



SYNTHESIS, SPECTRAL CHARACTERIZATION AND QUANTUM CHEMICAL COMPUTATIONAL STUDIES OF SOME SCHIFF BASES

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ABSTRACT

In the present study, (E)-N-(4-substitutedbenzylidene)-4-fluoro benzenesulfonamides (1-6) have been synthesized and their IR, ¹H and ¹³C NMR spectra were recorded. Density functional theory (DFT) has been used to optimize geometrical parameters, atomic charges, vibrational wavenumbers and intensity of vibrational bands were in good agreement with the corresponding experimental values. In addition, the molecular properties of HOMO-LUMO, MEP and atomic charges of carbon, nitrogen and oxygen were calculated using B3LYP/6-31G (d, p) basis set. The polarizability and first order hyperpolarizability of the synthesized compounds were calculated and interpreted. **Keywords:** DFT, HOMO – LUMO energies, Hyperpolarizability, MEP, NLO.

1. Introduction

Schiff base reactions are useful in making carbon-nitrogen bonds. Schiff bases appear to be important intermediates in a number of enzymatic reactions involving interaction of an enzyme with an amino or a carbonyl group of the substrate¹. Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields as sulfonamide Schiff's bases have been reported to possess antimicrobial activity², anti-inflammatory activity³, antikinoplastid antimitotic activity⁴, antitumor activity⁵, and anticonvulsant activity⁶. Schiff bases are associated with antibacterial, antifungal and anti-tubercular activities have diverse biological activities⁷⁻¹¹. The Schiff bases engrossed much

attention as they demonstrated anticancer¹², anticonvulsant¹³, diuretic¹⁴, herbicidal¹⁵, and anti HIV¹⁶ activities.

Schiff bases are studied widely due to their synthetic flexibility, selectivity and sensitivity towards the central metal atom; structural similarities with natural biological compounds and also due to presence of azomethine group (-N=CH-) which imports in elucidating the mechanism of transformation and racemization reaction biologically. The Schiff's base derivatives have been extensively investigated for more than a century and employed in different aspects including magneto chemistry, non-linear optics, photo physical studies, catalysis, materials chemistry, chemical analysis, absorption and transport of oxygen¹⁷.

Modern vibrational spectroscopy has proven to be an exceptionally powerful technique for solving many chemistry problems. Density functional theory (DFT)^{18, 19} has been accepted by the *ab initio* quantum chemistry community as a cost effective general procedure for studying physical properties of the molecules. In the framework of DFT approach, different exchange and correlation functionals are routinely used. Among those the B3LYP combination is most used since it proved its ability in reproducing various molecular properties, including vibrational spectra. The combined use of B3LYP functional and standard basis set 6-31G* provides an excellent balance between accuracy and computational efficiency of vibrational spectra for large and medium size molecules. The vibrational frequencies obtained by quantum chemical

calculations are typically larger and they have to be scaled by empirical scaling factors.

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-fluorobenzenesulfonamide with substituted aromatic benzaldehyde having extended conjugation. HOMO– LUMO energies, dipole moments, polarizabilities and first hyperpolarizabilities were determined by density functional theory (DFT) method.

2. Experimental methods

2.1 General procedure for synthesis of (E)-N-(4-substitutedbenzylidene)-4-fluorobenzenesulfonamides

The Schiff bases were obtained by 0.1M solution of 4-fluorobenzenesulfonamide was added to 0.1M solution of substituted aromatic benzaldehyde in ethanol, the addition reaction mixture is heated under reflux for 5-6 hours²⁰ at 70°C. After completion of reaction the precipitate are formed. The product filtered after cooling and purified with ethanol. The purity of product was checked by M. P. and TLC. The synthesized compounds were characterized by their Physical constants, IR, ¹H NMR and ¹³C NMR spectral data. The observed data are presented in **Table-1**.

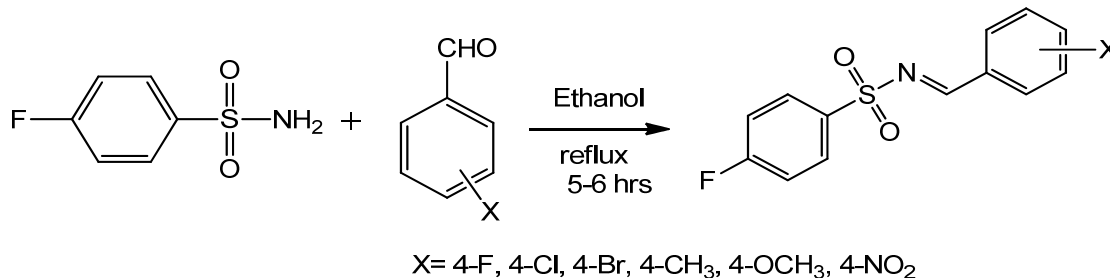


Table – 1 Physical analytical, melting point and spectral data of (E)-N-(4-substitutedbenzylidene)-4-fluorobenzenesulfonamides (**1-6**)

Entry	X	M.F	M.W	Yield (%)	m.p (°C)	IR	¹ H NMR ppm	¹³ C NMR ppm
						C=N	CH=N	C=N
1	4-F	C ₁₃ H ₉ F ₂ NO ₂ S	281	86	61-62	1595	8.42	175.767
2	4-Cl	C ₁₃ H ₉ ClFNO ₂ S	297.73	89	59-60	1564	8.422	175.653
3	4-Br	C ₁₃ H ₉ BrFNO ₂ S	342.18	83	57-58	1595	8.391	176.178
4	4-CH ₃	C ₁₄ H ₁₂ FNO ₂ S	277.31	82	55-56	1595	8.421	175.411
5	4-OCH ₃	C ₁₄ H ₁₂ FNO ₃ S	293.31	81	57-58	1579	8.392	175.822
6	4-NO ₂	C ₁₃ H ₉ FN ₂ O ₄ S	308.28	84	109-110	1579	8.399	175.706

2.2 Spectral measurements

The IR spectra were recorded in the 4000-400 cm⁻¹ range on SHIMADZU FT-IR spectrophotometer (Thermo Nicolet), the sample was mixed with KBr and the pellet technique and ¹H and ¹³C NMR Spectra of the

compounds were recorded under investigation using the NMR spectrophotometer by using BRUKER, 400MHz model Spectrometer.

2.3 Computational details

Initial molecular geometry was optimized using the DFT calculations with a hybrid

Functional B3LYP (Becke's Three parameter Hybrid Functional Using the LYP Correlation Functional) at 6-31G (d, p) basis set ²¹ were performed with the Gaussian 03W software package and Gauss view visualization program implemented on Pentium core 2 duo/3 GHz processor with 2GB RAM personal computer

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 6-31G (d, p) basis set and are presented in **Table-2**. Optimized structure of (*E*)-*N*-(4-substitutedbenzylidene)-4-fluorobenzenesulfonamides **1-6** shown in **Fig-1**.

Overall, as seen in optimized parameters Table, the most of the optimized bond lengths are slightly different from the experimental

results, since the molecular states are different during the experimental and theoretical processes. Many packing molecules are treated in condensed phase during experimental (XRD) measurements, while one isolated molecule is considered in gas phase during the theoretical (DFT) calculation.

The aromatic rings of the compounds **1-6** are somewhat irregular C-C bond lengths for aldehyde phenyl ring and sulfonyl-bound benzene ring, which is may be reason of substitution in aromatic leads to irregular C-C bond lengths. The atoms around the sulfonamide S₇ atom in the compound **1-6** are arranged in a slightly distorted tetrahedral arrangement configuration. The torsion angle C-S-N-C defining the conformation of the sulfonamide group is reported to planarity of sulfonamide group ²².

Table-2 Selected bond lengths, bond angles and dihedral angles of (*E*)-*N*-(4-substitutedbenzylidene)-4-fluorobenzenesulfonamides (**1-6**)

Bond length Å	XRD	1	2	3	4	5	6
C ₁ -C ₂	1.353	1.395	1.399	1.398	1.407	1.405	1.392
C ₁ -F ₁	1.36	1.374	1.752	1.905		1.356	1.476
C ₂ -C ₃	1.39	1.387	1.388	1.388	1.386	1.384	1.391
C ₃ -C ₄	1.391	1.408	1.406	1.406	1.407	1.408	1.404
C ₁ -C ₂ '	1.377	1.391	1.395	1.394	1.4	1.406	1.396
C ₂ '-C ₃ '	1.388	1.391	1.392	1.392	1.393	1.389	1.388
C ₃ '-C ₄	1.384	1.405	1.403	1.403	1.402	1.405	1.406
C ₄ -C ₅	1.479	1.461	1.463	1.463	1.46	1.455	1.463
C ₅ -N ₆	1.442	1.287	1.286	1.286	1.287	1.29	1.286
N ₆ -S ₇	1.66	1.721	1.723	1.723	1.719	1.715	1.723
S ₇ -O _{7A}	1.43	1.465	1.464	1.464	1.465	1.465	1.464
S ₇ -O _{BA}	1.43	1.465	1.464	1.464	1.473	1.465	1.464
S ₇ -C ₈	1.76	1.788	1.788	1.788	1.789	1.79	1.788
C ₈ -C ₉	1.386	1.398	1.398	1.398	1.398	1.396	1.398
C ₉ -C ₁₀	1.375	1.392	1.391	1.392	1.392	1.394	1.391
C ₁₀ -C ₁₁	1.375	1.393	1.393	1.393	1.393	1.391	1.393
C ₈ -C ₉ '	1.372	1.396	1.396	1.396	1.396	1.398	1.396
C ₉ '-C ₁₀ '	1.376	1.393	1.393	1.393	1.393	1.392	1.393
C ₁₀ '-C ₁₁	1.386	1.391	1.391	1.391	1.391	1.393	1.391
C ₁₁ -F ₁₁	1.36	1.375	1.372	1.374	1.372	1.373	1.374

Bond angle (°)							
C ₂ -C ₁ -C ₂ '	123.4	122.4	121.4	121.5	118.4	121	122.5
C ₃ -C ₄ -C ₃ '	118.6	119.3	119.2	119.3	118.9	118.6	119.3
N ₆ -S ₇ -C ₈	108.3	100.4	100.3	100.4	100.4	100.5	100.4
N ₆ -S ₇ -O _{7A}	106	105.9	105.8	105.8	105.9	106.2	105.8
N ₆ -S ₇ -O _{7B}	106.2	111.2	111.1	111.1	111.2	111.4	111.1
O _{7A} -S ₇ -C ₈	107.9	108.8	108.9	108.8	108.8	108.9	108.8
O _{7B} -S ₇ -C ₈	107.6	108.2	108.2	108.2	108.2	108.2	108.2
O _{7A} -S ₇ -O _{7B}	120.4	120.6	120.6	120.6	120.6	120.6	120.6
C ₉ -C ₈ -C ₉ '	120	121.5	121.5	121.5	121.5	121.5	121.5
C ₁₀ -C ₁₁ -C ₁₀ '	117.6	122.6	122.6	122.6	122.6	122.6	119.7
Dihedral angle (°)							
C ₈ -S ₇ -N ₆ -C ₅	84.5	-125.2	-125.2	-125.2	-125.1	-125.2	-125.5
C ₃ -C ₄ -C ₅ -N ₆	-	1.4	1.5	1.5	1.4	1.5	1.5
C ₃ '-C ₄ -C ₅ -N ₆	-	-178.6	-178.4	-178.4	-178.6	-178.4	-178.4
O _{7A} -S ₇ -C ₈ -C ₉	-	36.3	36.2	36.2	36.3	36.2	36.2
O _{7B} -S ₇ -C ₈ -C ₉	-	168.9	169	168.9	168.9	168.9	169
O _{7A} -S ₇ -C ₈ -C ₉ '	-	-142.9	-142.9	-142.9	-142.9	-142.9	-142.9
O _{7B} -S ₇ -C ₈ -C ₉ '	-	-10.3	-10.1	-10.3	-10.3	-10.3	-10.1
C ₃ '-C ₂ '-C ₁ -CH ₃	178.3				179.7		
C ₃ -C ₂ -C ₁ -CH ₃	177.6				177.7		

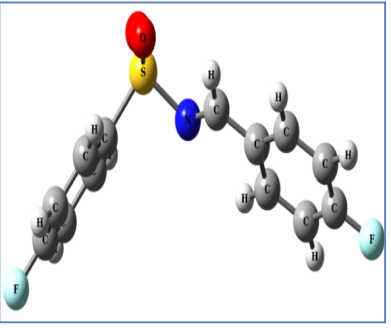
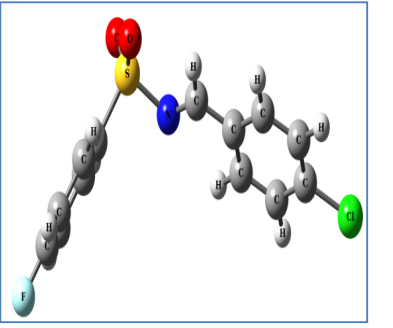
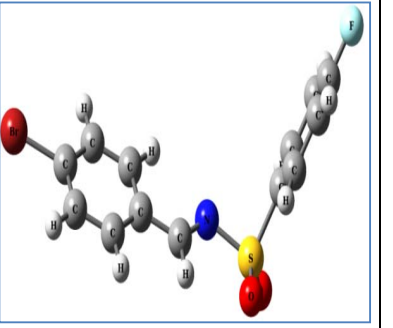
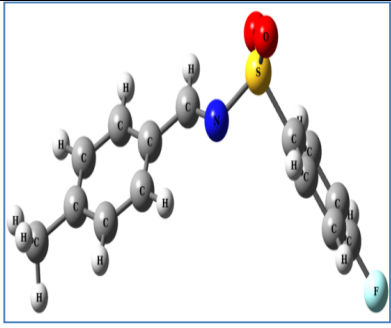
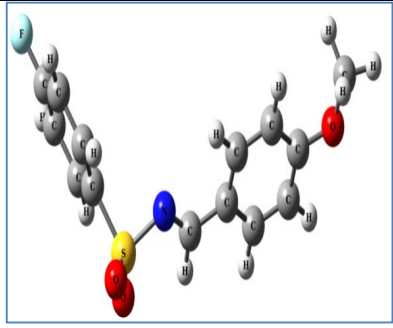
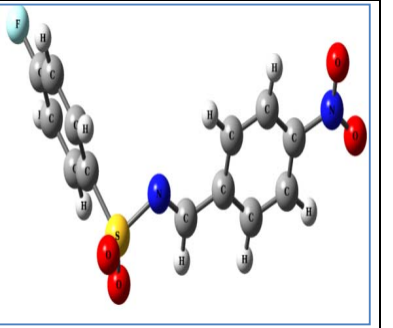
		
(1)	(2)	(3)
		
(4)	(5)	(6)

Fig -1 Optimized structure of (*E*)-*N*-(4-substitutedbenzylidene)-4-fluorobenzenesulfonamides (**1-6**)

3.2 Mulliken charge analysis

Results from Mulliken charge analysis **Table-3** and **Fig-2**, show that all the hydrogen atoms have a net positive charge. The obtained atomic charge shows that the C₁, C₈ atom has higher positive atomic charge than the other carbon atoms. This is due to the presence of electronegative group. From Mulliken charge

table, we can observe that sulphur atom has higher positive charge than the other atoms. The oxygen and nitrogen atoms on sulfonamide moiety in **1-6** exhibit a negative charge. The nitro group oxygen atoms have positive value about -0.38 a.u in compound **6**. These data clearly show that **1-6** are the most reactive towards substitution reactions.

Table-3 Mulliken atomic charges of

(*E*)-*N*-(4-substitutedbenzylidene)-4-fluorobenzenesulfonamides (**1-6**)

Atom	Atom Charge (a. u)		Atom Charge (a. u)	Atom Charge (a. u)	Atom	Atom Charge (a. u)	Atom	Atom Charge (a. u)
	1	2	3	4		5		6
C ₁	0.368	-0.088	0.059	0.133	C ₁	0.363	C ₁	0.251
F ₁	-0.283	0.003	-0.103		O ₁	-0.508	N ₁	0.392
C ₂	-0.144	-0.072	-0.093	-0.119	O _{1A}	-0.087	O _{1A}	-0.389
H ₂	0.116	0.123	0.121	0.091	C ₂	-0.133	O _{1B}	-0.388
C ₃	-0.117	-0.088	-0.116	-0.092	H ₂	0.098	C ₂	-0.092
H ₃	0.111	0.133	0.111	0.122	C ₃	-0.106	H ₂	0.148
C _{2'}	-0.14	-0.075	-0.089	-0.127	H ₃	0.125	C ₃	-0.132
H _{2'}	0.117	0.122	0.121	0.091	C _{2'}	-0.12	H ₃	0.118
C _{3'}	-0.092	-0.113	-0.091	-0.114	H _{2'}	0.107	C _{2'}	-0.089
H _{3'}	0.133	0.111	0.133	0.1	C _{3'}	-0.12	H _{2'}	0.148
C ₄	0.084	0.084	0.086	0.084	H _{3'}	0.103	C _{3'}	-0.106
C ₅	0.094	0.095	0.094	0.092	C ₄	0.084	H _{3'}	0.139
H ₅	0.145	0.146	0.144	0.143	C ₅	0.09	C ₄	0.101
N ₆	-0.523	-0.52	-0.521	-0.522	H ₅	0.141	C ₅	0.1
S ₇	1.191	1.193	1.193	1.19	N ₆	-0.527	H ₅	0.151
O _{7A}	-0.546	-0.544	-0.545	-0.547	S ₇	1.189	N ₆	-0.513
O _{7B}	-0.513	-0.512	-0.513	0.515	O _{7A}	-0.549	S ₇	0.196
C ₈	-0.178	-0.179	-0.179	-0.178	O _{7B}	-0.517	O _{7A}	-0.541
C ₉	-0.08	-0.08	-0.08	-0.08	C ₈	-0.175	O _{7B}	-0.508
H ₉	0.142	0.142	0.142	0.142	C ₉	-0.08	C ₈	-0.182
C ₁₀	-0.136	-0.136	-0.136	-0.136	H ₉	0.142	C ₉	-0.079
H ₁₀	0.117	0.118	0.118	0.117	C ₁₀	-0.136	H ₉	0.143
C _{9'}	-0.066	-0.066	-0.066	-0.066	H ₁₀	0.114	C ₁₀	-0.135
H _{9'}	0.142	0.142	0.142	0.142	C _{9'}	-0.065	H ₁₀	0.12
C _{10'}	-0.138	-0.138	-0.138	-0.138	H _{9'}	0.143	C _{9'}	-0.065
H _{10'}	0.118	0.118	0.118	0.118	C _{10'}	-0.138	H _{9'}	0.144
C ₁₁	0.365	0.365	0.365	0.364	H _{10'}	0.115	C _{10'}	-0.138
F ₁₁	-0.286	-0.285	-0.285	-0.287	C ₁₁	0.364	H _{10'}	0.121
					F ₁₁	-0.288	C ₁₁	0.36
							F ₁₁	-0.283

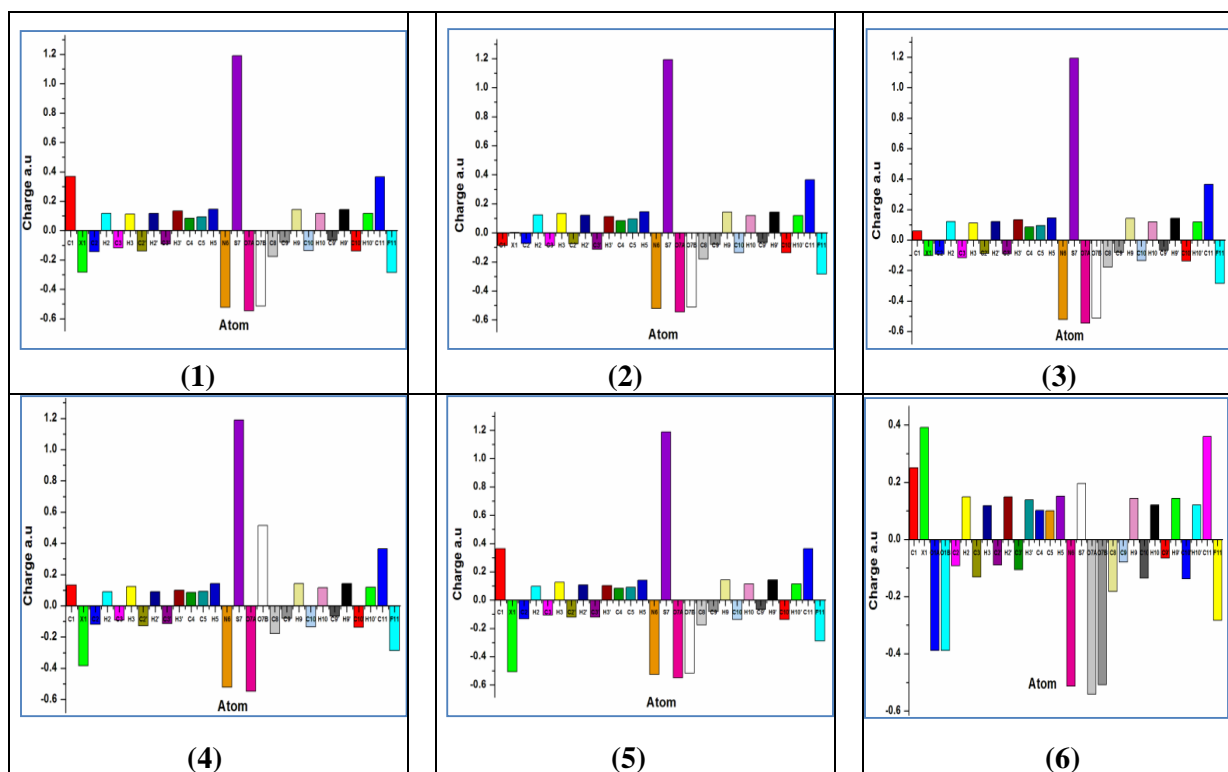
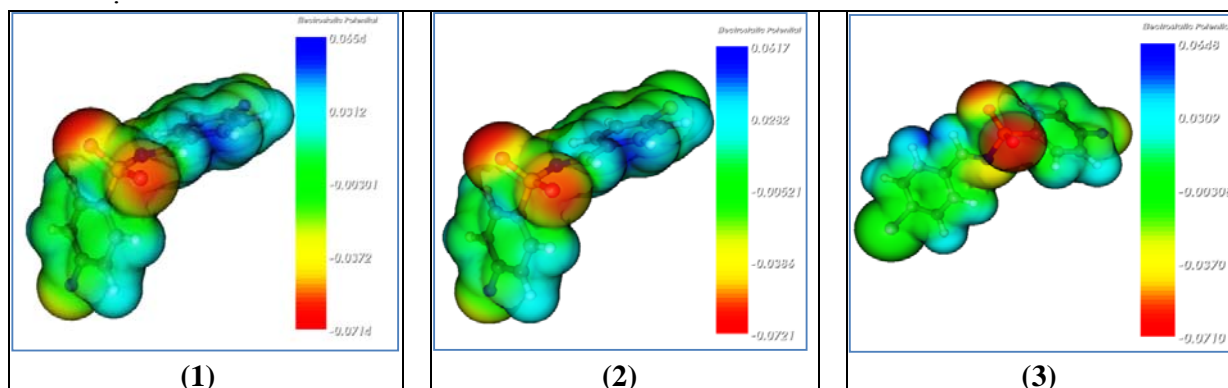


Fig-2 Mulliken charges of (*E*)-*N*-(4-substitutedbenzylidene)-4-fluorobenzenesulfonamides (**1-6**)

3.3 Molecular electrostatic potential analysis

Molecular electrostatic potential (MEP) is a helpful descriptor used to visualize the electrophilic or nucleophilic reactive sites of molecules²³, 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 reactivity²⁴. 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



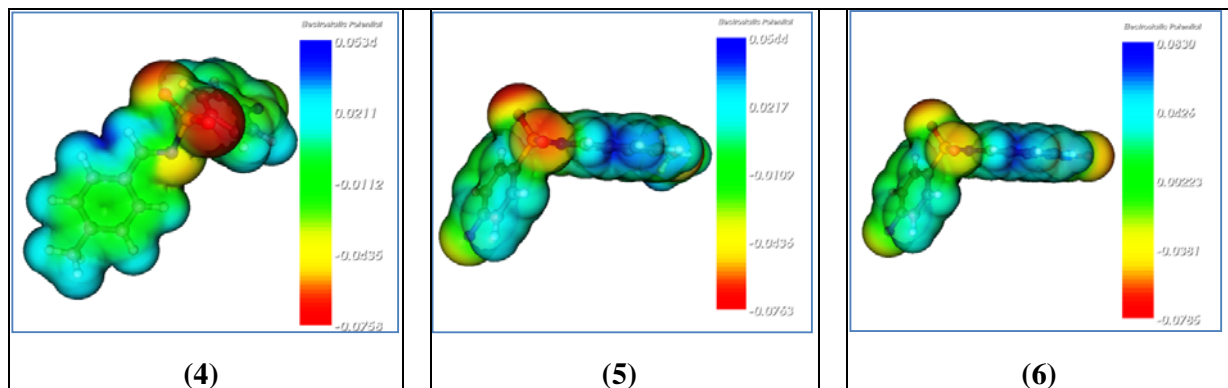


Fig-3 Molecular electrostatic potential diagrams of (*E*)-*N*-(4-substitutedbenzylidene)-4-fluorobenzenesulfonamides (**1-6**)

3.4 Frontier molecular orbital analysis

As seen from FMO results **Table-4** and **Fig-4**, the difference of the charge separation between the HOMO and LUMO of those structures 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 1-site of the phenyl core.

For a system 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 $6 < 5 < 3 < 2 < 4 < 1$. We can observe from HOMO-LUMO Table, the introduction of

different substituent at 1-site 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**²⁵. 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: $6 > 3 > 2 > 1 > 4 > 5$.

Table-4 Calculated energy values (eV) of (*E*)-*N*-(4-substitutedbenzylidene)-4-fluorobenzenesulfonamides (**1-6**) in gas phase.

B3LYP / 6-31 G(d,p)	1	2	3	4	5	6
E_{HOMO}	-7.01	-7.05	-6.97	-6.85	-6.42	-7.44
E_{LUMO}	-2.2	-2.37	-2.37	-2.07	-1.94	-3.25
$E_{\text{LUMO-HOMO}}$	4.81	4.68	4.6	4.78	4.49	4.19
$E_{\text{HOMO-1}}$	-7.38	-7.41	-7.37	-7.26	-7.15	-7.86
$E_{\text{LUMO+1}}$	-0.92	-0.98	-0.98	-0.82	-0.75	-1.86
$E_{(\text{LUMO+1})-(\text{HOMO-1})}$	6.46	6.42	6.39	6.44	6.4	6
Electronegativity(χ)	-4.61	-4.71	-4.67	-4.46	-4.18	-5.34

Hardness(η)	2.4	2.34	2.3	2.39	2.24	2.09
Electrophilicity index(ψ)	4.42	4.74	4.75	4.17	3.89	6.81
Softness(s)	154.04	158.12	161.02	155.03	164.93	176.71

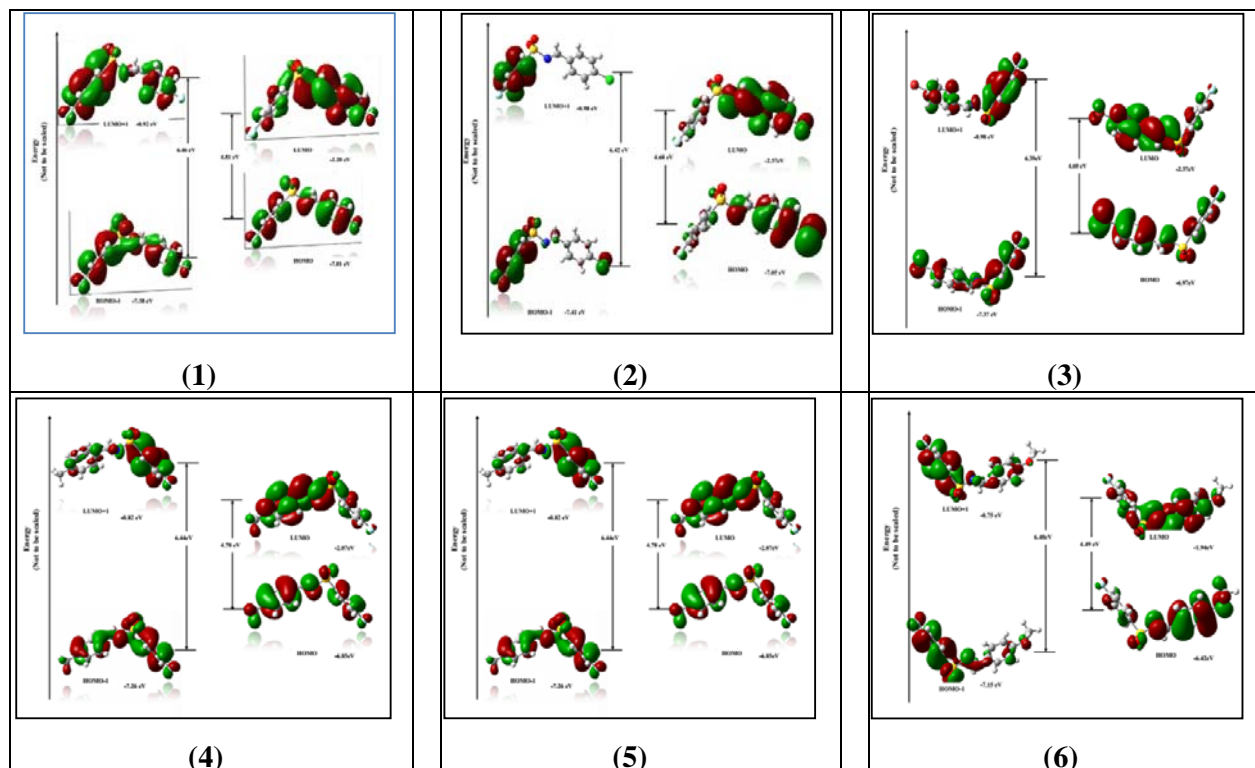


Fig-4 Molecular orbitals and energies for the HOMO and LUMO in gas phase (**1 - 6**)

3.11.5 Non-linear optical activity

NLO is important property providing key for areas such as telecommunications, signal processing and optical interactions^{26, 27}. 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-site in phenyl core.

From **Tables-5** the order of dipole moments for **1-6** is **5 > 4 > 1 > 3 > 6 > 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 F, Cl, Br, CH₃, OCH₃ and NO₂, groups at 1- site of the phenyl core. According to hypolarizability tables, all values of each mentioned molecules are greater than urea²⁸ values. Therefore, NLO properties of our compounds are better than urea. Results from Tables, the general ranking of NLO properties should be as follows: **3 > 6 > 5 > 4 > 2 > 1**. With results in hand, molecule **3** is the best candidate for NLO properties.

To sum up, it can be concluded that the presence of an electron withdrawing bromo atom in the phenyl ring contributes to increase the hyperpolarizability. The above results show that the synthesized molecules **1-6** can be the best material for NLO applications.

Table-5 Non-linear optical properties of (1–6) calculated using B3LYP method using 6-31G (d, p) basis set.

NLO behavior	1	2	3	4	5	6
Dipole moment(μ) D	4.1	1.63	3.8	5.77	6.59	3.05
Mean polarizability (α) esu	1.67×10^{-23}	1.81×10^{-23}	1.90×10^{-23}	1.63×10^{-23}	1.70×10^{-23}	2.00×10^{-23}
Anisotropy of the Polarizability ($\Delta\alpha$) esu	3.34×10^{-24}	3.93×10^{-24}	4.36×10^{-24}	3.58×10^{-24}	4.14×10^{-24}	7.23×10^{-24}
First order polarizability (β_0) esu	4.54×10^{-31}	5.47×10^{-31}	2.31×10^{-30}	9.57×10^{-31}	1.72×10^{-30}	2.16×10^{-30}

4. Conclusion

Synthesized Compounds of (*E*)-N-(4-substitutedbenzylidene)-4-fluorobenzenesulfonamides (1-6) were characterized by IR, ^1H and ^{13}C NMR spectral data. 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 reasonably good NLO properties.

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