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Computational study of the chemical reactivity properties of 4-[(1H-indol-3-ylmethylene)-amino] benzenesulfonamide derivatives

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Abstract
This study represents an integral approach towards understanding the electronic and structural aspects of 4-[(1H-indol-3-ylmethylene)-amino] benzenesulfonamide derivatives 1-4 by the DFT/B3LYP method and 6-31G (d,p) basis set. The geometrical parameters of title compounds are also obtained by the same method. From the MEP map it is evident that the negative electrostatic potential regions are mostly localized over the sulfamide function and are possible sites for electrophilic attack and positive regions are localized around the hydrogen atoms indicating possible sites for nucleophilic attack. The frontier molecular orbital is determined by means the HOMO and LUMO analysis which is used to explain the charge transfer within the molecule. The chemical reactivity descriptors were calculated to study the reactive sites within molecules and the results show that compound 3 is the most reactive. Furthermore the Mulliken population analysis on atomic charges is calculated and interpreted. Natural bond orbital (NBO) analysis was carried out to interpret the hyperconjugative interactions. Nonlinear optical property calculations of the compounds 1-4 indicate that these compounds cannot be used as a NLO material.

Keywords: sulfamide; density functional theory; computational chemistry; quantum chemical calculations.

1. Introduction

Sulfonamides were intensively investigated as the first effective antibacterial agents. They were the first effective chemotherapeutic agents used systematically for the prevention and cure of bacterial infections in humans and some animals, mainly because of their low cost, low toxicity and excellent activity against bacterial diseases [1]. Also the sulfonamide group is considered as a pharmacophore which is present in a number of biologically active molecules, particularly in antimicrobial agents [2-6].

Reactivity in chemistry is a key concept because it is intimately associated with reaction mechanisms thus allowing understanding chemical reactions and improving synthesis procedures to obtain new materials. The density functional theory (DFT) has become one of the most often used tool to investigate the properties of molecules [7].

The present paper gives a complete description of the molecular geometries, MEP, electronic transitions, global reactivity descriptors, Mulliken atomic charges, intramolecular interactions and NLO features of the 4-[(1H-indol-3-ylmethylene)-amino] benzenesulfonamide derivatives 1-4 illustrated in literature [8] at DFT/B3LYP method and 6-31G (d,p) basis set.

2. Materials and Methods

All calculations were performed by using Gaussian 09W package program [9] and the output files were visualized by means of the Gaussian View 5 software [10] at DFT and Becke-3-LeeeYangeParr (B3LYP) functional [11] supplemented with the 6-31G (d,p) basis set.

3. Results and Discussion

3.1 Molecular Geometry

The optimized molecular structures of 4-[(1H-indol-3-ylmethylene)-amino] benzene sulf on amide derivatives 1-4 with numbering scheme for the atoms were determined using Gaussian 09 program and shown in Figure 1. The geometrical parameters of these compounds 1-4 are calculated by B3LYP method with 6-31G (d,p) basis set and listed in Tables 1-4.
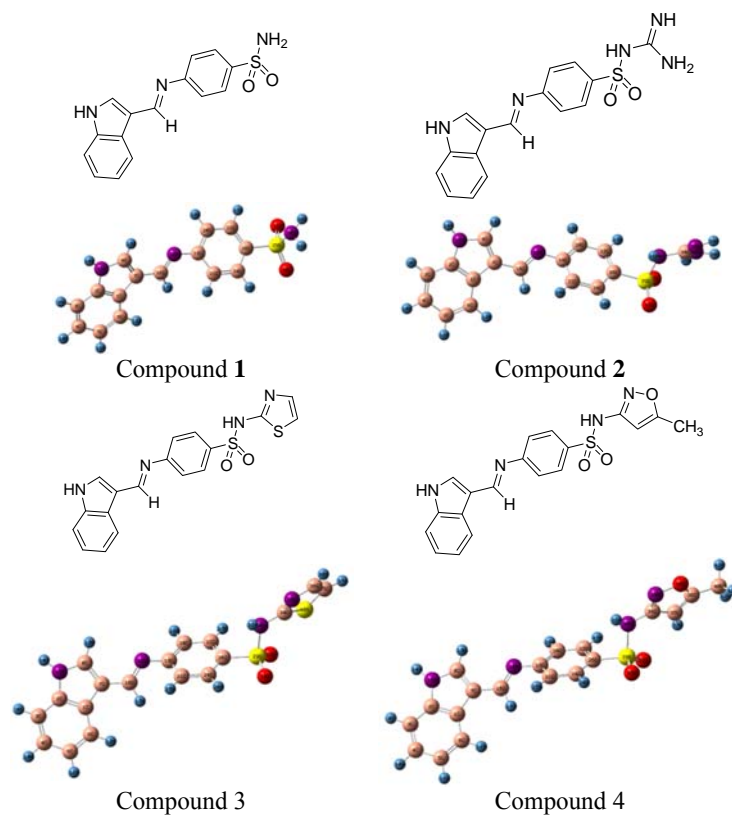
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Fig 1: Optimized molecular structure of 4-[(1H-indol-3-ylmethylene)-amino] benzenesulfonamide derivatives 1-4

Table 1: Optimized geometric parameters of compound 1

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.419	A(1,2,15)	107.127	D(10,4,5,6)	179.992
R(2,15)	1.387	A(3,2,15)	130.150	D(7,1,2,3)	179.966
R(7,16)	1.444	A(1,7,16)	127.505	D(16,7,8,15)	179.965
R(8,13)	1.080	A(8,7,16)	125.983	D(11,5,6,1)	179.963
R(14,15)	1.008	A(7,8,15)	109.658	D(1,2,15,14)	179.908
R(16,17)	1.100	A(7,16,17)	116.041	D(13,8,15,2)	179.903
R(16,18)	1.288	A(7,16,18)	122.689	D(15,2,3,4)	179.893
R(18,19)	1.399	A(17,16,18)	121.263	D(2,1,6,12)	179.858
R(19,20)	1.409	A(16,18,19)	119.781	D(18,19,20,22)	179.385
R(24,26)	1.395	A(26,29,30)	103.563	D(19,20,22,27)	178.089
R(26,29)	1.786	A(26,29,33)	108.469	D(1,7,16,18)	177.916
R(29,30)	1.701	A(26,29,34)	107.598	D(20,19,21,25)	177.132
R(29,33)	1.467	A(30,29,33)	105.273	D(24,26,29,33)	147.603
R(29,34)	1.468	A(33,29,34)	121.905	D(34,29,30,32)	111.048
R(30,31)	1.017	A(31,30,32)	110.847	D(26,29,30,31)	104.405

Table 2: Optimized geometric parameters of compound 2

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,7)	1.449	A(1,2,15)	107.138	D(7,1,2,3)	179.985
R(2,15)	1.388	A(7,8,15)	109.635	D(7,8,15,14)	179.947
R(7,8)	1.385	A(2,15,8)	109.881	D(15,2,3,4)	179.892
R(14,15)	1.008	A(8,15,14)	124.939	D(31,30,34,37)	179.494
R(16,17)	1.099	A(17,16,18)	121.182	D(18,19,20,22)	179.291
R(16,18)	1.289	A(16,18,19)	119.803	D(20,22,26,29)	179.273
R(18,19)	1.397	A(26,29,30)	99.969	D(8,7,16,17)	178.905
R(26,29)	1.781	A(26,29,32)	109.829	D(19,20,22,27)	178.811
R(29,32)	1.473	A(32,29,33)	119.514	D(1,7,16,18)	178.050
R(29,33)	1.467	A(29,30,31)	110.569	D(20,19,21,25)	176.787
R(30,31)	1.019	A(30,34,35)	115.559	D(32,29,30,31)	176.474
R(30,34)	1.430	A(30,34,37)	114.825	D(7,16,18,19)	176.177
R(34,35)	1.280	A(35,34,37)	129.368	D(35,34,37,38)	167.397
R(34,37)	1.375	A(34,35,36)	111.051	D(16,18,19,20)	140.954
R(37,38)	1.014	A(34,37,38)	117.193	D(24,26,29,32)	134.908

Table 3: Optimized geometric parameters of compound 3

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.419	A(1,2,15)	107.144	D(7,1,2,3)	180.002
R(7,8)	1.385	A(1,7,16)	127.522	D(7,8,15,14)	179.988
R(8,15)	1.366	A(7,8,15)	109.632	D(11,5,6,1)	179.954
R(14,15)	1.008	A(2,15,8)	109.884	D(15,2,3,4)	179.909
R(16,18)	1.289	A(8,15,14)	124.941	D(31,30,34,40)	179.452
R(18,19)	1.396	A(7,16,18)	122.767	D(40,35,36,38)	179.447
R(26,29)	1.781	A(16,18,19)	119.810	D(23,20,22,26)	179.332
R(29,30)	1.725	A(18,19,21)	123.148	D(18,19,20,22)	179.314
R(29,32)	1.465	A(21,24,26)	119.253	D(20,22,26,29)	179.307
R(29,33)	1.466	A(26,29,32)	110.431	D(19,20,22,27)	178.569
R(30,31)	1.019	A(32,29,33)	120.827	D(1,7,16,18)	177.965
R(30,34)	1.403	A(29,30,31)	111.087	D(37,35,40,34)	177.563
R(34,39)	1.303	A(29,30,34)	121.507	D(7,16,18,19)	176.170
R(34,40)	1.758	A(30,34,39)	120.630	D(30,34,40,35)	173.616
R(35,37)	1.080	A(39,34,40)	115.487	D(24,26,29,32)	138.395

Table 4: Optimized geometric parameters of compound 4

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.419	A(1,2,15)	107.145	D(7,8,15,14)	179.967
R(2,15)	1.388	A(8,7,16)	125.924	D(13,8,15,2)	179.942
R(14,15)	1.008	A(2,15,8)	109.879	D(15,2,3,4)	179.926
R(16,18)	1.289	A(2,15,14)	125.176	D(34,35,36,40)	179.749
R(18,19)	1.397	A(7,16,18)	122.731	D(20,22,26,29)	179.606
R(19,20)	1.410	A(16,18,19)	119.847	D(23,20,22,26)	179.295
R(26,29)	1.782	A(18,19,21)	123.176	D(18,19,20,22)	179.165
R(29,30)	1.723	A(26,29,30)	99.371	D(39,34,35,37)	179.134
R(29,32)	1.465	A(26,29,32)	110.307	D(19,20,22,27)	178.671
R(30,31)	1.019	A(32,29,33)	120.413	D(31,30,34,35)	177.083
R(30,34)	1.406	A(30,34,39)	118.246	D(32,29,30,31)	177.060
R(34,39)	1.317	A(38,36,40)	116.699	D(20,19,21,25)	176.905
R(36,38)	1.352	A(36,38,39)	109.402	D(30,34,35,36)	175.405
R(36,40)	1.489	A(34,39,38)	104.681	D(24,26,29,32)	138.660
R(38,39)	1.402	A(36,40,43)	110.883	D(35,36,40,43)	121.258

3.2 Molecular Electrostatic Potential (MEP)

The chemical reactivity of the molecules is investigated with the aid of molecular electrostatic potential (MEP) surface and it is plotted over the optimized electronic structures of the title compounds using density functional B3LYP level with 6-31G (d,p) basis set. The MEP originated in space around molecules by the charge distribution is very helpful in understanding the reactive sites for nucleophilic and electrophilic attack in hydrogen bonding interaction and in biological recognition process. The difference values for electrostatics potential are represented by different colors, red represent the negative regions of electrostatic potential, blue represent the positive region of electrostatic potential and green in the region of less positive potential. The potential increases in the order red < orange < yellow < green < blue [12]. The projection of such a MEP surface for the 4-[(1H-indol-3-ylmethylene)-amino] benzenesulfonamide derivatives 1-4 is given in Figure 2.

Compound 1   Compound 2

Compound 3   Compound 4

-4.094e-2 a.u ▬▬▬ 4.094e-2 a.u
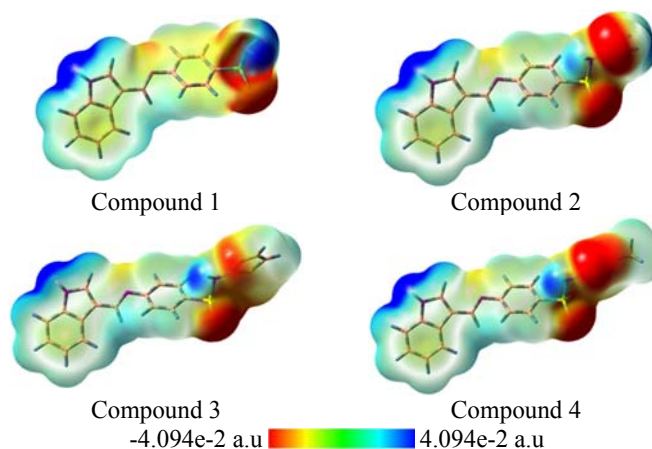
Fig 2: Molecular electrostatic potential surface of 4-[(1H-indol-3-ylmethylene)-amino] benzenesulfonamide derivatives 1-4

The regions exhibiting the negative electrostatic potential are localized on sulfamide function for all compounds also on amidine group for compound 2, thiazole for compound 3 and isoxazole for compound 4; while the regions presenting the

positive potential are localized vicinity of the hydrogen atoms.

3.3 Basin Analysis
The concept of basin was first introduced by Bader in his atom in molecular (AIM) theory, after that, this concept was transplant to the analysis of ELF by Savin and Silvi. In fact, basin can be defined for any real space function, such as molecular orbital, electron density difference, electrostatic potential and even Fukui function.

A real space function in general has one or more maxima, which are referred to as attractors or (3,-3) critical points. Each basin is a subspace of the whole space, and uniquely contains an attractor. The basins are separated with each other by interbasin surfaces (IBS), which are essentially the zero-flux surface of the real space functions; mathematically, such surfaces consist of all of the points r satisfying $\nabla f(r).n(r) = 0$, where n(r) stands for the unit normal vector of the surface at position r.

Interbasin surfaces (IBS) dissect the whole molecular space into individual basins, each IBS actually is a bunch of gradient paths derived from a (3,-1) critical points (CP). The interbasin surfaces of compounds 1-4 generated by (3,-1) critical points are illustrated below.
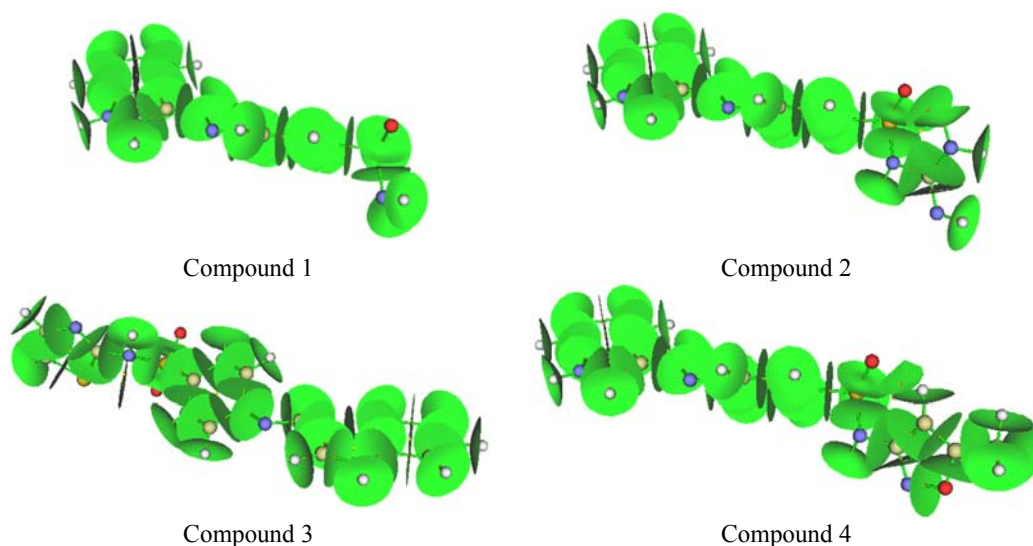
Compound 1

Compound 2

Compound 3

Compound 4

Fig 3: Plots of the interbasin surfaces of compounds 1-4

The number of interbasin surfaces is 36, 42, 44 and 47 for compounds 1-4 respectively.

3.4 Frontier Molecular Orbitals (FMOs)
The frontier molecular orbital theory plays an important role in the electric and optical properties. The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that largely acts as the electron acceptor [13]. HOMO and LUMO orbital not only determine the way in which the molecule interact with other species, but also their energy gap helps to characterize the chemical reactivity and kinetic stability of the molecule [14] and explains the eventual charge transfer interactions that take place within the molecules. HOMO and HOMO-1 and second highest and lowest unoccupied molecular orbitals LUMO and LUMO+1 and their transition state were obtained using DFT/B3LYP method and 6-31G (d,p) basis set and shown in Figure 4 for compound 3 which is the most reactive.
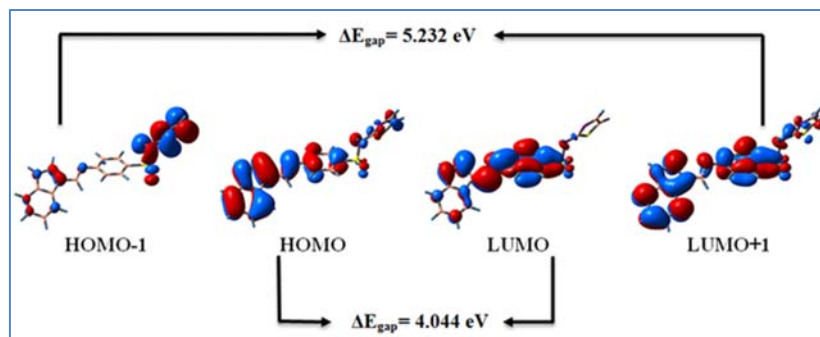
ΔE_{gap}= 5.232 eV

HOMO-1

HOMO

LUMO

LUMO+1

ΔE_{gap}= 4.044 eV

Fig 4: HOMO-LUMO Structure with the energy level diagram of compound 3

LUMO is confined over the benzene sulfonamide and HOMO-1 is confined over the thiazole, while HOMO and LUMO+1 are on the whole molecule for compound 3 which gives charge transfer process in the molecular system.

3.5 Global Reactivity Descriptors
The global chemical reactivity descriptors such as hardness (η), chemical potential (μ), softness (S), electronegativity (χ) and electrophilicity index (ω) can be calculated using HOMO and LUMO energy values for a molecule [15]. Namely, the larger HOMO-LUMO band gap is in accordance to the

chemical hardness, stability and chemically unreactive properties of the molecule whereas the smaller band gap points out the soft molecule [16]. The global parameters ionisation potential (*I*), electron affinity (*A*), electrophilicity (ω), electronegativity (χ), hardness (η) and softness (*S*) of the molecules 1-4 are determined using B3LYP/6-31G (d,p) basis set and displayed in Table 5.

Table 5: Quantum chemical descriptors of 4-[(1H-indol-3-ylmethylene)-amino] benzenesulfonamide derivatives 1-4

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
E_{HOMO} (eV)	-5.704	-5.825	-5.847	-5.832
E_{LUMO} (eV)	-1.593	-1.768	-1.803	-1.774
ΔE_{gap} (eV)	4.111	4.057	4.044	4.057
I (eV)	5.704	5.825	5.847	5.832
A (eV)	1.593	1.768	1.803	1.774
μ (eV)	-3.649	-3.796	-3.825	-3.803
χ (eV)	3.649	3.796	3.825	3.803
η (eV)	2.056	2.029	2.022	2.029
S (eV)	0.243	0.246	0.247	0.246
ω (eV)	3.238	3.552	3.618	3.565

The compound which has the lowest energy gap is the compound 3 (ΔE_{gap} = 4.044 eV). This lower gap allows it to be the softest molecule. The compound that has the highest energy gap is the compound 1 (ΔE_{gap} = 4.111 eV). The compound that has the highest HOMO energy is the compound 1 (E_{HOMO} = -5.704 eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound 3 (E_{LUMO} = -1.803 eV) which signifies that it can be the best electron acceptor. The two properties like *I* (potential ionization) and *A* (affinity) are so important, the determination of these two properties allows us to calculate the absolute electronegativity (χ) and the absolute hardness (η). These two parameters are related to the one-electron orbital energies of the HOMO and LUMO respectively. Compound 1 has the lowest value of the potential ionization (*I* = 5.704 eV), so that will be the better electron donor. Compound 3 has the largest value of the affinity (*A* = 1.803 eV), so it is the better electron acceptor. The chemical reactivity varies with the structure of molecules. Chemical hardness (softness) value of compound 3 (η = 2.022 eV, S = 0.247 eV) is lesser (greater) among all the molecules.

Thus, compound 3 is found to be more reactive than all the compounds. Compound 3 possesses higher electronegativity value (χ = 3.825 eV) than all compounds so; it is the best electron acceptor. The value of ω for compound 3 (ω = 3.618 eV) indicates that it is the stronger electrophiles than all compounds. Compound 3 has the smaller frontier orbital gap so, it is more polarizable and is associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule.

3.6 Mulliken Analysis
Mulliken charges predict the net atomic populations in the molecules and it is calculated by the B3LYP/6-31G (d, p) method of compound 3 which is the most reactive and are detailed in a Mulliken's plot as visualized in Figure 5. Mulliken atomic charge calculation has a significant role in the application of quantum chemical calculations to molecular systems because of atomic charges affect some properties of molecular systems including dipole moment and molecular polarizability [17].
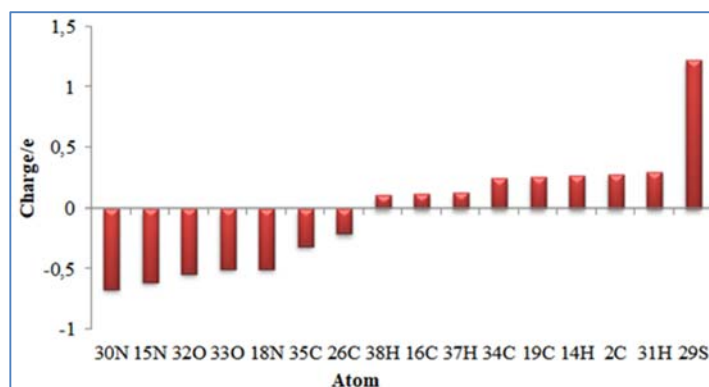

Fig 5: Mulliken's plot of compound 3

The atom 30N shows more negative (-0.666326e) charge and 29S more positive (1.225635e) charge, which suggests extensive charge delocalization in the entire molecule. The charge noticed on the 15N and 18N is smaller in the molecule and equal to -0.608489e, -0.498648e respectively. This can be explained by the high degree of conjugation, with a strong push-pull effect. Negatively charged oxygen (32O and 33O) atoms shows that charge is transferred from sulfur to oxygen and from carbon to oxygen. Carbon atoms 35C and 26C are more negatively charged which indicate that the charge transfer from sulfamide group to thiazole ring. The maximum atomic charge of carbons is obtained for 16C, 34C and 19C. This is due to the attachment of negatively charged azote. The positive charges are localized on the hydrogen atoms. Very similar values of positive charges are observed for the hydrogen atoms (38H, 37H, 14H and 31H (0.10~0.30e)) bonded to the negative atoms (36C, 35C, 15N and 30N) respectively.

3.7 Natural Bond Orbital Analysis (NBO)

Natural bond orbital (NBO) analysis is based on a method for optimally transforming a given wave function into localized form. It also provides a convenient basis for the investigation of charge transfer or conjugative interactions in molecular system [18]. The NBO analysis is already proved to be an effective tool for the chemical interpretation of hyperconjugative interaction and electron density transfer from the filled lone pair electron [19]. In Tables 6-9, the perturbation energies of significant donor-acceptor interactions are presented with the calculation done using DFT/B3LYP method and 6-31G (d,p) basis set. Greater the value of hyperconjugative interaction energy, higher will be the extent of delocalization, consequently greater will be the stability of whole molecular system.

Table 6: Second order perturbation theory analysis of Fock matrix on NBO of compound **1**

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F(i,j) a.u
LP (1) N15	1.60046	π*(C7-C8)	0.34049	40.43	0.30	0.099
LP (1) N15	1.60046	π*(C1-C2)	0.48070	33.24	0.30	0.091
π (C19-C21)	1.61886	π*(C24-C26)	0.39337	26.13	0.27	0.075
LP (3) O33	1.78542	σ*(S29-O34)	0.16160	21.80	0.56	0.100
π (C20-C22)	1.67910	π*(C19-C21)	0.37599	21.30	0.28	0.070
π (C24-C26)	1.69407	π*(C20-C22)	0.28327	20.58	0.30	0.070
π (C7-C8)	1.76396	π*(C16-N18)	0.17917	20.01	0.29	0.070
π (C5-C6)	1.72001	π*(C3-C4)	0.32670	19.56	0.28	0.067
π (C3-C4)	1.72692	π*(C1-C2)	0.48070	19.41	0.28	0.069
π (C1-C2)	1.59561	π*(C3-C4)	0.32670	18.95	0.28	0.066
π (C1-C2)	1.59561	π*(C5-C6)	0.30540	18.81	0.28	0.067
π (C5-C6)	1.72001	π*(C1-C2)	0.48070	17.96	0.28	0.066
π (C1-C2)	1.59561	π*(C7-C8)	0.34049	17.86	0.27	0.063
π (C3-C4)	1.72692	π*(C5-C6)	0.30540	17.64	0.29	0.064
π (C20-C22)	1.67910	π*(C24-C26)	0.39337	17.52	0.27	0.063
π (C7-C8)	1.76396	π*(C1-C2)	0.48070	17.50	0.29	0.068
LP (2) O34	1.81892	σ*(C26-S29)	0.19629	16.44	0.46	0.078
π (C19-C21)	1.61886	π*(C20-C22)	0.28327	16.26	0.29	0.062
LP (2) O33	1.81824	σ*(C26-S29)	0.19629	15.75	0.45	0.076
π (C24-C26)	1.69407	π*(C19-C21)	0.37599	15.30	0.29	0.061

Table 7: Second order perturbation theory analysis of Fock matrix on NBO of compound 2

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F(i,j) a.u
LP (1) N15	1.59829	π*(C7-C8)	0.34244	40.85	0.30	0.100
LP (1) N15	1.59829	π*(C1-C2)	0.47991	33.16	0.30	0.091
π (C19-C21)	1.61407	π*(C24-C26)	0.40031	27.19	0.27	0.076
LP (1) N37	1.79922	π*(C34-N35)	0.22871	23.84	0.44	0.092
LP (3) O33	1.77662	σ*(S29-N30)	0.27333	23.48	0.40	0.087
LP (2) O32	1.81039	σ*(S29-O33)	0.16122	21.77	0.57	0.100
π (C20-C22)	1.68081	π*(C19-C21)	0.37248	21.34	0.28	0.070
π (C24-C26)	1.70137	π*(C20-C22)	0.27574	20.51	0.30	0.071
π (C7-C8)	1.76039	π*(C16-N18)	0.18225	20.44	0.29	0.070
LP (3) O32	1.80698	σ*(S29-N30)	0.27333	20.27	0.40	0.083
π (C5-C6)	1.71918	π*(C3-C4)	0.32561	19.55	0.28	0.067
π (C3-C4)	1.72576	π*(C1-C2)	0.47991	19.48	0.28	0.070
π (C1-C2)	1.59652	π*(C3-C4)	0.32561	18.91	0.28	0.066
π (C1-C2)	1.59652	π*(C5-C6)	0.30488	18.75	0.28	0.067
LP (2) O33	1.80459	σ*(C26-S29)	0.18968	18.67	0.46	0.082
π (C5-C6)	1.71918	π*(C1-C2)	0.47991	18.05	0.27	0.066
π (C1-C2)	1.59652	π*(C7-C8)	0.34244	17.89	0.27	0.063
π (C3-C4)	1.72576	π*(C5-C6)	0.30488	17.69	0.29	0.065
π (C7-C8)	1.76039	π*(C1-C2)	0.47991	17.53	0.29	0.068
LP (1) N35	1.91596	σ*(C34-N37)	0.05111	17.11	0.82	0.106

Table 8: Second order perturbation theory analysis of Fock matrix on NBO of compound **3**

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F(i,j) a.u
LP(1) N15	1.59795	π*(C7-C8)	0.34284	40.92	0.30	0.100
LP(1) N15	1.59795	π*(C1-C2)	0.47978	33.15	0.30	0.091
LP(2) S40	1.64312	π*(C34-N39)	0.39710	29.47	0.24	0.076
π (C19-C21)	1.61334	π*(C24-C26)	0.40176	27.28	0.27	0.076
LP(3) O33	1.77077	σ*(S29-N30)	0.29272	25.57	0.38	0.090
LP(3) O32	1.79288	σ*(S29-N30)	0.29272	25.41	0.38	0.090

LP(1) N30	1.83315	π*(C34-N39)	0.39710	21.37	0.34	0.081
π (C20-C22)	1.68049	π*(C19-C21)	0.37251	21.36	0.28	0.070
π (C7-C8)	1.75993	π*(C16-N18)	0.18273	20.51	0.29	0.070
π (C24-C26)	1.70203	π*(C20-C22)	0.27510	20.48	0.30	0.071
π (C5-C6)	1.71901	π*(C3-C4)	0.32539	19.55	0.28	0.067
π (C3-C4)	1.72555	π*(C1-C2)	0.47978	19.50	0.28	0.070
LP(2) S40	1.64312	π*(C35-C36)	0.26232	19.05	0.27	0.065
π (C1-C2)	1.59672	π*(C3-C4)	0.32539	18.90	0.28	0.066
π (C1-C2)	1.59672	π*(C5-C6)	0.30471	18.73	0.28	0.067
π (C34-N39)	1.88080	π*(C35-C36)	0.26232	18.64	0.35	0.074
LP(2) O33	1.80668	σ*(C26-S29)	0.19144	18.37	0.46	0.082
π (C5-C6)	1.71901	π*(C1-C2)	0.47978	18.07	0.27	0.066
π (C1-C2)	1.59672	π*(C7-C8)	0.34284	17.89	0.27	0.063
LP(2) O32	1.80008	σ*(C26-S29)	0.19144	17.72	0.46	0.080

Table 9: Second order perturbation theory analysis of Fock matrix on NBO of compound 4

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F(i,j) a.u
LP(1) N15	1.59822	π*(C7-C8)	0.34256	40.87	0.30	0.100
LP(2) O38	1.72002	π*(C35-C36)	0.26169	35.12	0.36	0.101
LP(1) N15	1.59822	π*(C1-C2)	0.47991	33.16	0.30	0.091
π (C35-C36)	1.81652	π*(C34-N39)	0.37347	27.69	0.28	0.083
π (C19-C21)	1.61406	π*(C24-C26)	0.40005	27.13	0.27	0.076
LP(3) O33	1.77625	σ*(S29-N30)	0.28743	25.40	0.38	0.090
LP(3) O32	1.79732	σ*(S29-N30)	0.28743	24.35	0.39	0.088
π (C20-C22)	1.68033	π*(C19-C21)	0.37280	21.34	0.28	0.070
LP(1) N30	1.84687	π*(C34-N39)	0.37347	21.27	0.35	0.081
π (C24-C26)	1.70159	π*(C20-C22)	0.27637	20.51	0.30	0.071
π (C7-C8)	1.76031	π*(C16-N18)	0.18249	20.46	0.29	0.070
π (C5-C6)	1.71915	π*(C3-C4)	0.32557	19.55	0.28	0.067
π (C3-C4)	1.72570	π*(C1-C2)	0.47991	19.49	0.28	0.070
π (C1-C2)	1.59657	π*(C3-C4)	0.32557	18.91	0.28	0.066
π (C1-C2)	1.59657	π*(C5-C6)	0.30482	18.74	0.28	0.067
LP(2) O33	1.80529	σ*(C26-S29)	0.19277	18.57	0.46	0.082
LP(2) O32	1.80182	σ*(C26-S29)	0.19277	18.43	0.45	0.082
π (C5-C6)	1.71915	π*(C1-C2)	0.47991	18.05	0.27	0.066
π (C1-C2)	1.59657	π*(C7-C8)	0.34256	17.89	0.27	0.063
π (C3-C4)	1.72570	π*(C5-C6)	0.30482	17.69	0.29	0.065

The intra molecular interaction for the title compounds is formed by the orbital overlap between: π (C19-C21) and π*(C24-C26) for compound 1, π (C19-C21) and π*(C24-C26) for compound 2, π (C19-C21) and π*(C24-C26) for compound 3 and π (C35-C36) and π*(C34-N39) for compound 4 respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of π (C19-C21) to π*(C24-C26) for compound 1, π (C19-C21) to π*(C24-C26) for compound 2, π (C19-C21) to π*(C24-C26) for compound 3 and π (C35-C36) to π*(C34-N39) for compound 4 lead to highest stabilization of 26.13, 27.19, 27.28 and 27.69 kJ mol^{-1} respectively. In case of LP (1) N15 orbital to the π*(C7-C8) for compound 1, LP (1) N15 orbital to π*(C7-C8) for compound 2, LP (1) N15 orbital to π*(C7-C8) for compound 3, LP (1) N15 orbital to π*(C7-C8) for compound

4 respectively, show the stabilization energy of 40.43, 40.85, 40.92 and 40.87 kJ mol^{-1} respectively.

3.8 Nonlinear Optical Properties (NLO)
NLO is at the forefront of current research because it provides 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 [20, 21]. In discussing nonlinear optical properties, the polarization of the molecule by an external radiation field is often approximated as the creation of an induced dipole moment by an external electric field. The dipole moment (μ), polarizability (α), anisotropy of polarizability (Δα) and first hyperpolarizability (β$_0$) of 4-[(1H-indol-3-ylmethylene)-amino] benzenesulf onamide derivatives 1-4 were calculated using B3LYP/6-31G (d,p) basis set and illustrated in Table 10.

Table 10: Nonlinear optical properties of 4-[(1H-indol-3-ylmethylene)-amino] benzenesulfonamide derivatives 1-4

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
β$_{xxx}$	-110.3345	-38.7986	165.6257	-105.2677
β$_{yyy}$	-27.1661	-27.0166	-32.3832	-38.4765
β$_{zzz}$	-11.7501	8.5193	0.6042	2.1638
β$_{xyy}$	-59.9159	-92.6984	107.8692	-97.6920
β$_{xxy}$	-143.5081	-108.2708	-171.4802	-136.7863
β$_{xxz}$	-113.4145	62.7104	-2.5741	104.5457
β$_{xzz}$	35.7201	11.9655	-27.8376	21.9003

β_{yzz}	-0.0312	-1.0209	-4.2077	-2.2607
β_{yyz}	4.3623	4.0221	-2.2419	1.8699
β_{xyz}	-20.9601	-15.8825	-13.0391	-24.9822
β_0(esu)x10^{-33}	225.6196	196.2920	321.9609	275.8380
μ_x	-5.8036	-6.7928	7.4485	-6.9922
μ_y	-3.1458	-2.8105	-3.9632	-3.5441
μ_z	-2.5763	0.5474	0.8292	0.8723
μ (D)	7.0863	7.3717	8.4779	7.8875
α_{xx}	-108.8534	-110.4059	-121.6882	-115.3107
α_{yy}	-118.4889	-138.2946	-154.9882	-153.8494
α_{zz}	-129.9897	-152.0349	-166.6503	-167.2999
α_{xy}	-1.8524	6.7336	-2.1900	6.7323
α_{xz}	-12.4265	11.3251	2.8983	16.5787
α_{yz}	-0.6313	-2.5114	2.2015	-4.0639
α(esu)x10^{-24}	28.4723	44.7195	41.0776	56.5207
$\Delta\alpha$(esu)x10^{-24}	4.2196	6.6274	6.0877	8.3764

Since the values of the polarizabilities ($\Delta\alpha$) and the hyperpolarizabilities (β_0) of the GAUSSIAN 09 output are obtained in atomic units (a.u.), the calculated values have been converted into electrostatic units (e.s.u.) (for α; 1 a.u = 0.1482 x 10^{-24} e.s.u., for β; 1 a.u = 8.6393 x 10^{-33} e.s.u.). The calculated values of dipole moment (μ) for the title compounds were found to be 7.0863, 7.3717, 8.4779 and 7.8875 D respectively, which are approximately seven and eight times than to the value for urea (μ = 1.3732 D). Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore, it has been used frequently as a threshold value for comparative purposes. The calculated values of polarizability are 28.4723 x 10^{-24}, 44.7195 x 10^{-24}, 41.0776 x 10^{-24} and 56.5207 x 10^{-24} esu respectively; the values of anisotropy of the polarizability are 4.2196, 6.6274, 6.0877 and 8.3764 esu, respectively. The magnitude of the molecular hyperpolarizability (β_0) is one of the important key factors in a NLO system. The DFT/6-31G (d,p) calculated first hyperpolarizability value (β_0) of 4-[(1H-indol-3-ylmethylene)-amino] benzenesulfonamide derivatives are equal to 225.6196 x 10^{-33}, 196.2920 x 10^{-33}, 321.9609 x 10^{-33} and 275.8380 x 10^{-33} esu. The first hyperpolarizability of title molecules is approximately 0.65, 0.57, 0.94 and 0.80 times than those of urea (β of urea is 343.272 x10^{-33} esu obtained by B3LYP/6-311G (d,p) method). The above results show that the title compounds might have not the NLO applications.

4. Conclusion
In this study, we have performed the density functional calculations on 4-[(1H-indol-3-ylmethylene)-amino] benzenesulfonamide derivatives 1-4. Our objectives were to reproduce the molecular geometries, reactive sites, delocalization of electron density, energy gap and non-linear optical properties by B3LYP/6-31G (d,p) level. The optimized structural parameters such as bond lengths, bond angles and dihedral angles are calculated. MEP shows that the negative potential sites are on sulfamide function and the positive potential sites are around the hydrogen atoms. The lowering of the energy gap between HOMO and LUMO orbitals explains the eventual load transfer interactions that take place within the molecules. The calculated value of ionization potential, electron affinity, global hardness, electro negativity, global softness, chemical potential and global electrophilicity of 4-[(1H-indol-3-ylmethylene)-amino] benzenesulfonamide derivatives 1-4 display that that compound 3 is the most reactive. Mulliken's net charges have been calculated and results show that 30N is the more negative and 29S is the more positive charge, which Indicates extensive charge delocalization in the entire molecule. NBO analysis provides a satisfactory description of the title compounds analyzed. The results show that stability of the molecular structures arises from conjugative interactions, charge delocalization and E (2) energies confirm the occurrence of intra-molecular charge transfer within the molecule. A computation of the first hyperpolarizability (β_0) indicates that compounds 1-4 not be a good candidate as a NLO material.

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