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Quantum chemical characterization of arylsulfonylureido compounds by DFT approach

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Abstract

We reported in the present work, a theoretical study of arylsulfonylureido compounds 1-4 by DFT/B3LYP method using 6-31G (d,p) to predict their NLO applications. The geometrical parameters of the title compounds are obtained by the same method. The active sites in the molecules are determined by molecular electrostatic potential map. The calculation of frontier molecular orbitals show that the charge transfers within the molecules. The reactivity of the title compounds of interest was described by HOMO-LUMO energies and global descriptors. The Mulliken analysis was also determined. The NBO analysis is carried out to investigate the various intra and inter molecular interactions of molecular system and to study the stability of the molecules. The polarizability and first order hyperpolarizability of the title molecules were calculated and results show that the compounds 1-4 might have not the NLO behavior.

Keywords: sulfonamide, density functional theory, computational chemistry, quantum chemical calculations

1. Introduction

SO_2-NH group is a key constituent of sulfonamide pharmaceuticals, which are promising chemotherapeutic agents used for treatment of various diseases [1]. This functional group constitutes the largest class of antimicrobial agents and has been shown to be a transition state mimetic of peptide hydrolysis and, in particular, as the critical motif for potent, irreversible inhibitors of cysteine proteases [2-4].

Reactivity in chemistry is a key concept because it is intimately associated with reaction mechanisms thus allowing to understand chemical reactions and improve synthesis procedures to obtain new materials. A branch of Density Functional Theory (DFT) [5-7] called Conceptual DFT [8-10] has been developed and used in chemistry.

The present work deals with quantum chemical calculations to analyze the molecular structures, the MEP analysis, the distributions of the frontier molecular orbitals, chemical reactivity, the Mulliken atomic charges, various intra-molecular interactions and the non-linear optical properties of the arylsulfonylureido compounds 1-4 reported in literature [11] at DFT/B3LYP method and 6-31G (d,p) basis set.

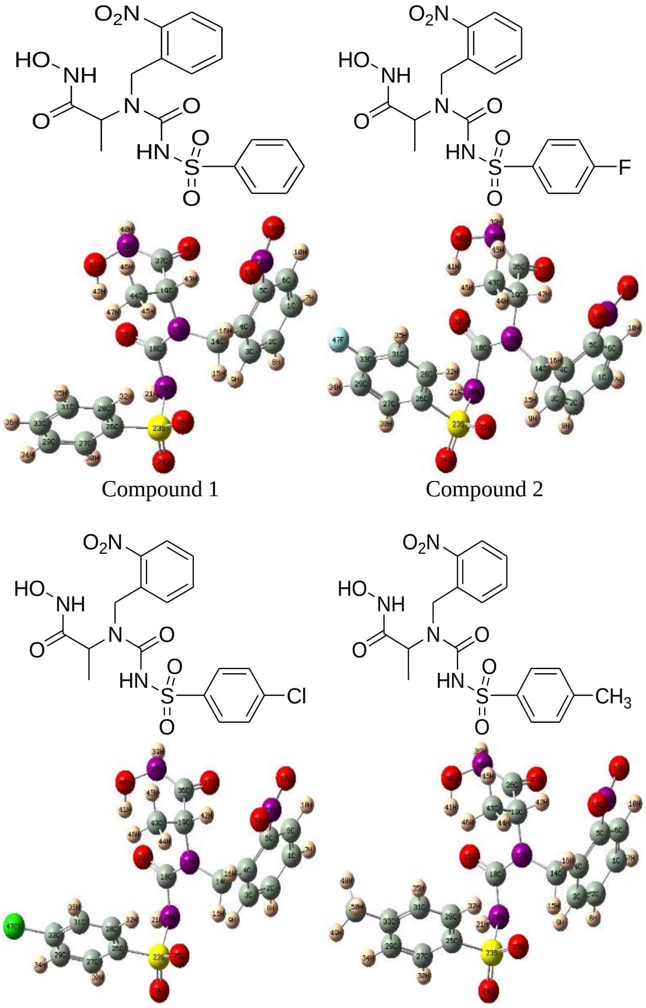
2. Materials and Methods

In the present paper, density functional theory was adopted by employing B3LYP/6-31G (d,p) basis set level to calculate the properties of the arylsulfonylureido compounds 1-4. All the quantum chemical computations, of the title molecules were carried out with the Gaussian 09W program [12].

3. Results and Discussion

3.1 Molecular Geometry

The optimized geometrical parameters of arylsulfonylureido compounds 1-4 obtained through DFT/B3LYP method using 6-31G (d,p) are listed in Tables 1-4 and there molecular structures depicted in Figure1.



Compound 1

Compound 2

Compound 3

Compound 4

Fig 1: Optimized molecular structure of arylsulfonyl uredo compounds 1-4

Table 1: Optimized geometric parameters of compound 1

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(3,4)	1.403	A(2,3,9)	119.446	D(28,31,33,36)	179.965
R(4,14)	1.528	A(4,5,11)	123.336	D(8,2,3,4)	179.620
R(11,12)	1.225	A(5,11,13)	118.778	D(2,3,4,14)	179.516
R(11,13)	1.237	A(12,11,13)	123.292	D(23,26,28,31)	179.365
R(17,18)	1.352	A(4,14,17)	113.948	D(27,26,28,32)	178.273
R(18,20)	1.439	A(18,17,19)	117.326	D(11,5,6,1)	177.750
R(18,22)	1.235	A(17,18,22)	124.806	D(21,20,23,25)	173.057
R(20,21)	1.019	A(20,18,22)	117.914	D(18,20,23,24)	165.558
R(20,23)	1.730	A(17,19,37)	109.791	D(44,19,37,38)	159.625
R(23,24)	1.461	A(17,19,44)	111.720	D(38,37,39,41)	159.342
R(23,25)	1.462	A(18,20,23)	121.671	D(24,23,26,28)	155.049
R(37,38)	1.228	A(20,23,26)	106.568	D(15,14,17,19)	151.848
R(37,39)	1.365	A(24,23,25)	122.585	D(3,4,14,16)	147.927
R(39,41)	1.395	A(38,37,39)	119.955	D(17,19,37,39)	115.556
R(41,42)	0.982	A(37,39,41)	123.231	D(14,17,19,37)	106.841

Table 2: Optimized geometric parameters of compound 2

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(4,14)	1.528	A(5,6,10)	118.400	D(28,31,33,47)	179.950
R(5,11)	1.478	A(5,11,13)	118.774	D(26,28,31,35)	179.659
R(11,12)	1.225	A(12,11,13)	123.303	D(2,3,4,14)	179.561
R(11,13)	1.237	A(4,14,17)	113.942	D(23,26,28,31)	179.483
R(14,17)	1.487	A(17,18,20)	117.222	D(34,29,33,31)	179.075
R(17,18)	1.352	A(17,18,22)	124.884	D(30,27,29,33)	178.596
R(18,20)	1.440	A(20,18,22)	117.871	D(27,26,28,32)	178.258
R(18,22)	1.235	A(18,20,23)	121.554	D(21,20,23,25)	172.975
R(19,36)	1.547	A(24,23,25)	122.717	D(18,20,23,24)	165.335
R(20,23)	1.729	A(24,23,26)	108.374	D(37,36,38,40)	159.544
R(23,24)	1.461	A(19,36,38)	120.916	D(43,19,36,37)	159.478
R(23,25)	1.461	A(37,36,38)	119.951	D(24,23,26,28)	155.442
R(23,26)	1.790	A(36,38,40)	123.308	D(15,14,17,19)	152.060
R(31,33)	1.392	A(39,38,40)	113.826	D(17,19,36,38)	115.422
R(33,47)	1.342	A(38,40,41)	103.329	D(14,17,19,36)	106.549

Table 3: Optimized geometric parameters of compound 3

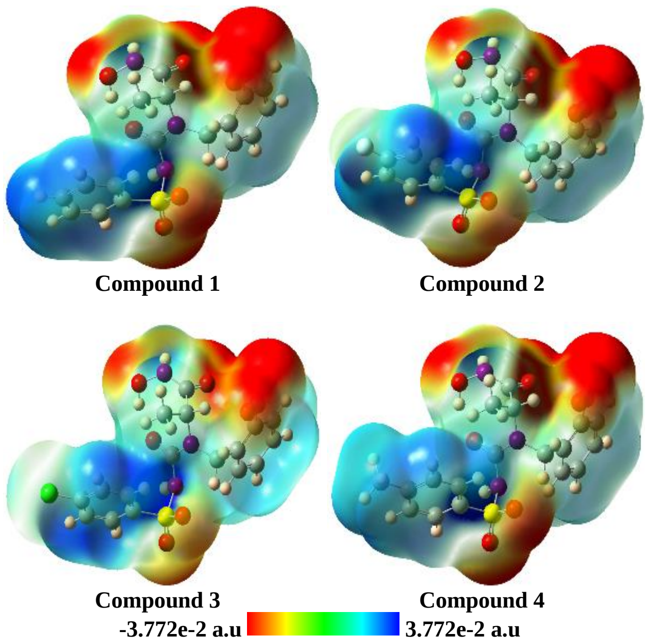
Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(5,11)	1.478	A(4,14,17)	113.963	D(28,31,33,47)	179.925
R(17,19)	1.490	A(18,17,19)	117.318	D(23,26,28,31)	179.613
R(18,20)	1.441	A(17,18,20)	117.160	D(2,3,4,14)	179.564
R(18,22)	1.235	A(17,18,22)	124.942	D(34,29,33,31)	179.115
R(19,36)	1.547	A(17,19,36)	109.758	D(30,27,29,33)	178.582
R(20,21)	1.019	A(18,20,21)	107.356	D(27,26,28,32)	178.225
R(20,23)	1.726	A(18,20,23)	121.548	D(21,20,23,25)	174.667
R(23,24)	1.461	A(20,23,24)	103.305	D(18,20,23,24)	167.131
R(23,25)	1.461	A(20,23,25)	107.043	D(37,36,38,40)	159.818
R(23,26)	1.792	A(20,23,26)	106.716	D(43,19,36,37)	159.461
R(33,47)	1.750	A(31,33,47)	119.256	D(24,23,26,28)	156.771
R(36,37)	1.228	A(19,36,37)	118.963	D(15,14,17,19)	151.821
R(36,38)	1.364	A(37,36,38)	119.952	D(3,4,14,16)	148.037
R(38,39)	1.015	A(36,38,39)	115.093	D(17,19,36,38)	115.326
R(38,40)	1.395	A(38,40,41)	103.379	D(14,17,19,36)	106.609

Table 4: Optimized geometric parameters of compound 4

Bond Length (Å)		Bond Angles (°)		Dihedral Angles (°)	
R(5,6)	1.396	A(12,11,13)	123.287	D(7,1,2,3)	179.904
R(5,11)	1.478	A(14,17,18)	123.601	D(26,28,31,35)	179.466
R(11,12)	1.225	A(17,19,36)	109.920	D(23,26,28,31)	179.348
R(11,13)	1.237	A(17,19,43)	111.728	D(34,29,33,31)	178.780
R(14,17)	1.487	A(18,20,23)	121.621	D(30,27,29,33)	178.567
R(17,18)	1.353	A(20,23,26)	106.571	D(27,29,33,47)	178.540
R(17,19)	1.489	A(24,23,25)	122.540	D(27,26,28,32)	178.060
R(18,20)	1.438	A(24,23,26)	108.661	D(21,20,23,25)	172.627
R(18,22)	1.236	A(29,33,47)	120.818	D(18,20,23,24)	165.043
R(19,36)	1.547	A(19,36,37)	119.031	D(37,36,38,40)	159.413
R(19,43)	1.532	A(37,36,38)	119.898	D(43,19,36,37)	159.246
R(20,23)	1.732	A(36,38,40)	123.276	D(24,23,26,28)	155.110
R(23,24)	1.461	A(39,38,40)	113.775	D(15,14,17,19)	152.093
R(23,25)	1.462	A(38,40,41)	103.288	D(29,33,47,50)	147.380
R(38,39)	1.015	A(19,43,44)	108.546	D(17,19,36,38)	115.254

3.2 Molecular Electrostatic Potential (MEP)

The use of molecular surfaces based on the molecular electron density, such as the molecular electrostatic potential (MEP), has a long tradition in the qualitative interpretation of chemical reactivity [13, 14]. Molecular electrostatic potentials (MEPs) have been used for interpreting and predicting the reactive behavior of a wide variety of chemical systems for both electrophilic and nucleophilic reactions. The molecular electrostatic potentials of the arylsulfonylureido compounds 1-4 were evaluated using the B3LYP/6-31G (d,p) method and the projection of MEP surface is given in Figure 2.


Compound 1 **Compound 2**

Compound 3 **Compound 4**

Fig 2: Molecular electrostatic potential surface of arylsulfonylureido compounds 1-4

In all molecules, the regions exhibiting the negative electrostatic potential are localized on sulfamide function, hydroxamic acid function and nitro group; 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 $\nabla f(\mathrm{r}).\mathrm{n}(\mathrm{r}) = 0$, 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.

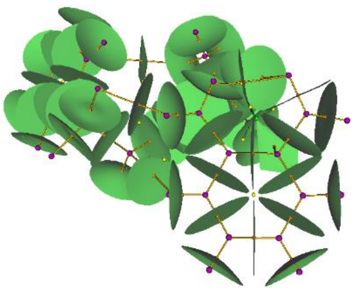


Fig 3: Plots of the interbasin surfaces of compound 1

The number of interbasin surfaces is 56 for compounds 1-3 and 59 for compounds 4.

3.4 Frontier Molecular Orbitals (FMOs)

The energies and distributions of the frontier molecular orbitals, HOMO and LUMO, are very important descriptors in computational Chemistry. They help in demonstrating the chemical reactivity, active sites, and kinetic stability of the molecule. The HOMO, in addition to HOMO-1, HOMO-2 etc. molecular orbitals, represents the ability to donate an electron and the LUMO. In addition to LUMO+1, LUMO+2 etc. molecular orbitals, it represents the ability to gain an electron. In order to evaluate the energetic behavior of the molecules under investigation, the FMO calculations of compound 4 (the most reactive compound) were carried out at DFT/B3LYP with 6-31G (d,p) basis set and visualized in Figure 4.

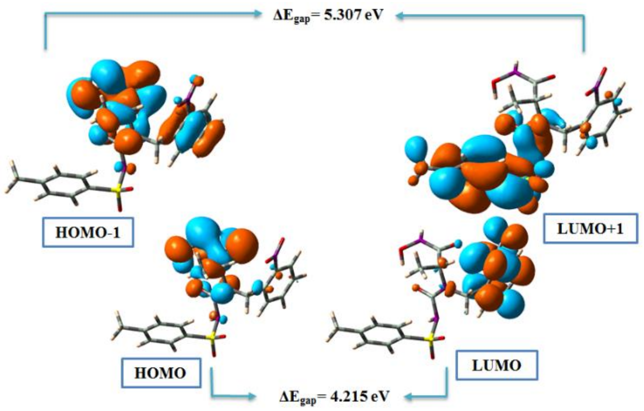


Fig 4: HOMO-LUMO Structure with the energy level diagram of compound 4

HOMO is confined over the hydroxamic acid and LUMO is confined over the nitrobenzene, while HOMO-1 is localised on both of the hydroxamic acid and the nitrobenzene and LUMO+1 is localised on 5-methyl-2-nitrophenyl for compound **4** which gives charge transfer process in the molecular system.

3.4 Global Reactivity Descriptors

The concept of hardness (η) and softness is related to a compound's reactivity and is a property that measures the extent of chemical reactivity to which the addition of a charge stabilizes the system. The chemical potential (μ) provides a global reactivity index and is related to charge transfer from a system of higher chemical potential to one of lower chemical potential. Electronegativity (χ) is the power to attract electrons and is directly related to all the previously mentioned properties. The HOMO and LUMO are also very popular quantum chemical parameters which determine the molecular reactivity. The HOMO and LUMO energies, the energy gap (ΔE), the ionization potential (*I*), the electron affinity (*A*), the absolute electronegativity (χ), the absolute hardness (η) and softness (*S*) for the arylsulfonylureido compounds 1-4 have been calculated at B3LYP/6-31G (d,p) basis set and the result are given in Table 5.

Table 5: Quantum chemical descriptors of arylsulfonylureido compounds 1-4

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
E_{HOMO} (eV)	-6.619	-6.669	-6.689	-6.592
E_{LUMO} (eV)	-2.402	-2.441	-2.457	-2.377
ΔE_{gap} (eV)	4.216	4.228	4.232	4.215
I (eV)	6.619	6.669	6.689	6.592
A (eV)	2.402	2.441	2.457	2.377
μ (eV)	-4.510	-4.555	-4.573	-4.484
χ (eV)	4.510	4.555	4.573	4.484
η (eV)	2.108	2.114	2.116	2.107
S (eV)	0.237	0.237	0.236	0.237
ω (eV)	4.825	4.908	4.941	4.771

The compound which has the lowest energy gap is the compound 4 (ΔE_{gap} = 4.215 eV). This lower gap allows it to be the softest molecule. The compound that has the highest energy gap is the compound 3 (ΔE_{gap} = 4.232 eV). The compound that has the highest HOMO energy is the compound 4 (E_{HOMO} = -6.592 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} = -2.457 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 4 has the lowest value of the potential ionization (*I* = 6.592 eV), so that will be the better electron donor. Compound 3 has the largest value of the affinity (*A* = 2.457 eV), so it is the better electron acceptor. The chemical reactivity varies with the structure of molecules. Chemical hardness (softness) value of compound 4 (η = 2.107 eV, S = 0.237 eV) is lesser (greater) among all the molecules. Thus, compound 4 is found to be more reactive than all the compounds. Compound 3 possesses higher electronegativity value (χ = 4.573 eV) than all compounds so; it is the best electron acceptor. The value of ω for compound 3 (ω = 4.941 eV) indicates that it is the stronger electrophiles than all compounds. Compound 4 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.

3.5 Mulliken Analysis

It is clear that Mulliken populations yield one of the simplest pictures of charge distribution and Mulliken charges render net atomic populations in the molecule. This calculation which depicts the charges of the every atom in the molecule distribution of positive and negative charges are vital to increase or decrease of bond length between the atoms. The atomic charges have an important role in the application of quantum chemical calculation to molecular system because atomic charges effect dipole moment, molecular polarizability, electronic structure, acidity-basicity behavior and a lot of properties of molecular system [15]. Mulliken charges predict the net atomic populations in the molecules 1-4 and it is calculated by the B3LYP/6-31G (d,p) method of compound 4 which is the most reactive and are detailed in a Mulliken's plot as visualized in Figure 5.

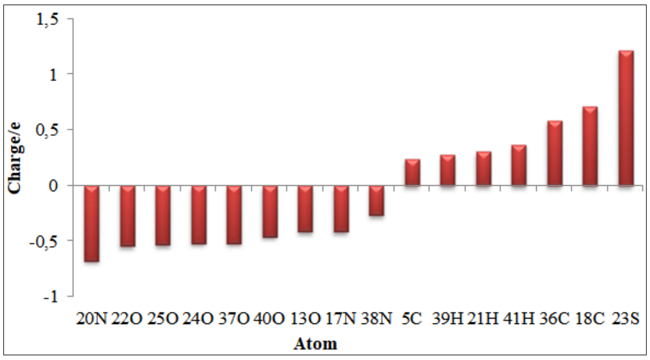


Fig 5: Mulliken's plot of compound 4

The atom 20N shows more negative (-0.677009e) charge and 23S more positive (1.218843e) charge, which suggests extensive charge delocalization in the entire molecule. The charge noticed on the 17N and 38N is smaller in the molecule and equal to -0.414057e, -0.267639e respectively. This can be explained by the high degree of conjugation, with a strong push-pull effect. Negatively charged oxygen (22O, 25O, 24O, 37O, 40O and 13O) atoms shows that charge is transferred from sulfur to oxygen and from azote to oxygen. The maximum atomic charge of carbons is obtained for 5C, 36C and 18C. This is due to the attachment of negatively charged azote and oxygen. The positive charges are localized on the hydrogen atoms. Very similar values of positive charges are observed for the hydrogen atoms (39H, 21H and 41H (0.27~0.36e)) bonded to the negative atoms (38N, 20N and 40O) respectively.

3.6 Natural Bond Orbital Analysis (NBO)

Natural bond orbital analysis provide an efficient method for studying intra and inter molecular bonding and interaction among bonds, and provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems [16]. The bonding-anti bonding interaction can be quantitatively described in terms of the NBO approach that is expressed by means of second-order perturbation interaction energy E (2) [17-19]. The stabilization energy E (2) values of the arylsulfonylureido compounds 1-4 were calculated on the basis of second-order Fock matrix perturbation theory using B3LYP/6-31G (d,p) basis set. The larger E (2) values were listed in Tables 6-9.

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 (3) O13	1.46704	π*(N11-O12)	0.59459	152.33	0.15	0.138
LP (1) N17	1.64148	π*(C18-O22)	0.37745	78.38	0.25	0.126
LP (1) N39	1.72833	π*(C37-O38)	0.23573	27.35	0.43	0.098
LP (2) O22	1.85250	σ*(C18-N20)	0.08543	26.83	0.63	0.118
π (C4-C5)	1.63590	π*(N11-O12)	0.59459	25.37	0.14	0.057
π (C31-C33)	1.63723	π*(C26-C28)	0.39102	24.64	0.26	0.072
LP (2) O38	1.85844	σ*(C37-N39)	0.07795	24.62	0.71	0.120
π (C2-C3)	1.63406	π*(C4-C5)	0.39929	22.39	0.27	0.071
π (C1-C6)	1.63950	π*(C2-C3)	0.31214	21.00	0.28	0.070
π (C27-C29)	1.64572	π*(C31-C33)	0.30901	20.76	0.28	0.069
π (C4-C5)	1.63590	π*(C1-C6)	0.29867	20.58	0.29	0.070
π (C26-C28)	1.68823	π*(C27-C29)	0.30008	20.56	0.30	0.070
π (C1-C6)	1.63950	π*(C4-C5)	0.39929	20.13	0.28	0.067
LP (2) O38	1.85844	σ*(C19-C37)	0.07961	19.88	0.60	0.099
LP (2) O12	1.89230	σ*(N11-O13)	0.06652	19.78	0.69	0.105
π (C27-C29)	1.64572	π*(C26-C28)	0.39102	19.44	0.27	0.065
LP (3) O25	1.77317	σ*(N20-S23)	0.28396	19.27	0.38	0.078
LP (2) O13	1.90349	σ*(N11-O12)	0.05419	19.16	0.72	0.106
π (C31-C33)	1.63723	π*(C27-C29)	0.30008	18.98	0.28	0.066
π (C2-C3)	1.63406	π*(C1-C6)	0.29867	18.45	0.28	0.066

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 (3) O13	1.46735	π*(N11-O12)	0.59405	152.14	0.15	0.138
LP (1) N17	1.64030	π*(C18-O22)	0.37806	78.79	0.25	0.126
LP (1) N38	1.72730	π*(C36-O37)	0.23626	27.51	0.43	0.098
LP (2) O22	1.85263	σ*(C18-N20)	0.08577	26.91	0.63	0.118
π (C31-C33)	1.62993	π*(C26-C28)	0.39972	25.32	0.28	0.075
π (C4-C5)	1.63603	π*(N11-O12)	0.59405	25.29	0.14	0.057
LP (2) O37)	1.85828	σ*(C36-N38)	0.07792	24.62	0.71	0.120
π (C27-C29)	1.66967	π*(C31-C33)	0.36044	24.06	0.28	0.074
π (C2-C3)	1.63409	π*(C4-C5)	0.39965	22.40	0.27	0.071
π (C26-C28)	1.69047	π*(C27-C29)	0.30719	22.40	0.29	0.073
LP (3) F47	1.90742	π*(C31-C33)	0.36044	21.67	0.42	0.091
π (C1-C6)	1.63890	π*(C2-C3)	0.31243	21.02	0.28	0.070
π (C4-C5)	1.63603	π*(C1-C6)	0.29845	20.55	0.29	0.070
π (C1-C6)	1.63890	π*(C4-C5)	0.39965	20.18	0.28	0.067
LP (2) O37	1.85828	σ*(C19-C36)	0.07964	19.90	0.60	0.099
LP (2) O12	1.89221	σ*(N11-O13)	0.06657	19.79	0.69	0.105
LP (2) O13	1.90346	σ*(N11-O12)	0.05417	19.15	0.72	0.106
LP (3) O25	1.77305	σ*(N20-S23)	0.28325	18.60	0.38	0.077
π (C2-C3)	1.63409	π*(C1-C6)	0.29845	18.43	0.28	0.066
LP (2) O24	1.80974	σ*(S23-C26	0.20311	18.37	0.45	0.082

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 (3) O13	1.46734	π*(N11-O12)	0.59378	152.12	0.15	0.138
LP (1) N17	1.63880	π*(C18-O22)	0.37817	79.18	0.25	0.126
LP (1) N38	1.72628	π*(C36-O37)	0.23623	27.52	0.43	0.098
LP (2) O22	1.85242	σ*(C18-N20)	0.08647	27.09	0.63	0.118
π (C4-C5)	1.63619	π*(N11-O12)	0.59378	25.20	0.15	0.057
LP (2) O37	1.85818	σ*(C36-N38)	0.07792	24.61	0.71	0.120
π (C31-C33)	1.65206	π*(C26-C28)	0.39291	22.54	0.28	0.072
π (C2-C3)	1.63415	π*(C4-C5)	0.39978	22.41	0.27	0.071
π (C27-C29)	1.65074	π*(C31-C33)	0.37394	21.87	0.27	0.069
π (C26-C28)	1.68336	π*(C27-C29)	0.29521	21.21	0.30	0.071
π (C1-C6)	1.63861	π*(C2-C3)	0.31259	21.03	0.28	0.070
π (C4-C5)	1.63619	π*(C1-C6)	0.29837	20.54	0.29	0.070
π (C1-C6)	1.63861	π*(C4-C5)	0.39978	20.20	0.28	0.067
LP (2) O37	1.85818	σ*(C19-C36)	0.07963	19.90	0.60	0.099
LP (2) O12	1.89216	σ*(N11-O13)	0.06661	19.79	0.69	0.105
LP (2) O13	1.90338	σ*(N11-O12)	0.05416	19.15	0.72	0.106
LP (2) O24	1.80940	σ*(S23-C26)	0.20518	18.52	0.45	0.082
LP (3) O25	1.77307	σ*(N20-S23)	0.28150	18.50	0.39	0.076
π (C27-C29)	1.65074	π*(C26-C28)	0.39291	18.49	0.27	0.064
π (C2-C3)	1.63415	π*(C1-C6)	0.29837	18.43	0.28	0.066

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 (3) O13	1.46700	π^*(N11-O12)	0.59472	152.33	0.15	0.138
LP (1) N17	1.64314	π^*(C18-O22)	0.37761	78.09	0.25	0.126
LP (1) N38	1.72843	π^*(C36-O37)	0.23607	27.44	0.43	0.098
π (C29-C33)	1.61689	π^*(C26-C27)	0.40144	26.90	0.26	0.075
LP (2) O22	1.85287	σ^*(C18-N20)	0.08473	26.66	0.63	0.118
π (C4-C5)	1.63577	π^*(N11-O12)	0.59472	25.40	0.14	0.058
LP (2) O37	1.85851	σ^*(C36-N38)	0.07797	24.62	0.71	0.120
π (C2-C3)	1.63420	π^*(C4-C5)	0.39897	22.40	0.27	0.071
π (C28-C31)	1.65534	π^*(C29-C33)	0.32504	21.77	0.29	0.071
π (C26-C27)	1.68905	π^*(C28-C31)	0.30065	21.09	0.30	0.071
π (C1-C6)	1.63992	π^*(C2-C3)	0.31202	20.99	0.28	0.070
π (C4-C5)	1.63577	π^*(C1-C6)	0.29884	20.60	0.29	0.070
π (C1-C6)	1.63992	π^*(C4-C5)	0.39897	20.10	0.28	0.067
LP (2) O37	1.85851	σ^*(C19-C36)	0.07956	19.86	0.60	0.099
LP (2) O12	1.89240	σ^*(N11-O13)	0.06642	19.77	0.69	0.105
LP (3) O25	1.77325	σ^*(N20-S23)	0.28637	19.35	0.38	0.078
LP (2) O13	1.90345	σ^*(N11-O12)	0.05425	19.16	0.72	0.106
π (C2-C3)	1.63420	π^*(C1-C6)	0.29884	18.46	0.28	0.066
π (C28-C31)	1.65534	π^*(C26-C27)	0.40144	18.43	0.27	0.063
LP (3) O24	1.77484	σ^*(N20-S23)	0.28637	18.42	0.38	0.076

The intra molecular interaction for the title compounds is formed by the orbital overlap between: π (C4-C5) and π^*(N11-O12) for compound 1, π (C31-C33) and π^*(C26-C28) for compound 2, π (C4-C5) and π^*(N11-O12) for compound 3 and π (C29-C33) and π^*(C26-C27) for compound 4 respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of π (C4-C5) to π^*(N11-O12) for compound 1, π (C31-C33) to π^*(C26-C28) for compound 2, π (C4-C5) to π^*(N11-O12) for compound 3 and π (C29-C33) to π^*(C26-C27) for compound 4 lead to highest stabilization of 25.37, 25.32, 25.20 and 26.90 kJ mol^{-1} respectively. In case of LP (3) O13 orbital to the π^*(N11-O12) for compound 1, LP (3) O13 orbital to π^*(N11-O12) for compound 2, LP (3) O13 orbital to π^*(N11-O12) for compound 3, LP (3) O13 orbital to π^*(N11-O12) for compound 4 respectively, show the stabilization energy of 152.33, 152.14, 152.12 and 152.33 kJ mol^{-1} respectively.

Nonlinear Optical Properties (NLO)

NLO effects arise from the interactions of electromagnetic fields with certain media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics [20]. Hyperpolarizability are very sensitive to the basis sets and level of theoretical approach employed [21, 22], that the electron correlation can change the value of hyperpolarizability. Theoretically calculated values of first order hyperpolarizability, dipole moments, total polarizability and anisotropy of the polarizability of title compounds are calculated at the DFT method with B3LYP/6-31G (d,p) basis set and mentioned in Table 10.

Table 10: Nonlinear optical properties of arylsulfonylureido compounds 1-4

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
β_{xxx}	-146.1759	-71.7268	-13.5606	-160.0303
β_{yyy}	23.0510	41.4421	41.1058	36.0247
β_{zzz}	-28.4566	-27.8100	-28.5620	-28.3283
β_{xyy}	43.5264	32.6256	26.9449	34.5995
β_{xxy}	-17.3776	-82.5928	-98.4063	-31.1814
β_{xxz}	-63.3170	-65.9337	-69.4944	-63.3416
β_{xzz}	-8.1067	-27.2937	-13.3124	-6.8155
β_{yzz}	9.0744	12.3936	8.7251	7.8758
β_{yyz}	-15.3220	-18.4986	-22.2643	-19.2896
β_{xyz}	-17.7700	-19.0174	-19.7793	-17.9473
β_{tot}(esu)x10^{-33}	154.0854	133.5425	129.7561	173.0979
μ_x	-4.3657	-3.1188	-2.6716	-4.8282
μ_y	-0.9186	-1.9104	-2.2682	-0.8066
μ_z	-2.3680	-2.3859	-2.4611	-2.3959
μ(D)	5.0508	4.3668	4.2824	5.4500
α_{xx}	-157.1862	-171.6961	-182.1261	-157.6446
α_{yy}	-182.2068	-189.4863	-197.7003	-191.5938
α_{zz}	-169.0579	-172.1649	-180.1996	-175.8922
α_{xy}	-24.6449	-17.1887	-15.9022	-25.1557
α_{xz}	-5.8841	-6.8517	-7.6200	-7.2258
α_{yz}	9.0780	9.0108	9.2732	8.5089
α(esu)x10^{-24}	51.4115	39.7385	38.3025	56.0205
$\Delta\alpha$(esu)x10^{-24}	7.6192	5.8892	5.6764	8.3022

Since the values of the polarizabilities (Δα) and the hyperpolarizabilities (β_{tot}) 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 5.0508, 4.3668, 4.2824 and 5.4500 D respectively, which are approximately four and five 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 51.4115 x 10^{-24}, 39.7385 x 10^{-24}, 38.3025 x 10^{-24} and 56.0205 x 10^{-24} esu respectively; the values of anisotropy of the polarizability are 7.6192, 5.8892, 5.6764 and 8.3022 esu, respectively. The magnitude of the molecular hyperpolarizability (β_{tot}) is one of the important key factors in a NLO system. The DFT/6-31G (d,p) calculated first hyperpolarizability value (β_{tot}) of arylsulfonylureido compounds are equal to 154.0854 x 10^{-33}, 133.5425 x 10^{-33}, 129.7561 x 10^{-33} and 173.0979 x 10^{-33} esu. The first hyperpolarizability of title molecules is approximately 0.44, 0.38, 0.37 and 0.50 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

Quantum chemical calculations of arylsulfonylureido compounds 1-4 have been performed at DFT level of theory using B3LYP functional and 6-31G (d,p) as basis set. The optimized parameters of the molecules 1-4 are determined. The MEP map shows that the negative potential sites are on sulfamide function, hydroxamic acid function and nitro group, while the positive potential sites are around the hydrogen atoms. The values of the energies gap between the HOMO and LUMO reveals that charge transfer may be taking place within molecules. Chemical activity has been measured by reactivity descriptors and the results show that compound 4 has the high chemical reactivity. In addition, Mulliken population analysis on atomic charges was also calculated and the result show that 23S atom has a largest positive atomic charge and 20N atom has a largest negative atomic charge. The NBO analysis shows strong intermolecular hyper conjugative interactions of π electron. The strong delocalization of π electron in the molecule leading to a stabilization of the molecule. The calculated first hyperpolarizability of the title compounds is lesser that of the standard NLO material urea and is not an attractive object for future studies of nonlinear optics.

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6. References

1. Hansch C, Sammes PG, Taylor JB. Comprehensive Medicinal Chemistry, vol.2, Pergamon Press, Oxford, (Chapter 7), 1990.
2. Hanson PR, Probst DA, Robinson RE, Yau M. Cyclic sulfonamides via the ring-closing metathesis reaction. Tetrahedron Lett. 1999; 40(26):4761-4764. https://doi. org/ 10.1016/S0040-4039(99)00878-3
3. McKerrow JH, James MNG. In Perspecti V es in Drug Discovery and Design; Anderson PS, Kenyon GL, Marshall GR, Eds.; ESCOM Science Publishers: Leiden. 1996; 6:1-120.
4. Roush WR, Gwaltney SL, Cheng J, Scheidt KA, McKerrow JH, Hansell E. Vinyl Sulfonate Esters and Vinyl Sulfonamides: Potent, Irreversible Inhibitors of Cysteine Proteases. J. Am. Chem. Soc. 1998; 120:42 10994-10995. https://doi.org/10.1021/ja981792o
5. Parr RG, Yang W. Density-Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.
6. Hohenberg P, Kohn W. Inhomogeneous Electron Gas. Phys. Rev. B. 1964; 136(3B):864-871. https:// doi. org/10.1103/PhysRev.136.B864
7. Kohn W, Sham LJ. Self-Consistent Equations Including Exchange and Correlation Effects. Phys. Rev. A. 1965; 140(4A): 1133-1138. https://doi.org/10. 1103/ PhysRev.140.A1133
8. Parr RG, Yang W. Density-Functional Theory of the Electronic Structure of Molecules. Annu. Rev. Phys. Chem. 1995; 46:701-728. https://doi.org/10.1146/ annurev.pc.46.100195.003413
9. Ayers PW, Parr RG. Variational Principles for Describing Chemical Reactions: The Fukui Function and Chemical Hardness Revisited. J. Am. Chem. Soc. 2000; 122(9):2010-2018. https://doi.org/ 10.1021/ja9924039
10. Geerlings P, Proft FDe, Langenaeker W. Conceptual density functional theory. Chem. Rev. 2003; 103(5):1793-1873. https://doi.org/10.1021/cr990029p
11. Clare BW, Scozzafava A, Supuran CT. Protease Inhibitors: Synthesis of a Series of Bacterial Collagenase Inhibitors of the Sulfonyl Amino Acyl Hydroxamate Type. J. Med. Chem. 2001; 44(13): 2253-2258. https://doi.org/10.1021/jm010087e
12. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09, Revision C.01; Gaussian Inc.: Wallingford, CT, USA, 2010.
13. Politzer P, Truhlar DG. Chemical Applications of Atomic and Molecular Electrostatic Potentials: Reactivity, Structure, Scattering and Energies of Organic, Inorganic and Biological Systems, Plenum, New York, 1981.
14. Ehresmann B, Martin B, Horn AHC, Clark T. Local molecular properties and their use in predicting reactivity. J. Mol. Model. 2003; 9(5):342-347. https://doi.org/10.1007/s00894-003-0153-x
15. Sidir I, Sidir YG, Kumalar M, Tasal E. Ab initio Hartree-Fock and density functional theory investigations on the conformational stability, molecular structure and vibrational spectra of 7-acetoxy-6-(2,3-dibromopropyl)-4,8-dimethylcoumarin molecule. J. Mol. Struct. 2010; 964(1-3): 134-151. https://doi.org/10.1016/j.molstruc.2009.11.023
16. Reed AE, Weinhold F. Natural localized molecular orbitals. J. Chem. Phys. 1985; 83(4): 1736-1740. https://doi.org/10.1063/1.449360
17. Reed AE, Weinhold RB, Weinhold F. Natural population analysis. J. Chem. Phys. 1985; 83(2): 735-746. https://doi.org/10.1063/1.449486

18. Reed AE, Weinhold F. Natural bond orbital analysis of near-Hartree-Fock water dimer. J. Chem. Phys. 1983; 78(6): 4066-4073. https://doi.org/10.1063/1.445134
19. Foster JP, Weinhold F. Natural hybrid orbitals. J. Am. Chem. Soc. 1980; 102(24):7211-7218. https://doi.org/10.1021/ja00544a007
20. Sun YX, Hao QL, Wei WX, Yu ZX, Lu LD, Wang X, Wang YS. Experimental and density functional studies on 4-(3, 4-dihydroxybenzylideneamino)antipyrine, and 4-(2,3,4-trihydroxybenzylideneamino)antipyrine. J. Mol. Struct. Theochem. 2009; 904(1-3):74-82. https://doi.org/10.1016/j.theochem.2009.02.036
21. Henriksson J, Saue T, Norman P. Quadratic response functions in the relativistic four-component Kohn-Sham approximation. J. Chem. Phys. 2008; 128(2):024105-1-024105-9. https://doi.org/10.1063/1.2816709
22. Hermann JP, Ricard D, Ducuing J. Optical nonlinearities in conjugated systems: β-carotene. Appl. Phys. Lett. 1973; 23(4):178-180. https://doi.org/10.1063/1.1654850