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Research Article

Quantum Chemical Calculations of (2-Amino, 3-Amino, 4-Amino and 4-Hydrazino) Benzene Sulfonamides Compounds by DFT

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Abstract

This study represents an integral approach towards understanding the electronic properties of (2-amino, 3-amino, 4-amino and 4-hydrazino) benzene sulfonamides compounds **1-4** by DFT/B3LYP method using 6-31G (d,p) to predict their applications. The geometrical parameters of these compounds are obtained by the same method. The predicted MEP figure revealed the negative regions of the molecules, was subjected to the electrophilic attack of this compounds. The calculated HOMO and LUMO energies confirm that charge transfer occurs within the molecules. The structure-chemical reactivity relations of the compounds were determined through global reactivity descriptors by conceptual DFT methods. Mulliken population analysis was also carried out.NBO analysis was made and it indicated the intra molecular charge transfer between the bonding and anti-bonding orbitals. The linear polarizability (α) and the first order hyper polarizability (β_{tot}) values of the title compounds have been computed and results illustrated that the compounds **1-4** might have not the NLO behavior.

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

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1. Introduction

The sulfonamide -SO_2NH- group occurs in numerous biologically active compounds that constitute an important class of drugs used extensively as pharmaceutical and agricultural agents [1]. Benzene sulfonamides have been showing an ample variety of biological activities such as antibacterial [2], insecticidal [3] antifungal [4], anti-hepatitis [5], anti-inflamatory [6] anti HIV [7] and anti-tubercular activities [8].

The density functional theory [9,10] is an effective tool in quantum chemistry for evaluation of the molecular structures, spectral analysis, intra-/intermolecular interactions and nature of chemical reactions. It is a computational method that derives properties based on a determination of the electron density.

The aim of the work is to investigate a complete description of the molecular structures, molecular electrostatic potential surface, frontier molecular orbital, quantum chemical descriptors, Mulliken atomic charge, natural bond orbital (NBO) analysis and NLO properties of (2-amino, 3-amino, 4-amino and 4-hydrazino) benzene sulfonamides compounds **1-4** described in literature [11] using the B3LYP with 6-31G (d,p) basis set in-view of its biological and pharmaceutical importance.

2. Materials and methods

All calculations were performed by a personal computer using GAUSSIAN 09 package program [12] and the obtained results were visualized with the aid of Gauss View 05 software [13].

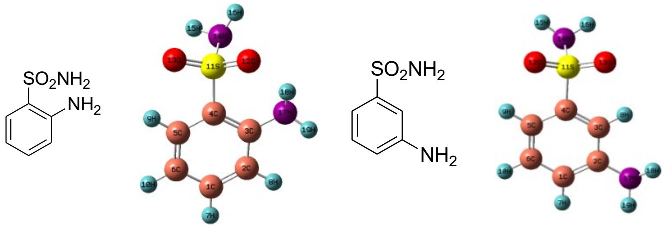
3. Results and discussion

3.1. Molecular Geometry

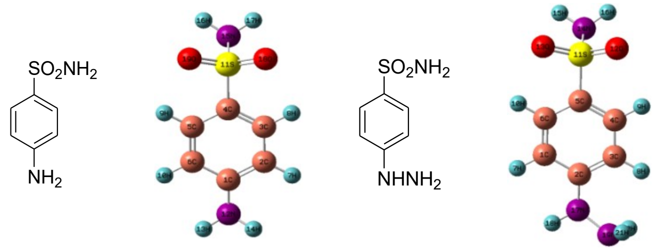
The molecular structures along with numbering of atoms of (2-amino, 3-amino, 4-amino and 4-hydrazino) benzene sulfonamides compounds **1-4** were obtained from Gaussian 09 and GAUSSVIEW programs as shown in Figure 1.

The optimized structural parameters (bond lengths, bond angles and dihedral angles) calculated by DFT (B3LYP) with 6-31G (d,p) basis set are given in Tables 1-4.

Figure 1: Optimized molecular structure of (2-amino, 3-amino, 4-amino and 4-hydrazino) benzene sulfonamides compounds **1-4**



Compound **1** Compound **2**



Compound **3** Compound **4**

Table 1: Optimized geometric parameters of compound **1**

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,6)	1.400	A(2,1,6)	121.042	D(7,1,6,5)	179.990
R(2,3)	1.412	A(3,2,8)	118.438	D(4,5,6,10)	179.958
R(2,8)	1.087	A(2,3,4)	116.699	D(8,2,3,4)	179.746
R(3,4)	1.419	A(2,3,17)	120.397	D(17,3,4,5)	179.508
R(3,17)	1.375	A(4,3,17)	122.879	D(6,1,2,8)	179.286
R(4,5)	1.400	A(4,11,14)	102.969	D(11,4,5,6)	178.868
R(4,11)	1.780	A(12,11,13)	120.359	D(3,4,5,9)	178.336
R(6,10)	1.084	A(12,11,14)	104.184	D(4,3,17,19)	164.874
R(11,12)	1.475	A(13,11,14)	110.203	D(5,4,11,12)	144.459
R(11,13)	1.466	A(11,14,15)	110.254	D(13,11,14,16)	96.879
R(11,14)	1.697	A(11,14,16)	108.014	D(4,11,14,15)	91.065
R(14,15)	1.018	A(15,14,16)	110.709	D(3,4,11,14)	74.832
R(14,16)	1.018	A(3,17,18)	116.432	D(4,3,17,18)	24.362
R(17,18)	1.013	A(3,17,19)	115.997	D(5,4,11,13)	11.522
R(17,19)	1.009	A(18,17,19)	115.216	D(8,2,3,17)	1.507

Table 2: Optimized geometric parameters of compound **2**

Bond Length(Å)		Bond Angles (°)		Dihedral Angles (°)	
R(1,2)	1.407	A(1,2,17)	120.914	D(2,3,4,11)	179.990
R(1,7)	1.087	A(3,4,11)	118.331	D(11,4,5,6)	179.882
R(2,3)	1.405	A(5,4,11)	119.141	D(7,1,2,3)	179.837
R(2,17)	1.392	A(4,11,12)	107.968	D(4,5,6,10)	179.741
R(3,4)	1.391	A(4,11,13)	107.797	D(1,2,3,8)	179.002
R(3,8)	1.085	A(4,11,14)	103.600	D(3,4,5,9)	178.078
R(4,11)	1.794	A(12,11,13)	122.144	D(17,2,3,4)	177.611
R(6,10)	1.086	A(12,11,14)	106.497	D(5,4,11,13)	162.015
R(11,12)	1.466	A(13,11,14)	107.346	D(3,2,17,19)	157.371
R(11,13)	1.468	A(11,14,15)	108.676	D(12,11,14,16)	130.805
R(11,14)	1.698	A(11,14,16)	109.226	D(4,11,14,15)	123.023
R(14,15)	1.017	A(15,14,16)	111.240	D(3,4,11,14)	96.152
R(14,16)	1.017	A(2,17,18)	115.557	D(5,4,11,12)	28.262
R(17,18)	1.010	A(2,17,19)	115.602	D(3,2,17,18)	23.382
R(17,19)	1.010	A(18,17,19)	112.249	D(12,11,14,15)	9.279

Table 3: Optimized geometric parameters of compound **3**

Bond Length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
R(1,2)	1.409	A(2,1,6)	118.744	D(2,3,4,11)	179.897
R(1,6)	1.409	A(2,1,12)	120.611	D(4,5,6,10)	179.782
R(1,12)	1.385	A(3,4,11)	119.806	D(6,1,2,7)	179.363
R(3,4)	1.397	A(4,11,15)	104.471	D(1,2,3,8)	178.636
R(3,8)	1.084	A(4,11,18)	107.841	D(3,4,5,9)	178.216
R(4,11)	1.779	A(4,11,19)	107.827	D(12,1,2,3)	177.634
R(5,6)	1.388	A(15,11,18)	106.534	D(2,1,12,13)	160.073
R(5,9)	1.084	A(15,11,19)	106.585	D(5,4,11,18)	156.459
R(11,15)	1.703	A(18,11,19)	122.247	D(19,11,15,17)	126.053
R(11,18)	1.468	A(1,12,13)	116.588	D(4,11,15,16)	119.498
R(11,19)	1.468	A(1,12,14)	116.589	D(3,4,11,15)	90.147
R(12,13)	1.010	A(13,12,14)	113.241	D(5,4,11,19)	22.646
R(12,14)	1.010	A(11,15,16)	108.556	D(2,1,12,14)	22.003
R(15,16)	1.017	A(11,15,17)	108.527	D(19,11,15,16)	5.496
R(15,17)	1.017	A(16,15,17)	110.847	D(12,1,6,10)	2.672

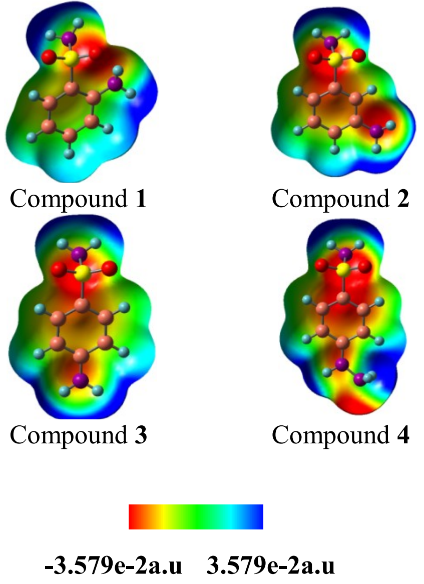
Table 4: Optimized geometric parameters of compound **4**

Bond Length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
R(1,6)	1.385	A(3,2,17)	121.849	D(8,3,4,5)	179.856
R(2,3)	1.408	A(4,5,11)	119.798	D(1,2,3,8)	179.634
R(2,17)	1.385	A(5,11,12)	107.933	D(7,1,6,5)	179.568
R(5,6)	1.400	A(5,11,14)	104.419	D(2,3,4,9)	178.887
R(5,11)	1.780	A(12,11,13)	122.276	D(17,2,3,4)	178.263
R(6,10)	1.084	A(12,11,14)	106.189	D(4,5,6,10)	178.109
R(11,12)	1.468	A(13,11,14)	106.987	D(3,2,17,18)	163.353
R(11,13)	1.468	A(11,14,15)	108.828	D(6,5,11,12)	155.972
R(11,14)	1.702	A(11,14,16)	108.365	D(18,17,19,20)	135.261
R(14,15)	1.017	A(15,14,16)	110.872	D(13,11,14,16)	122.797
R(14,16)	1.017	A(2,17,18)	116.347	D(5,11,14,15)	116.137
R(17,18)	1.010	A(2,17,19)	123.061	D(4,5,11,14)	89.214
R(17,19)	1.405	A(18,17,19)	112.145	D(2,17,19,21)	40.848
R(19,20)	1.017	A(17,19,21)	110.714	D(6,5,11,13)	22.157
R(19,21)	1.021	A(20,19,21)	108.033	D(3,2,17,19)	17.836

3.2. Molecular Electrostatic Potential (MEP)

Molecular electrostatic potential (MEP) mapping is very useful in the investigation of the molecular structure with its physiochemical property relationships [14-16].Molecular electrostatic potential (MEP) at a point in the space around a molecule gives an indication of the net electrostatic effect produced at that point by the total charge distribution (electron + nuclei) of the molecule and correlates with dipole moments, electron negativity, partial charges and chemical reactivity of the molecule [17,18]. Further it provides a visual method to understand the relative polarity of the molecules. The MEP was evaluated using the B3LYP/6-31G (d,p) method and the projection of MEP surface is shown in Figure 2.

Figure 2: Molecular electrostatic potential surface of (2-amino, 3-amino, 4-amino and 4-hydrazino) benzene sulfonamides compounds **1-4**


Compound **1** Compound **2**
Compound **3** Compound **4**

In all molecules, the regions exhibiting the negative electrostatic potential are localized on sulfamide function and amine group; while the regions presenting the positive potential are localized vicinity of the hydrogen atoms.

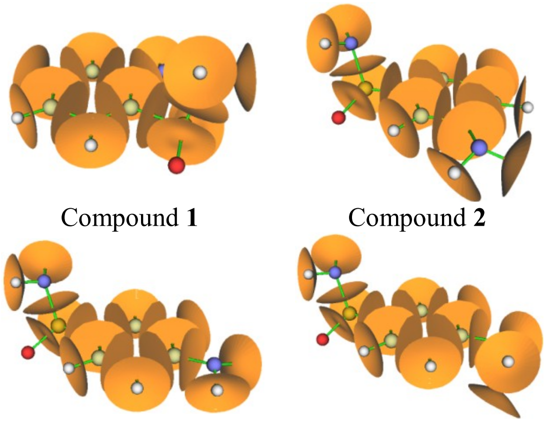
3.3. Basin Analysis

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.

Figure 3: Plots of the interbasin surfaces of compounds **1-4**



Compound **1** Compound **2**

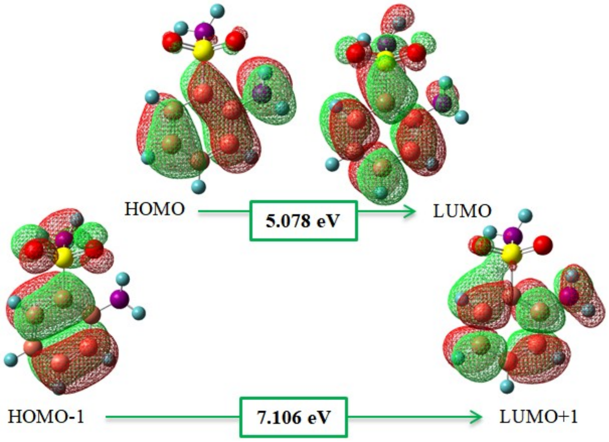
Compound **3** Compound **4**

The number of interbasin surfaces is 20, 19, 19 and 21 for compounds **1-4** respectively.

3.4. Frontier Molecular Orbitals (FMOs)

It is well known that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) which are the main orbitals taking part in chemical reaction are called as the frontier molecule orbitals (FMOs) [19]. The energy gap formed between HOMO and LUMO indicates the molecular chemical stability and is a critical parameter to determine molecular electrical transport properties and furthermore, the properties of the molecules such as the chemical reactivity, kinetic stability, polarizability, chemical hardness and softness, aromaticity and electronegativity can be determined by using this energy gap [20,21]. The molecules which have a large HOMO-LUMO energy gap are called as ‘‘hard molecules’’, while the molecules with a small HOMO-LUMO energy gap are called as ‘‘soft molecules’’. Therefore, the molecule with the least HOMO-LUMO gap becomes more reactive [20]. The HOMO-1, HOMO, LUMO and LUMO+1 orbitals and their transitions state were obtained using DFT/B3LYP method and 6-31G (d,p) basis set and shown in Figure 4 for compound **1** which is the most reactive.

Figure 4: HOMO-LUMO Structure with the energy level diagram of compound **1**



HOMO-1 is confined over the sulfamide function and benzene ring and LUMO is confined over the whole molecule, while HOMO and LUMO+1 are on amine group and benzene ring for compound **1** which gives charge transfer process in the molecular system.

3.5. Global Reactivity Descriptors

On the basis of frontier molecular orbitals (FMO) energies (HOMO, LUMO and Energy gap) the global reactivity descriptors such as electronegativity (χ), chemical potential (μ), global hardness (η), global softness (*S*) and global electrophilicity index (ω)[22] are calculated for (2-amino, 3-amino, 4-amino and 4-hydrazino) benzene sulfonamides compounds **1-4**using the DFT/B3LYP method and 6-31G (d,p) basis set and collected in Table 5. Considering, the chemical hardness, large HOMO-LUMO gap means a hard molecule and small HOMO-LUMO gap means a small molecule. One can also relate the stability of the molecule hardness, which means that the molecule with least HOMO-LUMO gap means it, is more reactive. Recently Parr *et al* have defined a new descriptor to quantity the global index which defines as quantitative classification of global electrophilic nature of the compounds.

Table 5: Quantum chemical descriptors of (2-amino, 3-amino, 4-amino and 4-hydrazino) benzene sulfonamides compounds **1-4**

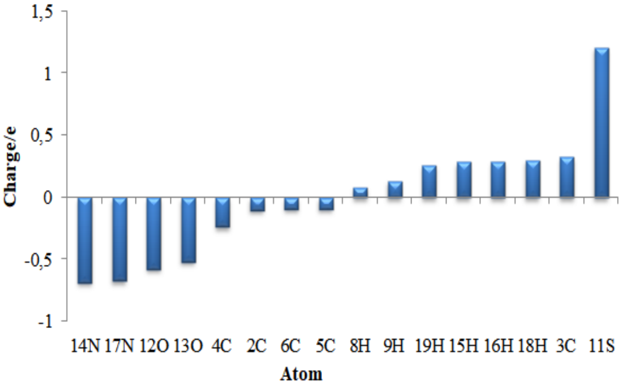
Parameters	Compound 1	Compound 2	Compound 3	Compound 4
E_{HOMO}(eV)	-5.863	-5.915	-5.983	-5.973
E_{LUMO}(eV)	-0.785	-0.777	-0.471	-0.588
ΔE_{gap} (eV)	5.078	5.137	5.512	5.385
I (eV)	5.863	5.915	5.983	5.973
A (eV)	0.785	0.777	0.471	0.588
μ (eV)	-3.324	-3.346	-3.227	-3.280
χ (eV)	3.324	3.346	3.227	3.280
η (eV)	2.539	2.569	2.756	2.693
S (eV)	0.197	0.195	0.181	0.186
ω (eV)	2.176	2.179	1.889	1.998

The compound which has the lowest energy gap is the compound **1** (ΔE_{gap} = 5.078 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} = 5.512 eV). The compound that has the highest HOMO energy is the compound **1** (E_{HOMO} = -5.863 eV). This higher energy allows it to be the best electron donor. The compound that has the lowest LUMO energy is the compound **1** (E_{LUMO} = -0.785 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* = 5.863 eV), so that will be the better electron donor. Compound **1** has the largest value of the affinity (*A* = 0.785 eV), so it is the better electron acceptor. The chemical reactivity varies with the structure of molecules. Chemical hardness (softness) value of compound **1** (η = 2.539 eV, **S** = 0.197 eV) is lesser (greater) among all the molecules. Thus, compound **1** is found to be more reactive than all the compounds. Compound **2** possesses higher electronegativity value (χ = 3.346 eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **2** (ω = 2.179 eV) indicates that it is the stronger electrophiles than all compounds. Compound **1** 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 atomic charge calculation has an important role in the application of quantum chemical calculation to molecular system because atomic charges affect dipole moment, molecular polarizability, electronic structure and more a lot of properties of molecular systems. Mulliken's population analysis provides a partitioning of either a total charge density or an orbital density [23-25]. The Mulliken population analysis of compound **1**which is the most reactive was performed in B3LYP/6-31G(d,p) level to obtain the values of the atomic charges and are detailed in a Mulliken's plot as visualized in Figure 5.

Figure 5: Mulliken's plot of compound **1**



The atom 14N shows more negative (-0.688288e) charge and 11S more positive (1.206882e) charge, which suggests extensive charge delocalization in the entire molecule. The charge noticed on the 17N is smaller and equal to -0.672336e. This can be explained by the high degree of conjugation, with a strong push-pull effect between the sulfamide group and amine group. Negatively charged oxygen (12O and 13O) atoms shows that charge is transferred from sulfur to oxygen. Carbon atoms 4C, 2C, 6C and 5C are more negatively charged which indicate that the charge transfer from sulfamide group to benzene ring. The maximum atomic charge of carbons is obtained for 3C. This is due to the attachment of negatively charged atom of azote 17N. The positive charges are localized on the hydrogen atoms. Very similar values of positive charges are observed for the hydrogen atoms (8H, 9H, 19H, 15H, 16H and 18H (0.082122, 0.131726, 0.260959, 0.285904, 0.292603 and 0.298273e) respectively) bonded to the negative atoms (2C, 5C, 17N, 14N, 14N and 17N) respectively.

3.7. Natural Bond Orbital Analysis (NBO)

Natural bond orbital analysis is an essential tool for studying intra- and intermolecular bonding interactions and also a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some orbitals are electron donor and some are acceptors, the energy difference between such bonding and anti-bonding orbitals makes the molecule susceptible for interactions [26,27]. The stabilization energy E (2) values of the (2-amino, 3-amino, 4-amino and 4-hydrazino) benzene sulfonamides 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 (1) N17	1.79203	π*(C3-C4)	0.47759	39.64	0.29	0.102
π (C3-C4)	1.65576	π*(C5-C6)	0.31958	25.08	0.30	0.078
π (C1-C2)	1.71367	π*(C3-C4)	0.47759	24.71	0.26	0.076
π (C5-C6)	1.68315	π*(C1-C2)	0.31686	24.11	0.28	0.074
LP (3) O12	1.79841	σ*(S11-O13)	0.15776	21.40	0.57	0.100
LP (3) O13	1.77831	σ*(S11-O12)	0.15489	21.15	0.55	0.098
LP (2) O13	1.81294	σ*(C4-S11)	0.18833	16.17	0.46	0.077
π (C1-C2)	1.71367	π*(C5-C6)	0.31958	15.11	0.29	0.059
LP (2) O12	1.82549	σ*(S11-N14)	0.24535	14.61	0.41	0.071
π (C5-C6)	1.68315	π*(C3-C4)	0.47759	14.60	0.26	0.057
LP (2) O13	1.81294	σ*(S11-N14)	0.24535	13.95	0.41	0.069
LP (2) O12	1.82549	σ*(C4-S11)	0.18833	13.94	0.46	0.072
LP (3) O13	1.77831	σ*(S11-N14)	0.24535	13.03	0.41	0.065
π (C3-C4)	1.65576	π*(C1-C2)	0.31686	12.73	0.30	0.055
LP (3) O12	1.79841	σ*(S11-N14)	0.24535	8.10	0.41	0.052
LP (1) N14	1.93133	σ*(S11-O13)	0.15776	7.13	0.64	0.062
π (C3-C4)	1.65576	σ*(S11-N14)	0.24535	5.08	0.39	0.041
σ (N17-H19)	1.98773	σ*(C3-C4)	0.03343	5.04	1.17	0.069
σ (C4-C5)	1.97494	σ*(C3-C4)	0.03343	4.60	1.24	0.068
LP (3) O12	1.79841	σ*(N17-H18)	0.02458	4.60	0.78	0.056

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) N17	1.83877	π*(C2-C3)	0.38942	28.00	0.32	0.090
π (C2-C3)	1.61086	π*(C4-C5)	0.41256	23.40	0.27	0.072
LP (3) O12	1.78109	σ*(S11-O13)	0.15774	21.39	0.56	0.100
π (C1-C6)	1.69549	π*(C2-C3)	0.38942	21.37	0.28	0.070
LP (3) O13	1.78195	σ*(S11-O12)	0.15401	20.96	0.57	0.099
π (C4-C5)	1.69237	π*(C1-C6)	0.33546	19.68	0.29	0.068
π (C1-C6)	1.69549	π*(C4-C5)	0.41256	18.79	0.27	0.066
π (C4-C5)	1.69237	π*(C2-C3)	0.38942	17.88	0.29	0.065
π (C2-C3)	1.61086	π*(C1-C6)	0.33546	17.31	0.28	0.063
LP (2) O13	1.82005	σ*(C4-S11)	0.19932	16.24	0.45	0.077
LP (2) O12	1.81866	σ*(C4-S11)	0.19932	16.18	0.45	0.076
LP (2) O12	1.81866	σ*(S11-N14)	0.24323	13.27	0.41	0.067
LP (2) O13	1.82005	σ*(S11-N14)	0.24323	12.98	0.41	0.066
LP (3) O13	1.78195	σ*(S11-N14)	0.24323	12.49	0.41	0.064
LP (3) O12	1.78109	σ*(S11-N14)	0.24323	11.96	0.41	0.063
σ (C4-C5)	1.97678	σ*(C3-C4)	0.02152	4.68	1.28	0.069
σ (C3-C4)	1.97518	σ*(C4-C5)	0.02349	4.66	1.29	0.069
π (C4-C5)	1.69237	σ*(S11-N14)	0.24323	4.39	0.39	0.037
σ (C3-H8)	1.97839	σ*(C4-C5)	0.02349	4.18	1.09	0.060
σ (N17-H18)	1.98858	σ*(C1-C2)	0.02281	4.17	1.20	0.063

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) N12	1.82141	π*(C1-C6)	0.40567	31.15	0.32	0.094
π (C1-C6)	1.60870	π*(C4-C5)	0.41733	28.79	0.27	0.080
π (C4-C5)	1.69091	π*(C2-C3)	0.31164	24.00	0.29	0.075
π (C2-C3)	1.70726	π*(C1-C6)	0.40567	22.91	0.28	0.073
LP (3) O18	1.78136	σ*(S11-O19)	0.15698	21.46	0.57	0.100
LP (3) O19	1.78129	σ*(S11-O18)	0.15684	21.44	0.57	0.100
LP (2) O19	1.82251	σ*(C4-S11)	0.19272	15.51	0.46	0.076
LP (2) O18	1.82252	σ*(C4-S11)	0.19272	15.50	0.46	0.076
π (C1-C6)	1.60870	π*(C2-C3)	0.31164	14.95	0.28	0.059
π (C2-C3)	1.70726	π*(C4-C5)	0.41733	14.83	0.27	0.059
π (C4-C5)	1.69091	π*(C1-C6)	0.40567	14.23	0.28	0.058
LP (2) O18	1.82252	σ*(S11-N15)	0.24694	13.76	0.41	0.068
LP (2) O19	1.82251	σ*(S11-N15)	0.24694	13.74	0.41	0.068
LP (3) O19	1.78129	σ*(S11-N15)	0.24694	11.52	0.40	0.061
LP (3) O18	1.78136	σ*(S11-N15)	0.24694	11.47	0.40	0.061
π (C4-C5)	1.69091	σ*(S11-N15)	0.24694	5.47	0.39	0.042
σ (C3-C4)	1.97658	σ*(C4-C5)	0.02398	4.39	1.27	0.067
σ (C4-C5)	1.97658	σ*(C3-C4)	0.02398	4.39	1.27	0.067
σ (N12-H13)	1.98872	σ*(C1-C2)	0.02278	4.10	1.20	0.063
σ (N12-H 14)	1.98872	σ*(C1-C6)	0.02278	4.10	1.20	0.063

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) N17	1.78431	π*(C2-C3)	0.01894	36.20	0.30	0.098
π (C2-C3)	1.62154	π*(C4-C5)	0.40358	28.15	0.27	0.079
π (C4-C5)	1.69842	π*(C1-C6)	0.29974	23.52	0.29	0.074
π (C1-C6)	1.71593	π*(C2-C3)	0.01894	22.28	0.28	0.073
LP (3) O12	1.78214	σ*(S11-O13)	0.15828	21.62	0.57	0.100
LP (3) O13	1.78023	σ*(S11-O12)	0.15563	21.30	0.57	0.100
LP (2) O13	1.82211	σ*(C5-S11)	0.19329	15.64	0.46	0.076
LP (2) O12	1.82225	σ*(C5-S11)	0.19329	15.45	0.46	0.076
π (C1-C6)	1.71593	π*(C4-C5)	0.40358	14.74	0.28	0.059
π (C2-C3)	1.62154	π*(C1-C6)	0.29974	14.54	0.29	0.059
LP (2) O12	1.82225	σ*(S11-N14)	0.24674	13.98	0.41	0.069
π (C4-C5)	1.69842	π*(C2-C3)	0.01894	13.81	0.28	0.057
LP (2) O13	1.82211	σ*(S11-N14)	0.24674	13.54	0.41	0.067
LP (3) O13	1.78023	σ*(S11-N14)	0.24674	11.91	0.41	0.062
LP (3) O12	1.78214	σ*(S11-N14)	0.24674	11.07	0.41	0.060
LP (1) N19	1.96434	σ*(C2-N17)	0.03466	8.18	0.79	0.072
LP (1) N17	1.78431	σ*(N19-H21)	0.01947	5.59	0.73	0.060
π (C4-C5)	1.69842	σ*(S11-N14)	0.24674	5.42	0.39	0.042
σ (C5-C6)	1.97652	σ*(C4-C5)	0.02395	4.38	1.28	0.067
σ (C4-C5)	1.97687	σ*(C5-C6)	0.02412	4.36	1.27	0.067

The intra molecular interaction for the title compounds is formed by the orbital overlap between: π (C3-C4) and π*(C5-C6) for compound **1**, π (C2-C3) and π*(C4-C5) for compound **2**, π (C1-C6) and π*(C4-C5) for compound **3** and π (C2-C3) and π*(C28-C30) for compound **4** respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of π (C3-C4) to π*(C5-C6) for compound **1**, π (C2-C3) to π*(C4-C5) for compound **2**, π (C1-C6) to π*(C4-C5) for compound **3** and π (C2-C3) to π*(C4-C5) for compound **4** lead to highest stabilization of 25.08, 23.40, 28.79 and 28.15 kJ mol^{-1} respectively. In case of LP (1) N17 orbital to the π*(C3-C4) for compound **1**, LP (1) N17 orbital to π*(C2-C3) for compound **2**, LP (1) N12 orbital to π*(C1-C6) for compound **3**, LP (1) N17 orbital to π*(C2-C3) for compound **4** respectively, show the stabilization energy of 39.64, 28.00, 31.15 and 36.20 kJ mol^{-1} respectively.

3.8. Nonlinear Optical Properties (NLO)

DFT calculations are efficient tool for designing non-linear optical (NLO) molecules and predicting some related properties such as molecular dipole moments, polarizabilities and hyperpolarizabilities [28-32]. The computation of polarizabilities and hyperpolarizabilities of the organic molecules are of great importance to studythe phenomenon induced by intermolecular interactions and nonlinear optical effects. In this direction, quantum chemical calculations of the title compounds were carried out using GAUSSIAN 09W package employing the B3LYP functional supplemented with standard 6-31G(d,p) basis set. The first static hyperpolarizability (β_{tot}) and its related properties (α, β and Δα) of (2-amino, 3-amino, 4-amino and 4-hydrazino) benzene sulfonamides compounds **1-4** have been calculated using B3LYP/6-31G (d,p) method based on finite-field approach and are presented in Table 10.

Table 10: Nonlinear optical properties of (2-amino, 3-amino, 4-amino and 4-hydrazino) benzene sulfonamides compounds **1-4**

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
β_{xxx}	8.9849	24.6345	56.0977	-38.8078
β_{yyy}	24.8543	-5.4141	-0.0534	1.4395
β_{zzz}	3.9603	-1.1527	-1.8710	-2.3422
β_{xyy}	-12.5526	15.2603	16.2771	25.9941
β_{xxy}	10.0213	-13.5854	-0.1005	-10.1867
β_{xxz}	24.8610	16.9129	13.2977	40.0686
β_{xzz}	19.0327	-17.0831	-17.8685	-7.2108
β_{yzz}	-4.5778	-6.4486	0.0793	-3.4072
β_{yyz}	-2.9814	2.5359	6.8205	6.9335
β_{xyz}	-0.9618	9.9007	0.0106	-1.5902
β_{tot}(esu)x10^{-33}	61.7493	38.7650	57.4796	50.4303
μ_x	-2.0093	3.3378	4.4262	3.1809
μ_y	1.4613	-0.3879	-0.0026	-0.1614
μ_z	2.2457	1.8739	1.9231	2.4296
μ(D)	3.3490	3.8475	4.8260	4.0059
α_{xx}	-64.2325	-57.8853	-53.6646	-73.9195
α_{yy}	-64.5936	-65.8198	-67.0539	-70.6885
α_{zz}	-72.6543	-74.0072	-74.4406	-78.6992
α_{xy}	0.5982	-2.4963	0.0198	-1.7239
α_{xz}	8.8503	-13.5540	-14.4146	-12.3780
α_{yz}	-3.7433	0.6767	0.0096	-0.9982
α(esu)x10^{-24}	18.6040	27.6795	30.9206	22.8096
$\Delta\alpha$(esu)x10^{-24}	2.7571	4.1021	4.5824	3.3804

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 3.3490, 3.8475, 4.8260 and 4.0059 D respectively, which are approximately three and four 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 18.6040 x 10^{-24}, 27.6795 x 10^{-24}, 30.9206 x 10^{-24} and 22.8096 x 10^{-24} esu respectively; the values of anisotropy of the polarizability are 2.7571, 4.1021, 4.5824 and 3.3804 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 (2-amino, 3-amino, 4-amino and 4-hydrazino) benzene sulfonamides compounds are equal to 61.7493 x 10^{-33}, 38.7650 x 10^{-33}, 57.4796 x 10^{-33} and 50.4303 x 10^{-33} esu. The first hyperpolarizability of title molecules is approximately 0.18, 0.11, 0.17 and 0.15 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 all studied compounds **1-4** might have not the NLO applications.

4. Conclusion

In this report we investigate a theoretical study of (2-amino, 3-amino, 4-amino and 4-hydrazino) benzene sulfonamides compounds **1-4** using DFT/B3LYP method and 6-31G (d,p) basis set. The optimized structural parameters have been optimized using the DFT method. The MEP map shows that the negative potential sites are on sulfamide function and amine group as well as the positive potential sites is around the hydrogen atoms. In addition, not only were HOMO and LUMO orbitals visualized and interpreted but also transition state and energy band gap were investigated for identification of the title compounds. Global reactivity descriptors of these molecules **1-4** have been frequently calculated and results show that compound **1** is the most reactive. Mulliken population analysis on atomic charges has been determined and interpreted. NBO analysis gives the information about intermolecular and intra molecular charge transfer within the molecules. The first order hyperpolarizability value of the title compounds is smaller than the value of urea which indicates that the compounds **1-4** might have not the NLO applications.

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