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Molecular structure, hyperpolarizability, NBO and Fukui function analysis of a serie of 1,4,3,5-oxathiadiazepane-4,4-dioxides derived of proline

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ABSTRACT

This study represents an integral approach towards understanding the electronic and structural aspects of a serie of 1,4,3,5-oxathiadiazepane 4,4-dioxides derived of proline. The molecular geometry, highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy gaps were calculated using DFT (B3LYP) method using 6-31G (d,p) basis set. From the optimized geometry of the molecule, molecular electrostatic potential (MEP) distribution, frontier molecular orbitals (FMOs) of the title compound have been calculated in the ground state theoretically. The dipole moment (μ), polarizability (α), anisotropy polarizability ($\Delta\alpha$) and first order hyperpolarizability (β) of oxathiadiazepane 4,4-dioxides have been discussed. The stability and charge delocalization of the molecule was studied by Natural Bond Orbital (NBO) analysis. The reactivity of molecule using various descriptors such as Fukui functions, local softness, electrophilicity, electronegativity, Hardness, HOMO-LUMO gap are calculated and discussed. Finally, Fukui function analyses on atomic charges, electrophilic and nucleophilic descriptors of the title molecules have been calculated.

Keywords: Oxathiadiazepane; Density functional theory; Computational chemistry; Quantum chemical calculations

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INTRODUCTION

Heterocyclic structures, components of a large number of molecules, have been studied since the mid-1800s due to their wide occurrence in nature, such as in the Heme and Chlorophyll A, and the discovery of their usefulness in organic chemistry, creating an interesting new branch, which continues today. From the first applications of simple heterocycles in main fields of research, such as in medicine, pharmaceutical, agrochemical and energy materials, polyheteroatomic heterocycles have achieved a remarkable position in the development of new products for clinical use with most advantageous features that allow different interactions with the biological target, not always possible with a simple heterocyclic ring. Nitrogen, oxygen, and sulphur are the most commonheteroatom [1], the presence of heteroatoms results in significant changes in the cyclic molecular structure due to the availability of unshared pairs of electrons and the difference in electronegativity between heteroatoms and carbon. As a result there is an unique feature of these heterocycles which are considered as promising materials in different areas of pharmaceutical research and also more recently as compounds with interesting physical properties especially for magnetism and conductivity. In recent decades, computer simulation has become an important tool in various fields such as mechanical engineering, chemistry, physics and materials [2-4]. In particular, computer simulations that take account of electronic structures [5]. At the present time, the computer simulation is one of the main tools to identify the regularities of behavior of the molecular systems under various external influences[6]. Molecular modeling is the computer simulation of molecular structures, which concerns the distances and angles of bonds in chemical molecules, alsothe results of introduction and substitution of atoms or groups of atoms in the molecule . Molecular modeling is the sum of theoretical methods and computational techniques that is used to predict molecular behaviours specifically interactions between molecules[7]. Molecular modeling has been introduced as a valuable methodology for scientific research providing useful tools for the analysis and estimate of the physicochemical parameters and/or biological activity [8]. Theoretical studies on bioactive compounds are of interest in order to gain a deeper insight on their action and thus helping in the design of new compounds with therapeutic effects. The knowledge of physico-chemical properties and sites of reaction of investigated compound will provide a deeper insight of its probable action. Particularly, molecular electrostatic potential (MESP) is related to the electronic density and is a very useful descriptor in understanding sites for electrophilic attack and nucleophilic reactions as well as hydrogen bonding interactions.In previous work [9], we have synthesized and characterized a new class of heterocyclic compounds: 1,4,3,5-oxathiadiazepane 4,4-dioxides, in this paper and in the aim to study their properties and to predict their applications, we give a complete description of the molecular geometry, natural bond orbital (NBO) analysis, nonlinear optical (NLO) properties, and chemical reactivity as HOMO-LUMO energy gap, chemical hardness, chemical potential of a new series of1,4,3,5-oxathiadiazepane 4,4-dioxides derived of proline.

MATERIALS AND METHODS

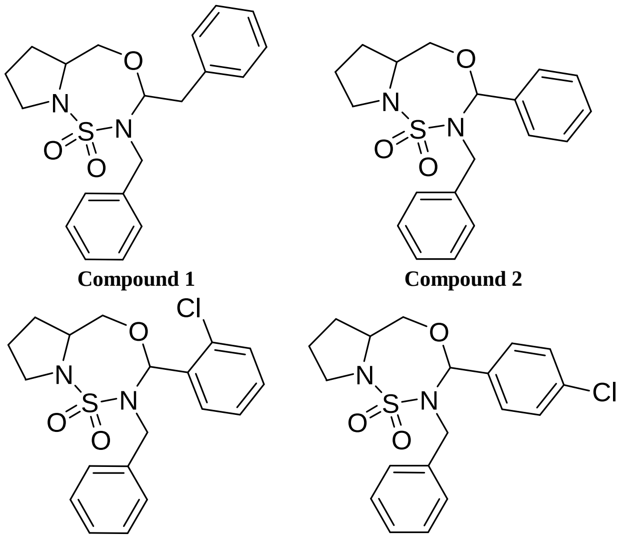
All computational calculations have been performed on personal computer using the Gaussian 09W program packages developed by Frisch and coworkers. The Becke's three parameter hybrid functional using the LYP correlation functional (B3LYP), one of the most robust functional of the hybrid family, was herein used for all the calculations, with 6.31G(d,p) basis set. Gaussian output files were visualized by means of GAUSSIAN VIEW 05 software.

RESULTS AND DISCUSSION

3.1. Chemistry:

Previously[9], we have described the synthesis of a new class of 1,4,3,5-oxathiadiazepane 4,4-dioxides derived of proline **1-4** indicated in Scheme 1. The synthesis of these compounds was carried out using a cycolodehydration reaction of substituted amino alcohols and various aromatic aldehydes by treatment with sulfuric acid (cat.) in dichloromethane at ambient temperature, these new heterocycles were obtained in 55%, 45%, 40% and 42% yields, respectively.

Scheme 1.Generalsynthesisofoxathiadiazepane 4,4-dioxides1-4



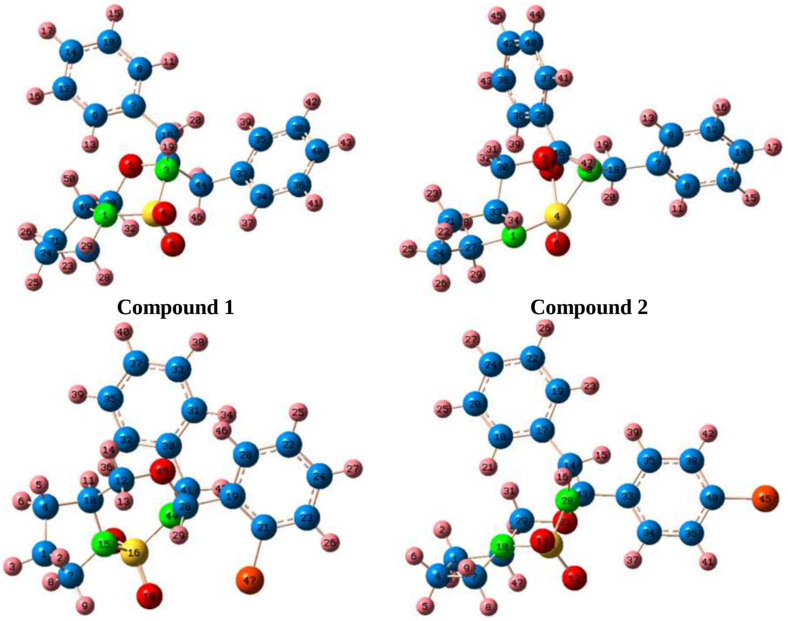
Compound 1 **Compound 2**

Compound 3 **Compound 4**

3.2. Molecular Geometry:

The geometric parameters of 1,4,3,5-Oxathiadiazepane 4,4-dioxides derived of proline**1-4** were optimized with B3LYP method at 6-31G (d,p) level. No solvent corrections were made with these calculations. The computations were converged upon a true energy minimum, which were supported by the absence of imaginary frequencies. The chemical structure of compounds **1-4** are shown in scheme 1 and the final optimized molecular structures of compounds in accordance with the atom numbering scheme were shown in Fig. 1. The optimized energy for compounds varies between -1930.17Arbitr Units and -1470.60Arbitr Units, which indicate that these compounds were stable. Based on these, some structural parameters such as bond distances and bond angles have been calculated. From the optimized geometries, various molecular properties such as energy of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), energy gap ΔE_{gap}, ionization potential (I), electron affinity (A) and global reactivity parameters were also calculated to analyze the reactivity of title molecules. Some selected geometrical parameters calculated with 6-31G (d,p) basis set are listed in Table 1-4.

Fig.1.Optimized molecular structure of compounds1-4



Compound 1 **Compound 2**

Compound 3 **Compound 4**

Table 1: Optimized geometric parameters of compound 1

Bond length(Å)		Bond Angles (°)		Dihedral Angles (°)	
N_1S_4	1.688	$S_4N_1C_{49}$	120.600	$C_{18}N_3C_{47}H_{48}$	9.741
S_4O_6	1.461	$N_1S_4N_3$	103.793	$H_{29}C_{47}N_1S_4$	77.744
N_3S_4	1.664	$N_1S_4O_6$	105.658	$N_3S_4N_1C_{49}$	52.033
N_1C_{27}	1.489	$N_1S_4O_5$	110.410	$H_{28}C_{27}N_1C_{49}$	97.060
N_1C_{49}	1.504	$O_6S_4O_5$	118.884	$N_1C_{49}C_{21}H_{22}$	149.462
O_2C_{30}	1.424	$S_4N_3C_{47}$	122.229	$O_6S_4N_1C_{49}$	166.644
N_3C_{47}	1.474	$C_{30}O_2C_{47}$	118.346	$N_3C_{47}C_{44}H_{45}$	179.531
C_7C_{18}	1.516	$N_1C_{49}C_{21}$	103.452	$O_6S_4N_3C_{47}$	168.510
C_8H_{11}	1.087	$N_3C_{18}C_7$	115.709	$H_{29}C_{27}N_1S_4$	77.744
$C_{21}C_{24}$	1.533	$O_2C_{47}N_3$	114.078	$N_1S_4N_3C_{18}$	87.348

Table 2: Optimized geometric parameters of compound 2

Bond length(Å)		Bond Angles (°)		Dihedral Angles (°)	
N_1S_4	1.685	$S_4N_1C_{33}$	119.228	$H_{31}C_{30}C_{33}H_{21}$	61.226
S_4O_5	1.744	$N_1S_4O_5$	100.121	$H_{34}C_{33}N_1C_{27}$	145.109
N_1C_{27}	1.473	$N_1S_4O_6$	105.872	$S_4N_3C_{18}H_{19}$	114.121
N_3C_{18}	1.465	$C_{30}O_2C_{47}$	116.751	$C_{27}N_1C_{33}C_{21}$	25.826
N_1C_{33}	1.481	$N_1C_{33}C_{21}$	103.216	$C_{21}C_{33}C_{30}O_2$	178.837
O_2C_{30}	1.427	$N_3C_{18}C_7$	111.193	$O_6S_4N_1C_{46}$	107.650
$C_{21}C_{24}$	1.546	$O_2C_{46}N_3$	102.945	$N_3C_{46}C_{35}C_{36}$	122.074
N_3C_{46}	1.438	$O_2C_{30}C_{33}$	110.998	$H_{28}C_{27}N_1C_{33}$	78.333
$C_{46}C_{35}$	1.531	$O_2C_{46}C_{35}$	111.936	$H_{29}C_{27}N_1S_4$	74.335
C_8H_{11}	1.087	$N_1C_{27}C_{24}$	100.842	$N_1C_{33}C_{21}H_{22}$	121.777

Table 3: Optimized geometric parameters of compound 3

Bond length(Å)		Bond Angles (°)		Dihedral Angles (°)	
$N_{15}S_{16}$	1.675	$S_{16}N_{15}C_{10}$	119.742	$N_{44}C_{28}O_4C_{12}$	81.688
$C_{10}N_{15}$	1.488	$N_{15}S_{16}N_{44}$	99.275	$H_{11}C_{10}N_{15}S_{16}$	25.660
$S_{16}O_{17}$	1.471	$N_{15}S_{16}O_{17}$	113.512	$N_{44}S_{16}N_{15}C_{10}$	50.296
$nS_{16}N_{44}$	1.679	$N_{15}S_{16}O_{18}$	104.913	$H_8C_7N_{15}C_{10}$	92.564
$N_{44}C_{41}$	1.482	$O_{17}S_{16}O_{18}$	117.666	$N_{15}C_{10}C_{12}O_{45}$	68.875
$C_{10}C_{12}$	74.967	$S_{16}N_{44}C_{28}$	119.046	$O_{17}S_{16}N_{44}C_{28}$	152.716
$C_{12}O_{45}$	1.421	$C_{12}O_{45}C_{28}$	116.416	$N_{44}C_{28}C_{19}C_{20}$	109.889
$C_{10}C_4$	1.547	$C_4C_{10}N_{15}$	103.318	$S_{16}N_{44}C_{28}H_{29}$	25.930
$N_{15}C_7$	1.483	$O_{45}C_{28}N_{44}$	111.443	$H_9C_7N_{15}S_{16}$	69.932
$C_{21}Cl_{47}$	1.756	$C_{19}C_{21}Cl_{47}$	120.703	$N_{15}S_{16}N_{44}C_{28}$	34.775

Table 4: Optimized geometric parameters of compound 4

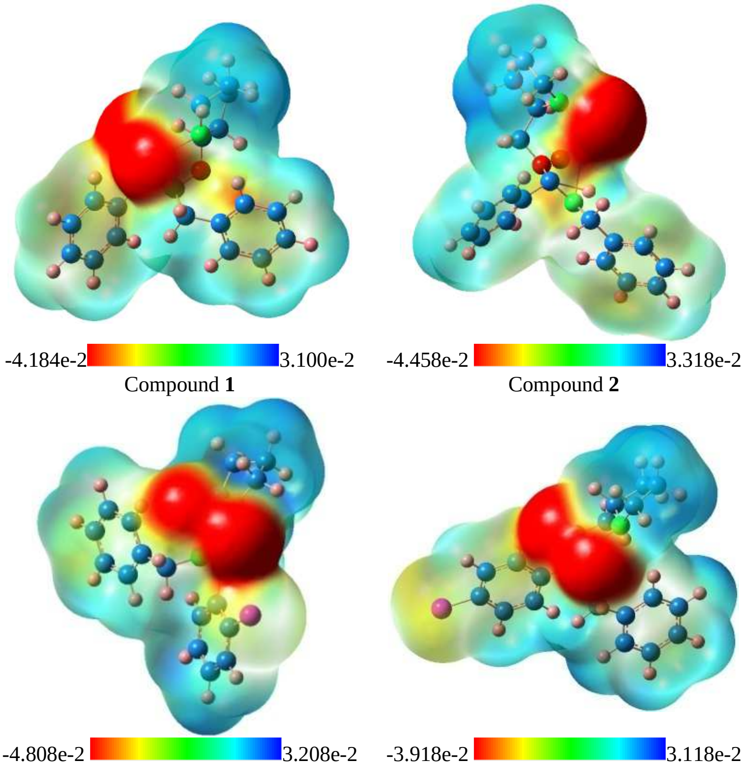
Bond length(Å)		**Bond Angles (°)**		**Dihedral Angles (°)**	
$N_{10}S_{11}$	1.709	$S_{11}N_{10}C_{46}$	115.654	$N_{28}C_{43}O_{32}C_{29}$	61.679
$S_{11}O_{12}$	1.466	$N_{10}S_{11}N_{28}$	102.413	$H_{47}C_{46}N_{10}S_{11}$	56.476
$S_{11}O_{13}$	1.462	$N_{10}S_{11}O_{12}$	109.680	$C_7N_{10}S_{11}O_{12}$	79.495
$S_{11}N_{28}$	1.666	$N_{10}S_{11}O_{13}$	105.526	$H_8C_7N_{10}C_{46}$	75.527
$N_{10}C_{46}$	1.481	$O_{12}S_{11}O_{13}$	120.157	$N_{10}C_{46}C_{29}O_{32}$	72.945
$C_{29}C_{46}$	1.523	$S_{11}N_{28}C_{43}$	123.029	$H_{30}C_{29}O_{32}C_{43}$	141.656
$C_{29}O_{32}$	1.431	$C_{29}O_{32}C_{43}$	116.363	$N_{28}C_{43}C_{33}C_{34}$	69.197
$O_{32}C_{43}$	1.402	$N_{28C43}O_{32}$	112.404	$H_3C_1N_{46}C_{29}$	86.665
C_1C_{46}	1.540	$N_{10}C_{46}C_1$	119.383	$H_9C_7N_{10}S_{11}$	67.330
$C_{40}Cl_{45}$	107.113	$C_{l45}C_{40}C_{36}$	119.383	$N_{28}S_{11}N_{10}C_{46}$	73.059

3.3. Molecular Electrostatic Potential (MEP):

The MEP is a very useful feature to study reactivity given that an approaching electrophile will be attracted to negative regions (the electron distribution in where effect is dominant). In the majority of the MEPs, while the maximum negative region which preferred site for electrophilic attack indications as red color, the maximum positive region which preferred site for nucleophilic attack symptoms as blue color. The importance of MEP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative and neutral electrostatic potential (MEP) of compound is shown in Fig. 2. The MEP is a plot of electrostatic potential mapped onto the constant electron density surface.

The different values of the electrostatic potential at the surface are represented by different colors. Potential increases in the order red < orange < yellow < green < blue. The color code of these maps is in the range between -4.808e-2 a.u. (deepest red) and 3.318e-2 a.u. (deepest blue) in compounds **1-4**, where blue shows the strongest attraction and red shows the strongest repulsion. Regions of negative V(r) are usually associated with the lone pair of electronegative atoms. As can be seen from the MEP map of the title molecules, while regions having the negative potential are over the electronegative atoms (oxygen atoms in the sulfoxide group), the regions having the positive potential are over the hydrogen atoms.

Fig.2.Molecular electrostatic potential surfaceofcompounds1-4



Compound **1**

Compound **2**

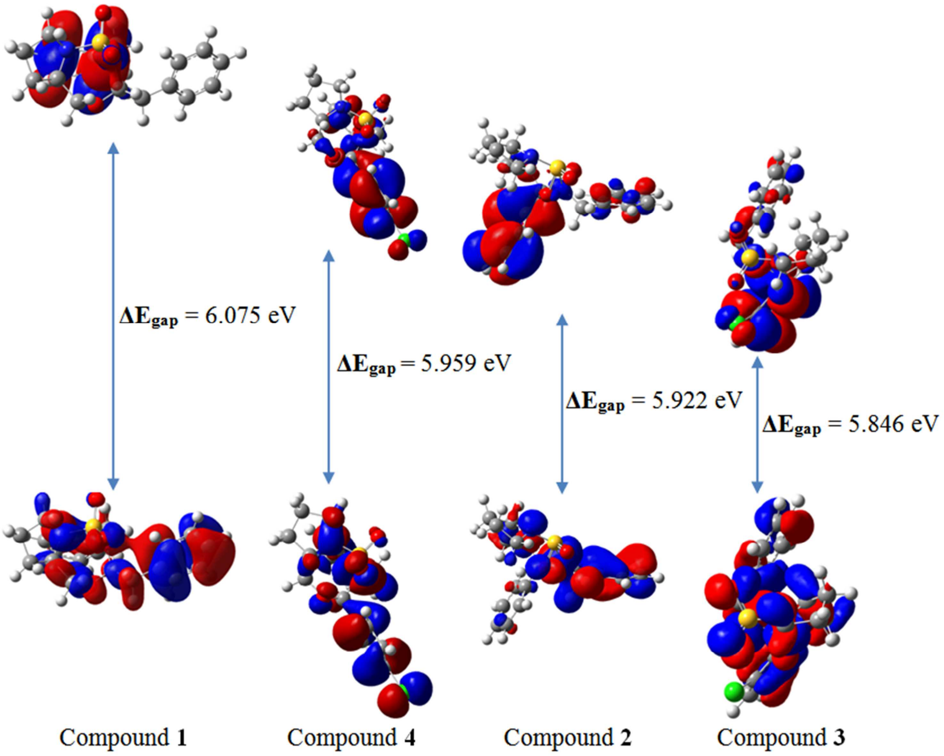
Compound **3**

Compound **4**

3.4. Frontier Molecular Orbitals (FMOs):

The frontier molecular orbital determine the way in which the molecule interacts with other species. HOMO (highest occupied molecular orbital), which can be thought the outermost orbital containing electrons, tends to give these electrons such as an electron donor. On the other hand, LUMO (lowest unoccupied molecular orbital) can be thought the innermost orbital containing free places to accept electrons [10]. Therefore, while the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structures [11], in this case, the order of stability of the title compounds is **1**, **4**, **2** and **3**. HOMO-LUMO helps to characterize the chemical reactivity and kinetic stability of the molecule [12]. A molecule with a small gap is more polarized and is known as soft molecule. Recently, the energy gap between HOMO and LUMO has been used to prove the bioactivity from intramolecular charge transfer (ICT) [13,14] because it is a measure of electron conductivity. The frontier molecular orbitals HOMO and LUMO of 1,4,3,5-oxathiadiazepane 4,4-dioxides **1**-**4**, with B3LYP/6-31G(d,p) method is plotted in Fig. 3 and given in Table 5.

Fig.3.Frontier molecular orbitals of compounds1-4



3.5. Global Reactivity Descriptors:

The frontier orbital (HOMO and LUMO) of the chemical species are very important in defining its reactivity [15, 16]. Energies of HOMO and LUMO are popular quantum mechanical descriptors. It has been shown [17] that these orbital's play a major role in governing many chemical reactions, and are also responsible for charge transfer complexes [18]. The energy of the HOMO is directly related to the ionization potential and characterizes the susceptibility of the molecule towards attack of electrophiles. The energy of LUMO is directly related to the electron affinity and characterizes the susceptibility of the molecule towards attack of nucleophiles. The concept of hard and soft nucleophiles and electrophiles has been also directly related to the relative energies of the HOMO and LUMO orbital's. Hard nucleophiles have a low energy HOMO, soft nucleophiles have a high energy HOMO, hard electrophiles have a high energy LUMO and soft electrophiles have a low energy LUMO [19]. HOMO-LUMO gap is an important stability index [20].Molecular orbital energies are molecular properties whereas orbital densities are atomic properties, and provide useful information about donor acceptor interaction [21]. According to frontier electron reactivity theory, the chemical reaction takes place at a position where overlap of the HOMO and LUMO are the maximum [22]. In the case of donor molecule the HOMO density and in case of acceptor molecule the LUMO density is important for any reaction. Frontier orbital densities can strictly be used to describe the reactivity of different atoms in the same molecule [22]. The electronegativity and hardness are of course used extensively to make predictions about chemical behavior. According to, the Koopmans' theorem, Ionization potential (IE), Electron affinity (EA), Global Electronegativity(χ), Chemical hardness (η), Global softness(S) and Global Electrophilicity index (ω) can be expressed as follows.

$$IE = -E_{HOMO}$$

$$EA = -E_{LUMO}$$

$$\chi = (IE + EA)/2$$
$$\eta = (IE - EA)/2$$
$$S = 1/\eta$$
$$\omega = \mu^2 / 2\eta$$

The highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies, hardness (η), ionization energy (IE), Electronegativity (χ), total energy and dipole moment have been calculated and are given in Table 5.

Table 5: Energetic parameters of compounds1-4

Parameters	Compound1	Compound2	Compound3	Compound4
E_{HOMO} (eV)	-6.356	-6.239	-6.452	-6.499
E_{LUMO} (eV)	-0.281	-0.317	-0.606	-0.540
ΔE_{gap}(eV)	6.075	5.922	5.846	5.959
IE (eV)	6.356	6.239	6.452	6.499
EA (eV)	0.281	0.317	0.606	0.540
μ(eV)	-3.318	-3.278	-3.529	-3.519
x(eV)	3.318	3.278	3.529	3.519
η(eV)	3.037	2.961	2.923	2.979
S(eV)	0.164	0 .169	0.171	0.168
ω(eV)	1.812	1.814	2.130	2.078

An electronic system with a larger HOMO-LUMO gap should be less reactive than one having smaller gap [23]. The ionization energy (IE) can be expressed through HOMO orbital energies as IE and electron affinity (EA) can be expressed through LUMO orbital energies [24] as EA. The hardness (η) corresponds to the gap between the HOMO and LUMO orbital energies. The larger the HOMO-LUMO orbital energy gap, the harder the molecule. The hardness has been associated with the stability of the chemical system.

As shown in table 5, the compound that has the highest HOMO energy is the compound **2** (E_{HOMO} = -6.239eV). 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} = -0.606eV) which signifies that it can be the best electron acceptor. The compound which have the lowest energetic gap is the compound **3** (ΔEgap = 5.846eV). This lower gap allows it to be the softest molecule. The compound that have the highest energy gap is the compound **1** (ΔEgap = 6.075eV). The two properties like I (potential ionization) and A (affinity) are so important, the determination of these two properties allow us to calculate the absolute electronegativity (χ) and the absolute hardness (□). These two parameters are related to the one-electron orbital energies of the HOMO and LUMO respectively. Compound **2** has lowest value of the potential ionization (I = 6.239eV), so that will be the better electron donor. Compound **3** also has the largest value of the affinity (A = 0.606eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules. Chemical hardness (softness) value of compound **3** (η = 2.923eV) 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 (□ = 3.529eV) than all compounds so; it is the best electron acceptor. The value of ω for compound **3** (ω = 2.130eV) 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. Local Reactivity Descriptors:

The Fukui function is among the most basic and commonly used reactivity indicators. The Fukui function is given as the change in the density function ρ(r) of the molecule as a consequence of changing the number of electrons N in the molecule, under the constraint of a constant external potential. The Fukui function is defined as:

$$F(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_r$$

Where ρ(r) is the electronic density, N is the number of electrons and r is the external potential exerted by the nuclease. Fukui functions are introduced, which are advocated as reactivity descriptors in order to identify the most reactive sites for electrophilic or nucleophilic reactions within a molecule. The Fukui function indicates the propensity of the electronic density to deform at a given position upon accepting or donating electrons [25-26]. Also, it is possible to define the corresponding condensed or atomic Fukui functions on the j_{th} atom site as,

$$f_j^+ = \left[q_j(N+1) - q_j(N)\right]$$
$$f_j^- = \left[q_j(N) - q_j(N\text{-}1)\right]$$
$$f_j^0 = \left[q_j(N+1) - q_j(N\text{-}1)\right]/2$$

For an electrophilic $f_i^-(r)$, nucleophilic or free radical attack $f_i^+(r)$, on the reference molecule, respectively. In these equations, q_i is the atomic charge (evaluated from Mulliken population analysis, electrostatic derived charge, etc.) at the j_{th} atomic site in the neutral (N), anionic (N + 1) or cationic (N - 1) chemical species.

Table 6: Values of the Fukui function considering MULLIKEN charges of compound 1and 2

	Compound 1					**Compound 2**			
Atom	C_9	C_{34}	C_7	N_1	**Atom**	C_{35}	N_1	O_6	C_7
f^+	0.037	0.026	0.02	0.017	f^+	0.056	0.042	0.013	0.007
Atom	C_7	S_4	C_{33}	C_{49}	**Atom**	O_2	S_4	C_7	C_{37}
f^-	0.031	0.001	0.001	-0.007	f^-	0.006	0.005	0.005	0.004
Atom	C_7	C_{33}	C_9	N_1	**Atom**	N_1	C_{35}	C_7	C_9
f^0	0.025	0.007	0.005	-0.001	f^0	0.016	0.013	0.006	-0.003

Table 7: Values of the Fukui function considering MULLIKEN charges of compound 3 and 4

	Compound 3					**Compound 4**			
Atom	C_{19}	O_{45}	C_{32}	N_{15}	**Atom**	N_{10}	C_{19}	N_{28}	O_{32}
f^+	0.043	0.035	0.027	0.024	f^+	0.007	0.005	0.003	-0.006
Atom	C_{30}	C_{21}	N_{15}	C_{19}	**Atom**	C_{18}	C_{33}	C_{17}	C_{40}
f^-	0.044	0.012	0.011	0.001	f^-	0.027	0.023	0.016	-0.001
Atom	C_{19}	N_{15}	O_{45}	C_{21}	**Atom**	C_{17}	N_{10}	C_{33}	C_{19}
f^0	0.022	0.017	0.008	0.002	f^0	-0.005	-0.005	-0.008	-0.009

In this study, gross charges were calculated by using Mulliken charge analysis in order to calculate the condensed Fukui functions. The condensed Fukui functions for the compounds are given in Table 6 and 7. These tables show that the most reactive site of compounds **1**, **2**, **3** and **4** are the C_9, C_{35}, C_{19} and N_{10} respectively, for the nucleophilic attack and C_7, O_2, C_{30} and C_{18} respectively, for electrophilic attack and C_7, N_1, C_{19} and C_{17} respectively, for radical attack

3.7. Natural Bond Orbital Analysis(NBO):

The Natural Bond Orbital (NBO) calculations were performed using NBO 3.1 program as implemented in the Gaussian09 package at the B3LYP/6-31G (d,p) level in order to understand various second-order interactions between the filled orbital of one subsystem and vacant orbital of another subsystem, which is a measure of the inter-molecular delocalization or hyper-conjugation. NBO analysis provides the most accurate possible ‘natural Lewis structure’ picture of 'j' because all orbital details are mathematically chosen to include the highest possible percentage of the electron density. A useful aspect of the NBO method is that it gives information about interactions of both filled and virtual orbital spaces that could enhance the analysis of intra and inter-molecular interactions. The second-order Fock-matrix was carried out to evaluate the donor-acceptor interactions in the NBO basis. The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non- Lewis orbital. For each donor (i) and acceptor (j) the stabilization energy (E2) associated with the delocalization i→j is determined as[27]:

$$E(2) = \Delta E_{ij} = q_i \frac{(F_{ij})^2}{(E_j - E_i)}$$

where, q_i → donor orbital occupancy, E_i , Ej→ diagonal elements and F_{ij}→ the off diagonal NBO Fock matrix element.

In NBO analysis large E(2) value shows the intensive interaction between electron-donors and electron- acceptors, and greater the extent of conjugation of the whole system, the possibleintensiveinteractionaregiveninTables8-11.The intra molecular interaction for the title compounds is formed by the orbital overlap between: $\pi(C_7\text{-}C_8)$ and $\pi^*(C_{10}\text{-}C_{14})$ for compound **1**, $\pi(C_7\text{-}C_8)$ and $\pi^*(C_{10}\text{-}C_{14})$ for compound **2**, $\pi(C_{30}\text{-}C_{31})$ and $\pi^*(C_{33}\text{-}C_{37})$ for compound **3** and $\pi(C_{17}\text{-}C_{19})$ and $\pi^*(C_{22}\text{-}C_{27})$ for compound **4** respectively, which result into intermolecular charge transfer (ICT) causing stabilization of the system. The intra molecular hyper conjugative interactions of $\pi(C_7\text{-}C_8)$ to $\pi^*(C_{10}\text{-}C_{14})$ for compound **1**, $\pi(C_7\text{-}C_8)$ to $\pi^*(C_{10}\text{-}C_{14})$ for compound **2**, $\pi(C_{30}\text{-}C_{31})$ to $\pi^*(C_{33}\text{-}C_{37})$ for compound **3** and $\pi(C_{17}\text{-}C_{19})$ to $\pi^*(C_{22}\text{-}C_{27})$ for compound **4** lead to highest stabilization of 20.28, 20.89, 20.65 and 20.35 kJ mol^{-1} respectively. In case of LP(2) O_5 orbital to the $\sigma^*(N_1\text{-}S_4)$ for compound **1**, LP(1) N_1 orbital to $\sigma^*(S_4\text{-}N_5)$ for compound **2**, LP(3) O_{17}

orbital to $\sigma^*(N_{15}-S_{16})$ for compound **3** and LP(2) O_{12} and LP(3) O_{12} orbitals to $\sigma^*(N_{10}-S_{11})$ and $\sigma^*(S_{11}-O_{13})$ for compound **4** respectively, show the stabilization energy of 23.53, 16.09, 24.28 and (21.95, 21.04) kJ mol^{-1} respectively.

Table 8:Secondorder perturbation theory analysis of Fock matrix on NBO of compound1

Donor(i)	**ED/e**	**Acceptor(j)**	**ED/e**	**E(2) Kcal/mol**	**E(j)-E(i) a.u**	**F (i.j) a.u**
$\sigma(C_{30}-H_{31})$	1.97554	$\sigma^*(N_1-C_{49})$	0.04255	5.72	0.81	0.061
		$\sigma^*(O_2-C_{47})$	0.05438	3.36	0.81	0.047
$\sigma(C_{47}-H_{48})$	1.96648	$\sigma^*(O_2-C_{30})$	0.02304	4.10	0.82	0.052
		$\sigma^*(N_3-S_4)$	0.24647	5.67	0.68	0.059
$\sigma(N_1-S_4)$	1.96883	$\sigma^*(S_4-O_5)$	0.17570	3.23	1.04	0.054
		$\sigma^*(S_4-O_6)$	0.14430	3.14	1.05	0.053
$\sigma(N_3-S_4)$	1.97088	$\sigma^*(S_4-O_5)$	0.17570	3.47	1.08	0.057
$\sigma(S_4-O_5)$	1.97987	$\sigma^*(N_1-S_4)$	0.26357	2.89	1.11	0.054
$\sigma(C_7-C_8)$	1.97589	$\sigma^*(C_7-C_9)$	0.02371	3.40	1.27	0.059
$\pi(C_7-C_8)$	1.66444	$\sigma^*(N_3-C_{18})$	0.03470	5.37	0.56	0.053
		$\pi^*(C_{10}-C_{14})$	0.01563	20.28	0.28	0.068
LP(2) O_2	1.91338	$\sigma^*(C_{30}-C_{49})$	0.03588	8.16	0.67	0.067
		$\sigma^*(N_3-C_{47})$	0.06404	10.66	0.62	0.073
LP(1) N_3	1.83439	$\sigma^*(N_1-S_4)$	0.26357	11.73	0.42	0.064
		$\sigma^*(O_2-C_{47})$	0.05438	11.90	0.57	0.076
		$\sigma^*(S_4-O_5)$	0.17570	3.26	0.55	0.038
LP(2) O_5	1.81360	$\sigma^*(N_3-S_4)$	0.24647	8.67	0.45	0.056
		$\sigma^*(N_1-S_4)$	0.26357	23.53	0.43	0.092
LP(3) O_5	1.79134	$\sigma^*(S_4-O_6)$	0.14430	18.88	0.57	0.094
		$\sigma^*(N_3-S_4)$	0.24647	15.14	0.45	0.074

Table 9:Secondorder perturbation theory analysis of Fock matrix on NBO of compound2

Donor(i)	**ED/e**	**Acceptor(j)**	**ED/e**	**E(2) Kcal/mol**	**E(j)-E(i) a.u**	**F (i.j) a.u**
$\sigma(C_{30}-H_{31})$	1.98037	$\sigma^*(N_1-C_{33})$	0.03715	4.50	0.84	0.055
		$\sigma^*(O_2-C_{46})$	0.07711	2.34	0.80	0.039
$\sigma(C_{30}-H_{32})$	1.98706	$\sigma^*(C_{33}-H_{34})$	0.02095	2.31	0.99	0.043
$\sigma(N_1-S_4)$	1.97731	$\sigma^*(S_4-O_6)$	0.03377	1.76	1.02	0.038
$\sigma(N_3-C_{46})$	1.98226	$\sigma^*(O_2-C_{30})$	0.02208	2.40	1.04	0.045
$\sigma(S_4-O_5)$	1.97712	$\sigma^*(N_1-S_4)$	0.17234	1.80	0.81	0.036
		$\sigma^*(S_4-O_6)$	0.03377	1.87	0.94	0.038
$\sigma(N_3-C_{18})$	1.98097	$\sigma^*(O_2-C_{46})$	0.07711	2.04	0.98	0.040
$\sigma(C_7-C_8)$	1.97600	$\sigma^*(C_7-C_9)$	0.02372	3.45	1.27	0.059
$\pi(C_7-C_8)$	1.65908	$\sigma^*(N_3-C_{18})$	0.01650	2.56	0.60	0.038
		$\pi^*(C_{10}-C_{14})$	0.33250	20.89	0.28	0.068
LP(1) O_2	1.95632	$\sigma^*(N_3-C_{46})$	0.05554	2.50	0.94	0.043
LP(2) O_2	1.90236	$\sigma^*(C_{30}-C_{33})$	0.04075	6.32	0.67	0.059
LP(1) N_1	1.83430	$\sigma^*(C_{30}-C_{33})$	0.04075	6.55	0.66	0.060
		$\sigma^*(S_4-O_5)$	0.30284	16.09	0.34	0.068
LP(1) N_3	1.88500	$\sigma^*(C_{35}-C_{46})$	0.05793	1.78	0.67	0.031
		$\sigma^*(C_{18}-H_{20})$	0.02690	7.47	0.74	0.068
LP(1) O_5	1.96694	$\sigma^*(N_3-C_{46})$	0.05554	1.70	1.02	0.037
LP(2) O_5	1.89905	$\sigma^*(N_3-C_{46})$	0.05554	8.44	0.69	0.069
		$\sigma^*(N_1-S_4)$	0.17234	5.92	0.47	0.048

Table 10:Second order perturbation theory analysis of Fock matrix on NBO of compound3

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F (i.j) a.u
$\sigma(C_{12}-H_{13})$	1.98699	$\sigma^*(C_{10}-H_{11})$	0.02466	2.58	0.99	0.045
$\sigma(C_{12}-H_{14})$	1.97801	$\sigma^*(C_{10}-N_{15})$	0.03853	4.10	0.82	0.052
		$\sigma^*(C_{28}-O_{45})$	0.05817	3.65	0.81	0.049
$\sigma(N_{15}-S_{16})$	1.97058	$\sigma^*(S_{16}-O_{18})$	0.15830	3.32	1.07	0.055
$\sigma(C_{30}-C_{31})$	1.97623	$\sigma^*(C_{30}-C_{32})$	0.02325	3.35	1.27	0.058
$\pi(C_{30}-C_{31})$	1.65834	$\sigma^*(C_{41}-N_{44})$	0.03494	5.34	0.56	0.053
		$\pi^*(C_{33}-C_{37})$	0.32993	20.65	0.28	0.068
LP(2) O_{45}	1.90747	$\sigma^*(C_{10}-C_{12})$	0.03992	6.62	0.66	0.060
		$\sigma^*(C_{28}-N_{44})$	0.06725	12.73	0.63	0.080
LP(1) N_{15}	1.87161	$\sigma^*(C_{10}-C_{12})$	0.03992	4.14	0.66	0.048
		$\sigma^*(C_7-H_8)$	0.02285	5.42	0.75	0.059
		$\sigma^*(S_{16}-O_{17})$	0.16791	11.49	0.59	0.074
LP(1) N_{44}	1.82856	$\sigma^*(C_{28}-O_{45})$	0.05817	14.03	0.55	0.081
		$\sigma^*(N_{15}-S_{16})$	0.25739	5.06	0.42	0.042
LP(2) O_{17}	1.81762	$\sigma^*(S_{16}-O_{18})$	0.15830	19.49	0.57	0.095
		$\sigma^*(S_{16}-N_{44})$	0.26111	13.72	0.43	0.070
LP(3) O_{17}	1.78588	$\sigma^*(N_{15}-S_{16})$	0.25739	24.28	0.43	0.093
		$\sigma^*(S_{16}-N_{44})$	0.26111	10.07	0.43	0.060
LP(2) Cl_{47}	1.96806	$\sigma^*(C_{19}-C_{21})$	0.03360	4.35	0.87	0.055
LP(3) Cl_{47}		$\pi^*(C_{19}-C_{21})$	0.03360	12.98	0.32	0.064

Table 11:Second order perturbation theory analysis of Fock matrix on NBO of compound4

Donor(i)	ED/e	Acceptor(j)	ED/e	E(2) Kcal/mol	E(j)-E(i) a.u	F (i.j) a.u
$\sigma(C_{29}-H_{30})$	1.97989	$\sigma^*(N_{10}-C_{46})$	0.03656	4.58	0.83	0.055
$\sigma(N_{10}-S_{11})$	1.96393	$\sigma^*(S_{11}-O_{12})$	0.17461	3.42	1.02	0.055
		$\sigma^*(S_{11}-O_{13})$	0.14111	3.14	1.02	0.052
$\sigma(S_{11}-O_{12})$	1.97972	$\sigma^*(N_{10}-S_{11})$	0.26910	3.28	1.10	0.057
$\sigma(C_{17}-C_{19})$	1.97562	$\sigma^*(C_{17}-C_{18})$	0.02362	3.44	1.27	0.059
$\pi(C_{17}-C_{19})$	1.66598	$\sigma^*(C_{14}-N_{28})$	0.02853	3.71	0.57	0.045
		$\pi^*(C_{22}-C_{24})$	0.32454	20.35	0.28	0.068
LP(2) O_{32}	1.90496	$\sigma^*(C_{29}-C_{46})$	0.03058	6.44	0.68	0.060
		$\sigma^*(N_{28}-C_{43})$	0.07567	12.79	0.60	0.079
LP(1) N_{10}	1.89482	$\sigma^*(C_7-H_8)$	0.02419	5.42	0.78	0.059
		$\sigma^*(S_{11}-O_{12})$	0.17461	7.69	0.62	0.063
LP(1) N_{28}	1.83888	$\sigma^*(N_{10}-S_{11})$	0.26910	10.61	0.39	0.059
		$\sigma^*(C_{14}-H_{15})$	0.01889	4.15	0.71	0.050
LP(2) O_{12}	1.80485	$\sigma^*(S_{11}-N_{28})$	0.25163	13.67	0.44	0.070
		$\sigma^*(N_{10}-S_{11})$	0.26910	21.95	0.41	0.087
LP(3) O_{12}	1.78014	$\sigma^*(N_{10}-S_{11})$	0.26910	3.85	0.41	0.036
		$\sigma^*(S_{11}-O_{13})$	0.14111	21.04	0.57	0.099
		$\sigma^*(S_{11}-N_{28})$	0.25163	11.81	0.44	0.065
LP(2) Cl_{45}	1.97354	$\sigma^*(C_{36}-C_{40})$	0.02686	3.81	0.87	0.052
LP(3) Cl_{45}	1.93135	$\pi^*(C_{38}-C_{40})$	0.38205	12.12	0.33	0.061

3.8. Nonlinear Optical Properties (NLO):

The nonlinear optical effects arise due to the interactions of electromagnetic fields in various media to produce new fields which are altered in frequency, phase and amplitude or other propagation characteristics from the incident fields [28]. Computational approach is an inexpensive, yet an effective way to design molecules by analyzing their potential which helps to determine the molecular NLO properties. In this direction, The first static hyperpolarizability (β_{tot}) and its related properties (α, β and $\Delta\alpha$) of 1,4,3,5-oxathiadiazepane 4,4-dioxides **1-4** have been calculated using B3LYP/6-31G (d,p) method based on finite-field approach and are presented in Table 12. To calculate all the electric dipole moment and the first hyperpolarizability tensor components for a given system will depend on the choice of the Cartesian co-ordinate system (x, y, z)=(0, 0, 0) was chosen at own centre of mass of molecule. The polarizability of this novel molecular system for which $\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$ is said to be isotropic. The polarizability is isotropic or is the same in all directions for a molecular system whose electron density is spherically symmetrical. If the molecule is perfectly isotropic (P) and (E) will have the same direction and is then a simple scalar quantity. The polarizability of this novel molecular system for which $\alpha_{xx} \neq \alpha_{yy} \neq \alpha_{zz}$ (P) will no longer have the same direction as (E).

In the presence of an applied electric field, the energy of a system is a function of the electric field and the first order hyperpolarizability is a third rank tensor that can be described by a 3×3×3 matrices. The 27 components of the 3D matrix can be reduced to 10 components because of the Kleinman symmetry [29]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the 3×3×3 matrices is tetrahedral. The components of β are defined as the coefficients in the Taylor series expansion of energy in an external electric field. The external electric field is weak and homogeneous, this expansion becomes.

$$E = E^{0} - \mu_i F_i - 1/2\alpha_{ij} F_i F_j - 1/6\beta_{ijk} F_i F_j F_k + \ldots$$

where E^0 is the energy of the unperturbed molecules, F_i is the field at the origin and μ_i , α_{ij} , β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability and the hyperpolarizability, respectively. The total static dipole moment (μ), the mean polarizability (α), the anisotropy of the polarizability (Δα) and the mean first hyperpolarizability (β_{tot}), using the x, y, z components can be calculated using the following equations:

$$\mu_{tot} = \left[\mu_x^2 + \mu_y^2 + \mu_z^2\right]^{1/2}$$

$$\alpha = \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)/3$$

$$\Delta\alpha = 2^{-1/2}\left[\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2\right]^{1/2}$$

$$\beta_{tot} = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2}$$

$$\beta_x = \beta_{xxx} + \beta_{xyz} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

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 x10^{-24} e.s.u., for β; 1 a.u = 8.6393 x10^{-33} e.s.u.). The calculated values of dipole moment (μ) for the title compounds were found to be 3.8140, 4.0319, 5.1951 and 5.7787 D respectively, which are approximately 3 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 -22.7496 x 10^{-24}, -21.5868 x 10^{-24},-23.5011 x 10^{-24} and -24.1871 x 10^{-24} esu respectively; the values of anisotropy of the polarizability are 3.9655, 3.1655, 4.9960 and 3.8666 esu, respectively. The magnitude of the molecular hyperpolarizability (β) is one of important key factors in a NLO system. The DFT/6-31G (d,p) calculated first hyperpolarizability value (β) of oxathiadiazepane 4,4-dioxides are equal to 717.0213 x 10^{-33}, 710.7318 x 10^{-33}, 587.8715 x 10^{33} and 1457.2175 x 10^{-33} esu. The first hyperpolarizability of title molecules is approximately 2.08, 2.07, 1.71 and 4.25 times than those of urea (β of urea is 343.272 x10^{-33} esu obtained by HF/6-311G(d,p) method).

Table 12: The dipole moments μ (D) polarizability α, the average polarizability α, the anisotropy of the polarizability Δα, and the first hyperpolarizability β of 1,4,3,5-oxathiadiazepane 4,4-dioxides 1-4 calculated by B3LYP/6-31G(d,p) method

Parameters	Compound 1	Compound 2	Compound 3	Compound 4
β_{xxx}	51.8944	-76.5672	5.4749	-146.9438
B_{xxy}	-3.6220	-41.8921	-20.6390	-24.8812
B_{xyy}	28.8176	3.9420	-16.7907	-11.3872
β_{yyy}	9.9718	38.6422	14.6392	7.7472
B_{zxx}	-16.7567	21.3909	30.8597	-13.5634
B_{xyz}	-9.2137	25.3379	18.6806	-6.0976
B_{zyy}	18.7223	7.4866	24.3654	-18.6269
B_{xzz}	0.2080	-8.6755	-2.3938	-2.2114
B_{yzz}	-14.4639	11.4897	-4.1325	-6.4065
β_{zzz}	14.5975	7.0525	12.0625	-13.8816
B_{tot}(esu) x10^{-33}	717.0213	710.7318	587.8715	1457.2175
μ_x	2.7723	-2.6088	-0.0806	-4.1811
μ_y	1.3891	2.0663	1.9115	2.1201
μ_z	2.2206	2.2761	4.8300	-3.3788
μ_{tot}(D)	3.8140	4.0319	5.1951	5.7787
α_{xx}	-142.2037	-134.0736	-139.7545	-163.4994
α_{yy}	-154.7431	-151.1193	-165.9448	-155.3450
α_{zz}	-163.5723	-151.7880	-170.0329	-170.7746
α_{xy}	-10.2599	-3.6164	2.8195	9.0906
α_{xz}	3.4763	-3.4815	-9.3954	8.7697
α_{yz}	-2.4525	-5.1074	-3.5631	2.7888
α_0 (esu) x10^{-24}	-22.7496	-21.5868	-23.5011	-24.1871
$\Delta\alpha$ (esu) x10^{-24}	3.9655	3.1655	4.9960	3.8666

CONCLUSION

In the present work, All theoretical calculations is performed with DFT/B3LYP/6-31G(d,p). The theoretically calculated values of both bond lengths and bond angles of the structure of the minimum energy were investigated. The MEP map contour shows that the negative potential sites are on electronegative atoms as well as the positive potential sites are around the hydrogen atoms. The movement of π-electron cloud from donor to acceptor i.e. intramolecular charge transfer can make the molecules more polarized and the HOMO-LUMO energy gap must be responsible for the NLO properties of molecules. The titled compounds exhibited good NLO property and were much greater than that of urea. We can conclude that the titled molecule is an attractive object for future studies of non-linear optical properties. The values of electronegativity, chemical hardness, softness, and electrophilicity index have been calculated. Fukui function helps to identifying the electrophilic and nucleophilic nature of a specific site within a molecule. According to stability of the molecule to softness, this means that the molecule with least HOMO-LUMO gap and means that it is more reactive molecule. NBO analysis reveals that the some important intramolecular charge transfer can induce large nonlinearity to the title molecule and the intramolecular conjugative interaction around the sulfonamide group can induce the large bioactivity in the compound. We conclude that the title compound and its derivatives are an attractive object for future studies of nonlinear optical properties.

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