DFT Based Simulations Study for Comparative Prediction of Reactivity and Stability of Thiadiazoles

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Abstract

HOMO and LUMO energies and thermodynamics of a set of thiadiazoles have been evaluated based on Density Functional Theory (DFT) at B3LYP level of theory at 6-31G* in the Gaussian program. The results of HOMO density of frontier orbitals indicate that thiadiaoles, sequence of donor ability is in the order, 2-methyl-1,3,4-thiadiazole > 2,5-dimethyl-1,3,4-thiadiazole > 5-methyl-1,3,4-thiadiazol-2-amine > 1,3,4-thiadiazol-2-amine > 1,3,4-thiadiazole-2,5-diamine. The electron charge density allowed to find out different molecular properties such us the electrostatic potential and the dipole moment, which were finally subject to a comparison leading to a good match obtained between studied molecules. The intramolecular charge transfer has also been confirmed by an HOMO-LUMO analysis.

Keywords: Thiadiazole, DFT, HOMO, LUMO.

Introduction

Density Functional Theory (DFT) has become a general method for calculating the ground state properties of interacting many electron systems such as atoms, molecules or solids [1–6] and attempts have been made to extend it to obtain excited-states [7,8]. Since its inception DFT has become very popular among researchers in physics, chemistry and material science, due to ease of its implementation and due to the development of accurate density functionals. The theory originates from the pioneering work due to Thomas [9] and Fermi [10] in the early thirties of the twentieth century and further re-finements by Hartree [11], Dirac [12], Fock [13] and Slater [14]. The application of density functional theory (DFT) [15] has given a new concept to chemical system. This concept focuses on the one electron density function instead of wave function [16]. For every chemical system there is a quantity μ called the electronic chemical potential. A chemical system is an atom, molecule, ion or radical or several such unit in a state of interaction [17]. A band gap is defined as the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels in the molecule [18].

$$Eg=ELOMO - EHOMO \text{ (ev)} \dots\dots\dots\dots (1)$$

Energy-gap is common knowledge that similar to the way electrons occupy the atomic orbitals, electrons occupy the molecular orbitals surrounding the molecule. The formations of molecular orbitals are from the linear combination of atomic orbitals or more specific, from the wave interaction of atomic orbitals. The study of energies of pairs of frontier orbitals, namely HOMO and LUMO of molecules provide reliable and quantitative data for straightforward prediction and comparative study of stabilities of molecules both from chemical and thermodynamic viewpoints. It has been reported earlier that HOMO-LUMO energy gap (ΔE) is an important stability index [19]. Dipole Moment is an important parameter that helps in the understanding of interaction between atoms in the same or different molecules is the dipole moment. It is a measure of the net molecular polarity, which is the magnitude of charge at the either ends of the molecular dipole time the distance between the charges. Dipole moment increases with increase in electronegativity of atoms [20]. Chemical reactivity usually increases with increase in dipole moment. In the present paper, the thiadiazoles named "1,3,4-thiadiazole-2,5-diamine (1); 5-methyl-1,3,4-thiadiazol-2-amine (2); 2,5-dimethyl-1,3,4-thiadiazole (3); 1,3,4-thiadiazol-2-amine (4) and 2-methyl-1,3,4-thiadiazole (5)" were chosen to be studied by DFT methods, their

structures as in Scheme (1), electronic properties, and chemical reactivity's were investigated and compared.

1   **2**

3   **4**   **5**
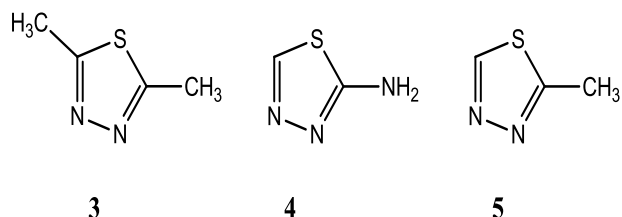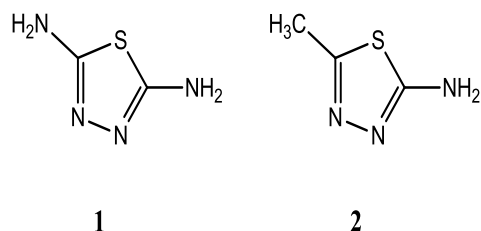
Scheme (1): The structures of thiadiazoles.

Experimental Details

Density functional theory (DFT) is a popular quantum mechanical calculation tool for probe into structures and reactivity of chemical molecules. In this study, DFT at the B3LYP/6-31G*basis set level is used to calculate the orbitals energies (HOMO and LUMO), optimized geometric structures, dipole moments, total energies, energy gaps, hardness and softness properties of thiadiazoles named "1,3,4-thiadiazole-2,5-diamine(1); 5-methyl-1,3,4-thiadiazol-2-amine (2); 2,5-dimethyl-1,3,4-thiadiazole (3); 1,3,4-thiadiazol-2-amine (4) and 2-methyl-1,3,4-thiadiazole (5)". These parameters are calculated using Chem Office software. The calculated values were correlated with the reactivity and stability of the 1,3,4-thiadiazole-2,5-diamine (1); 5-methyl-1,3,4-thiadiazol-2-amine (2); 2,5-dimethyl-1,3,4-thiadiazole (3); 1,3,4-thiadiazol-2-amine (4) and 2-methyl-1,3,4-thiadiazole (5) and the results obtained were used as a basis for comparison.

Results and Discussion

The ground state geometry optimization of the thiadiaoles derivatives: 1,3,4-thiadiazole-2,5-diamine (1); 5-methyl-1,3,4-thiadiazol-2-amine (2); 2,5-dimethyl-1,3,4-thiadiazole (3); 1,3,4-thiadiazol-2-amine (4) and 2-methyl-1,3,4-thiadiazole (5) were performed by using the DFT/B3LYP/6-311G** method and shown in Fig.(2).
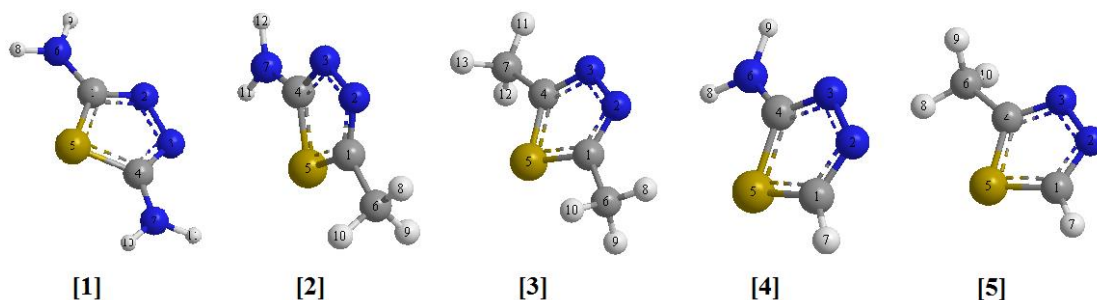

[1]   **[2]**   **[3]**   **[4]**   **[5]**

Fig.(1): Optimized ground state geometry of thiadiaoles derivatives: 1,3,4-thiadiazole-2,5-diamine (1); 5-methyl-1,3,4-thiadiazol-2-amine (2); 2,5-dimethyl-1,3,4-thiadiazole (3); 1,3,4-thiadiazol-2-amine (4) and 2-methyl-1,3,4-thiadiazole (5).

The calculated bond lengths and bond angles of thiadiaoles (1 to 5) are in good indication for the validity of the computational method. The similarity of the derivatives to the parent molecule explains the similarity in bond lengths and bond angles in all the molecules especially as we move farther away from the substituents (amine or/and amine). All the optimized geometries of thiadiaoles derivatives kept good planarity. Details of the resulted calculated structural parameters for all five molecules are presented in Table (1).

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Table (1)
***Calculated bond lengths (Å), dipole moments (Debye) and energies (hartree) for the studies
molecules using the DFT/B3LYP/6-311G** method.***

No.	Bonds Actual (°A)		Bonds Optimal (°A)	
1	N(7)-H(11)	1.0124	N(7)-H(11)	1.0500
	N(7)-H(10)	1.0103	N(7)-H(10)	1.0500
	N(6)-H(9)	1.0124	N(6)-H(9)	1.0500
	N(6)-H(8)	1.0103	N(6)-H(8)	1.0500
	C(1)-S(5)	1.7172	C(1)-S(5)	1.6575
	C(4)-S(5)	1.7172	C(4)-S(5)	1.6575
	N(3)-C(4)	1.3132	N(3)-C(4)	1.3580
	N(2)-N(3)	1.3819	N(2)-N(3)	1.3330
	C(1)-N(2)	1.3132	C(1)-N(2)	1.3580
	C(4)-N(7)	1.3410	C(4)-N(7)	1.4620
	C(1)-N(6)	1.3410	C(1)-N(6)	1.4620
2	N(7)-H(12)	1.0126	N(7)-H(12)	1.0500
	N(7)-H(11)	1.0103	N(7)-H(11)	1.0500
	C(6)-H(10)	1.0948	C(6)-H(10)	1.1130
	C(6)-H(9)	1.0948	C(6)-H(9)	1.1130
	C(6)-H(8)	1.0947	C(6)-H(8)	1.1130
	C(1)-S(5)	1.7169	C(1)-S(5)	1.6575
	C(4)-S(5)	1.7188	C(4)-S(5)	1.6575
	N(3)-C(4)	1.3140	N(3)-C(4)	1.3580
	N(2)-N(3)	1.3817	N(2)-N(3)	1.3330
	C(1)-N(2)	1.3153	C(1)-N(2)	1.3580
	C(4)-N(7)	1.3402	C(4)-N(7)	1.4620
	C(1)-C(6)	1.4839	C(1)-C(6)	1.4970
3	C(7)-H(13)	1.0945	C(7)-H(13)	1.1130
	C(1)-C(6)	1.4835	C(1)-C(6)	1.4970
	C(4)-C(7)	1.4835	C(4)-C(7)	1.4970
	C(1)-N(2)	1.3161	C(1)-N(2)	1.3580
	N(2)-N(3)	1.3799	N(2)-N(3)	1.3330
	N(3)-C(4)	1.3159	N(3)-C(4)	1.3580
	C(4)-S(5)	1.7183	C(4)-S(5)	1.6575
	C(1)-S(5)	1.7182	C(1)-S(5)	1.6575
	C(6)-H(8)	1.0946	C(6)-H(8)	1.1130
	C(6)-H(9)	1.0945	C(6)-H(9)	1.1130
	C(6)-H(10)	1.0945	C(6)-H(10)	1.1130
	C(7)-H(11)	1.0946	C(7)-H(11)	1.1130
	C(7)-H(12)	1.0945	C(7)-H(12)	1.1130
4	C(4)-N(6)	1.3397	C(4)-N(6)	1.4620
	C(1)-N(2)	1.3140	C(1)-N(2)	1.3580
	N(2)-N(3)	1.3823	N(2)-N(3)	1.3330
	N(3)-C(4)	1.3147	N(3)-C(4)	1.3580
	C(4)-S(5)	1.7203	C(4)-S(5)	1.6575
	C(1)-S(5)	1.7129	C(1)-S(5)	1.6575
	C(1)-H(7)	1.0807	C(1)-H(7)	1.1000
	N(6)-H(8)	1.0104	N(6)-H(8)	1.0500
	N(6)-H(9)	1.0124	N(6)-H(9)	1.0500
5	C(6)-H(10)	1.0947	C(6)-H(10)	1.1130
	C(4)-C(6)	1.4846	C(4)-C(6)	1.4970
	C(1)-N(2)	1.3146	C(1)-N(2)	1.3580
	N(2)-N(3)	1.3808	N(2)-N(3)	1.3330
	N(3)-C(4)	1.3172	N(3)-C(4)	1.3580
	C(4)-S(5)	1.7193	C(4)-S(5)	1.6575
	C(6)-H(9)	1.0947	C(6)-H(9)	1.1130
	C(6)-H(8)	1.0945	C(6)-H(8)	1.1130
	C(1)-H(7)	1.0807	C(1)-H(7)	1.1000
	C(1)-S(5)	1.7141	C(1)-S(5)	1.6575

The Carbon-Nitrogen bond length values for compounds 1 to 5 were [(1)1.3132, 1.3410; (2) 1.3402; (4) 1.3397] Å respectively and this is very close to the optimal Carbon-Nitrogen bond length. The computed computed dipole moment was for the compound 2-methyl-1,3,4-thiadiazole and this predicts that 2-methyl-1,3,4-thiadiazole is the most stable compound in selected studied compounds due to its lowest dipole moment value. Since 1,3,4-thiadiazol-2-amine > 1,3,4-thiadiazole-2,5-diamine are very polar, the conditions of the substitution reaction will dictate the stability of the product. The energies of frontier orbitals: the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were computed. Fig.(3)

illustrates the energies (in hartrees) of frontier molecular orbitals and their gaps (ΔE) at the B3LYP/6-311G** level. It can be seen that the values of EHOMO increase in the order 2-methyl-1,3,4-thiadiazole < 2,5-dimethyl-1,3,4-thiadiazole < 5-methyl-1,3,4-thiadiazol-2-amine < 1,3,4-thiadiazol-2-amine < 1,3,4-thiadiazole-2,5-diamine. The same trend is seen for the ELUMO.
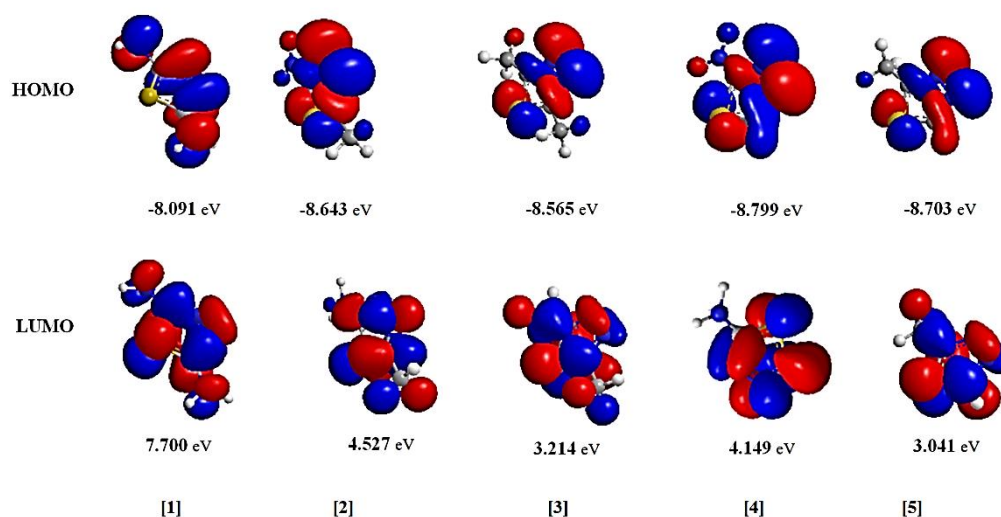

Fig.(3): The frontier orbitals of the molecules of 2-methyl-1,3,4-thiadiazole; 2,5-dimethyl-1,3,4-thiadiazole; 5-methyl-1,3,4-thiadiazol-2-amine; 1,3,4-thiadiazol-2-amine and 1,3,4-thiadiazole-2,5-diamine. The highest occupied molecular orbital (HOMO) are shown at the bottom and the lowest unoccupied molecular orbital (LUMO) are shown at the top. The values for EHOMO (eV) and ELUMO (eV) are shown on the graph.

Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the main orbitals taking part in the chemical reaction. It is common knowledge that similar to the way electrons occupy the atomic orbitals, electrons occupy the molecular orbitals surrounding the molecule. The formations of molecular orbitals are from the linear combination of atomic orbitals or more specific, from the wave interaction of atomic orbitals. The study of energies of pairs of frontier orbitals, namely

HOMO and LUMO of molecules provide reliable and quantitative data for straightforward prediction and comparative study of stabilities of molecules both from chemical and thermodynamic viewpoints. It has been reported earlier that HOMO-LUMO energy gap (ΔE) is an important stability index [21]. A large energy gap implies higher stability and lower chemical reactivity and vice versa. From the calculations made using DFT at the B3LYP/6-31G* basis set level, energy gab of compounds 1 to 5 were (-0.991;

-4.116; -5.251; -4.650 and -5.662 eV) respectively. Compound 5 is greater than the others, also compound 3 has the highest EHOMO and compound 1 has the highest ELUMO. This suggests than compound 1 and 4 would be of higher reactivity. The higher reactivity of would indicate a lower stability relative to other compounds. It could further be seen from the calculated amount of ΔE values that compounds 3 and 5 have higher band gaps energy than other compounds. Thermodynamically, a lower energy is representative of higher stability of molecules and low reactivity. However, a molecule may be thermodynamically stable but kinetically unstable. Therefore, the proposed higher stability of compound 3 may be ascribed to kinetic stability due to resonance and inductive effect and also steric handers.

Conclusions

On the basis of this study, it has been concluded that compounds 1,3,4-thiadiazole-2,5-diamine (1); 5-methyl-1,3,4-thiadiazol-2-amine (2); 2,5-dimethyl-1,3,4-thiadiazole (3); 1,3,4-thiadiazol-2-amine (4) and 2-methyl-1,3,4-thiadiazole (5)" were chosen to be studied by DFT methods. Compound 3 would show higher chemical reactivity than other from the values of their band gaps energy differences, total energies and dipole moments.

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الخلاصة

طاقات أعلى مدار جزيئي مشغول وطاقات أدنى مدار جزيئي غير مشغول والتي يرمز له اختصاراً HOMO و LUMO للمدارات الجزيئية من حيث شغلها بالإلكترونات لمجموعة من الثايوديازولات تم تقيمها بالاعتماد على نظرية دالة الحالة Density Functional Theory (DFT) باستخدام المستوى–B3LYP level of theory at 6 *31G باستخدام برنامج كاوسين Gaussian program. نتائج الـ HOMO و LUMO للجزيئات المدروسة اعتمادا علة قابلية هبة الالكترونات والاستقرارية بالترتيب التالي. 2-. methyl-1,3,4-thiadiazole > 2,5-dimethyl-1,3,4-thiadiazole > 5-methyl-1,3,4-thiadiazol-2-amine > 1,3,4-thiadiazol-2-amine > 1,3,4-thiadiazole-2,5-diamine. ان كثافة شحنة الإلكترون سمحت بمعرفة الخصائص الجزيئية المختلفة مثل ثنائي القطب وغيرها من الدوال والتي كانت في النهاية حققت معرفة تامة لنا لعلاقات الجزيئات المدروسة وتاثير المجاميع المعوضة والتي شملتها الدراسة.