

***Electronic Structure, Thermodynamics functions and Physical properties and charges study for derivatives ring 4(1,3,4-thiadiazol-2-yl)benzene-1,3-diols by using Ab Intio calculation (RHF Method).***

Received :5/3/2015

Accepted :31/5/2015

*Manal. A. Mohammad and Shatha A. Gawad*

*Mn.ab69@yahoo.com*

**Abstract:**

This study involved the adoption of the program (Gaussian 03) to use the method of calculation the total (Ab initio of method) according to the Hartree – Fock method (RHF), for the purpose of the expense of dimensional geometric (lengths and angles bond) when the geometry of a balanced, functions thermodynamic, some physical properties, charges for derivatives ring 4-(1,3,4-thiadiazol-2-yl)benzene-1,3-diols.

Calculation results have shown that the compound (R-NHC<sub>6</sub>H<sub>5</sub>) has highest value of thermodynamic functions ( $E^0$ ,  $H^0$ ,  $G^0$ ,  $A^0$ ) but the compound (R-NHC<sub>6</sub>H<sub>4</sub>-Cl) has the highest value of heat capacity and Entropy ( $C_V$ ,  $C_P$ ,  $S^0$ ). The results showed that both nitrogen atoms ( $N_9$ ,  $N_8$ ) has the highest negative charge when the compound (R-NH<sub>2</sub>), which makes it a strong legend when Linked to metal and the formation of the complex.

For (R-NH<sub>2</sub>, R-NHC<sub>6</sub>H<sub>5</sub>, R-NHC<sub>6</sub>H<sub>4</sub>-Cl, R-NHC<sub>6</sub>H<sub>4</sub>-F) molecules the calculated some of physical properties (dipole moment  $\mu$  in Debye), orbital energies ( $E_{HOMO}$ ,  $E_{LUMO}$  in eV), IP (in eV), (measurement stability  $\Delta$ ), hardness  $\eta$  and Electron Affinity  $E_A$ ). Also For these molecules the calculated ( $\Delta H_f^0$  (in kJ/mole) by using (semi-empirical method AM1 model in MOPAC program). Calculation results have shown that the compound (R-NHC<sub>6</sub>H<sub>4</sub>-F) the lower value of the heat of formation (the more Stability) as well as has less value of IP that means it's the highest active between the compounds. When the compound (R-NH<sub>2</sub>) has less value of orbital energies ( $E_{HOMO}$ ,  $E_{LUMO}$ ) and  $\Delta E$  that means this compound more active than other compounds, This difference in results come according to the difference of substituted groups.

***Key words: RHF study, 4-(1,3,4-thiadiazol-2-yl)benzene-1,3-diols, thermodynamics functions***

**Chemistry Classification QD 450-801**

**Introduction.**

Heterocyclic moieties can be found in a large number of compounds which display biological activity. The biological activity of the compounds is mainly dependent on their molecular structures [1]. 1, 3, 4-thiadiazoles are very interesting compounds due to their important applications in many pharmaceutical, biological and analytical field [2, 3]

Thiadiazole and its derivatives are used for biological activities such as antiviral, antibacterial, antifungal and antitubercular [10]. The antileukemic action and host toxicity of the thiadiazoles were blocked by administration of nicotinamide. 1, 3, 4 - Thiadiazole are diversified biocidal activities probably by virtue of a toxophoric -N=C-S-Grouping. A large number of 4-thiazolidinones have been reported to be antifungal, antibacterial and antileukemic properties. These observations prompted us to synthesis the title compound with a presumption that incorporation thiadiazole and thiazolidinones would produce new compound with significant fungicidal properties[4].

The term **theoretical chemistry** may be defined as the mathematical description of Chemistry[5 , 6] . The term **computational chemistry** is usually used when a mathematical method is sufficiently well developed that it can be automated for implementation on a computer[7]. The most important numerical techniques are ab-initio, semi-empirical and molecular mechanics. Definitions of these terms are helpful in understanding the use of computational techniques for chemistry. Ab-initio : a group of methods in which molecular structures can be calculated using nothing but the

Schrödinger equation, the values of the fundamental constants and the atomic numbers of the atoms present. The most common type of ab-initio calculation is called Hartree-Fock calculation[8,9,10].

For hydrogen the exact wave function is known . For helium and lithium , very accurate wave function have been calculated by including inter electronic distances in the variation functions[11,12]. For atoms of higher atomic number, the best approach to finding a good wave function lies in first calculating an approximate wave function using the Hartree-Fock procedure , which we shall outline in this research [13]. The Hartree-Fock method is the basis for the use of atomic and molecular orbitals in many – electron systems.

$$\underline{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \frac{Ze^2}{r_i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{e^2}{r_{ij}}$$

The first sum refers to kinetic energy operators for the n- electrons. The second sum is the potential energy for the attractions between the electrons and nucleus of charge  $Ze^2$ . for neutral atom,  $Z = n$ . The last sum the potential energy of the nucleus of electronic repulsions, the restriction  $j > i$  avoids counting the same inter electronic repulsions twice and avoids terms like  $(e^2 / r_{ii})$ [14,15,16]. The Hartree-Fock SCF Method. Because of inter electronic repulsions terms  $(e^2 / r_{ij})$  the Schrödinger equation for an atom is not separable. The zero th – order wave function would be a product of n hydrogen like (one –electron) orbitals:

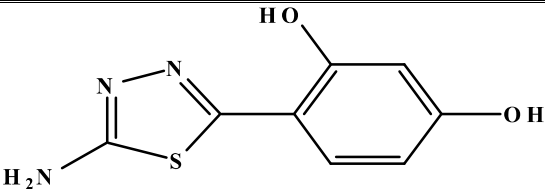
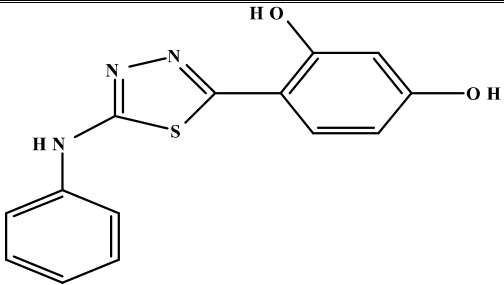
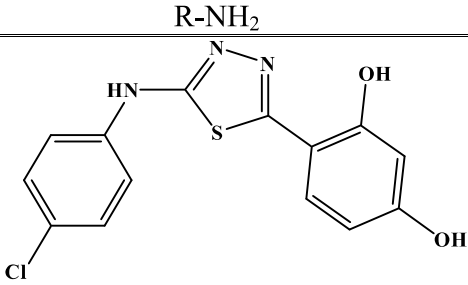
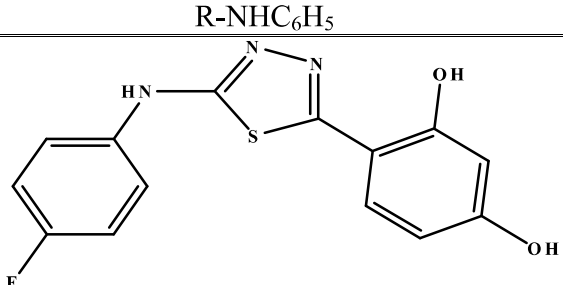
$$\psi = f_1(r_1, \theta_1, \phi_1) f_2(r_2, \theta_2, \phi_2) \dots f_n(r_n, \theta_n, \phi_n)$$

where the hydrogen like orbitals are  $f = R_n(r) Y_l^m(\theta, \phi)$  then the

Schrödinger equation for Hartree-Fock SCF :

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 + V_1(\mathbf{r}_1) \right] \psi_1(\mathbf{r}_1) = \epsilon_1 \psi_1(\mathbf{r}_1)$$

V:potential energy ,  $\epsilon$  is the energy of the orbital of electron 1. Also this equation used for molecules which contain many electrons [17,18,19].

 <p>4-(5-Amino-[1,3,4]thiadiazol-2-yl)-benzene-1,3-diol</p>	 <p>4-(5-Phenylamino-[1,3,4]thiadiazol-2-yl)-benzene-1,3-diol</p>
 <p>4-[5-(4-Chloro-phenylamino)-[1,3,4]thiadiazol-2-yl]-benzene-1,3-diol</p>	 <p>4-[5-(4-Fluoro-phenylamino)-[1,3,4]thiadiazol-2-yl]-benzene-1,3-diol</p>
<p>R-NHC<sub>6</sub>H<sub>4</sub>-Cl</p>	<p>R-NHC<sub>6</sub>H<sub>4</sub>-F</p>

## Results and Discussion.

### **Geometrical parameter.**

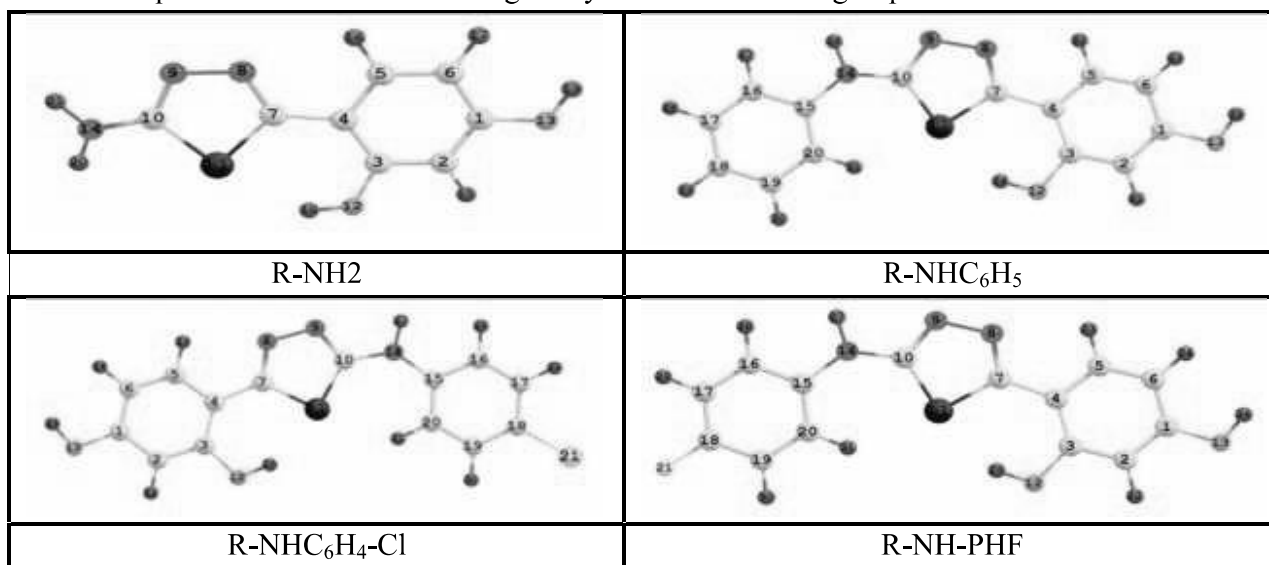
In this research calculated the molecules geometry such as (bond lengths and bond angles) of the four molecules of derivatives 4-(1,3,4-thiadiazol-2-yl) benzene-1,3-diol (R-NH<sub>2</sub>, R-NHC<sub>6</sub>H<sub>5</sub>, R-NHC<sub>6</sub>H<sub>4</sub>-Cl, R-NHC<sub>6</sub>H<sub>4</sub>-F), using the Ab initio method of according to the Hartree – Fock method (RHF). According to the results calculated and recorded in the (table 1 and fig. 1). Show that each the bonds (C<sub>10</sub>-N<sub>14</sub>) and (C<sub>10</sub>-N<sub>9</sub>) in compound R-NH<sub>2</sub> has less value compared to other compounds

studies this value may be return to the Ion pair in nitrogen atom and electron with drawing of substituted groups of the other compound. Where the bond (C<sub>10</sub>-S<sub>11</sub>) the compound R-NH<sub>2</sub> has high value compare with the other this value this caused by electron pair on S atom in this bond length that caused conjugated effect with substituted groups.

Also the change of the group substituted had effect on the value of the angles of the compounds studied in this research, have shown calculation in the (table 1 and fig.1).

That the angle ( $\angle C_{10}N_{14}S_{15}$ ) showed that in R-NHC<sub>6</sub>H<sub>4</sub>-F and R-NHC<sub>6</sub>H<sub>4</sub>-Cl larger than the other compound because the large size of substituted group in the compounds when the angle ( $\angle C_7S_{11}C_{10}$ ) the compound R-NH-PHF has larger value than the other's because of the Ion pair on S with the electronegativity

of the substituted groups. Also the result showed that the angle ( $\angle N_9C_{10}S_{11}$ ) the compound R-NH-PHF has larger value than the other's return to difference in molecular weight of substituted groups on C<sub>10</sub> with the difference of electro-negative the substituted groups.



**Fig.(1):** The geometric equilibrium for the derivatives of 4 (1,3,4- thiadiazol-2-yl) benzene – 1, 3- diol.

**Table ( 1 ) :** Calculated geometric parameters (bond lengths in Angstrom length angles in degree) of the derivatives 4 (1,3,4- thiadiazol-2-yl) benzene– 1, 3- diol.

R- NH2		R-NHC6H4F		R-NHC6H4Cl		R-NHC6H5	
Para. Geo	Bond Length and Angle	Para. Geo	Bond Length and Angle	Para. Geo	Bond Length and Angle	Para. Geo	Bond Length and Angle
R(4-7)	1.466	R(4-7)	1.497	R(4-7)	1.497	A(2-1-6)	119.5
R(5-6)	1.374	R(5-6)	1.374	R(5-6)	1.374	A(2-1-13)	117.6
R(9-10)	1.284	R(9-10)	1.315	R(9-10)	1.314	A(1-13-25)	105.4
R(10-11)	1.803	R(10-11)	1.739	R(10-11)	1.739	A(3-2-21)	118.8
R(10-14)	1.346	R(10-14)	1.404	R(10-14)	1.407	A(2-3-4)	120.1
R(12-18)	0.946	R(12-25)	0.985	R(12-25)	0.985	A(2-3-12)	113.5
R(13-19)	0.950	R(13-26)	0.989	R(13-26)	0.989	A(4-3-12)	126.4
R(14-20)	0.989	R(14-15)	1.428	R(14-15)	1.423	A(3-4-5)	117.4
R(14-21)	0.992	R(14-27)	1.020	R(14-27)	1.020	A(3-4-7)	126.4
A(7-11-10)	85.6	A(7-11-10)	87.0	A(7-11-10)	86.9	A(7-11-10)	87.0
A(8-9-10)	113.8	A(8-9-10)	111.0	A(8-9-10)	111.0	A(8-9-10)	111.0

A(9-10-11)	113.2	A(9-10-11)	115.2	A(9-10-11)	115.2	A(9-10-11)	115.2
A(9-10-14)	124.7	A(9-10-14)	118.3	A(9-10-14)	118.3	A(9-10-14)	118.3
A(11-10-14)	122.1	A(11-10-14)	126.5	A(11-10-14)	126.5	A(11-10-14)	126.5
A(10-14-20)	122.6	A(10-14-15)	132.3	A(10-14-15)	132.4	A(10-14-15)	132.4
A(10-14-21)	118.1	A(10-14-27)	112.0	A(10-14-26)	112.0	A(10-14-26)	112.0
---	---	A(15-14-27)	115.7	A(15-14-26)	115.7	A(15-14-26)	115.7
---	---	A(14-15-16)	116.6	A(14-15-16)	116.6	A(14-15-16)	116.6
---	---	A(14-15-20)	124.5	A(14-15-20)	124.5	A(14-15-20)	124.5
---	---	A(9-10-11)	115.2	A(9-10-11)	115.2	A(16-15-20)	119.0
---	---	A(9-10-14)	118.3	A(9-10-14)	118.3	---	---
---	---	A(16-15-20)	118.8	A(16-15-20)	119.0	---	---
---	---	A(15-16-17)	120.9	A(15-16-17)	120.5	---	---
---	---	A(15-16-28)	119.2	A(15-16-27)	119.2	---	---
---	---	A(15-20-19)	120.3	A(15-20-19)	119.9	---	---
---	---	A(15-20-31)	120.9	A(15-20-31)	120.9	---	---
---	---	A(17-16-28)	119.9	A(17-16-27)	120.3	---	---
---	---	A(16-17-18)	119.8	A(16-17-18)	120.5	---	---
---	---	A(16-17-29)	120.6	A(16-17-28)	119.4	---	---
---	---	A(18-17-29)	119.6	A(18-17-28)	120.1	---	---
---	---	A(17-18-19)	119.6	A(17-18-19)	119.2	---	---

**Physical properties.**

Depending on the Ab initio method of calculation Hartree – Fock method (RHF) , is calculate some physical properties of the molecules studied in this research; Dipole moments ( $\mu$  in Debye) , energies (e V) of the high Occupied Molecular Orbital ( $E_{HOMO}$ ) and the Lower Unoccupied Molecular Orbital ( $E_{LUMO}$ ) and according Koopmans theorem (the negative  $E_{HOMO}$  is equal to the ionization potential) the calculation has been ionization energies (eV) , Also calculated the energy difference ( $\Delta E$  , eV), And finally calculated (Molecular Hardness)Hardness( $\eta$ ) =  $\frac{1}{2}(E_{HOMO} - E_{LUMO})$ , (Electron Affinity)  $EA = -E_{LUMO}$  according Koopmans theorem for N system of electrons.

Shown this results (table :2) that compound R-NH<sub>2</sub> has high value for each of (Dipole moments , IP),And less value in

$E_{HOMO}$ (less the value of a negative energy),And  $\Delta E$ (sense of activity of this compound is high)and( Hardness  $\eta$  , Electron Affinity  $E_A$ ) where the compound R-NH<sub>2</sub> has less value in (IP ,  $E_{LUMO}$ )this means that this compound has more ability to lose electrons and be easier ionization compared to other compounds[20-23].

Also ,The MOPAC computational packages (semi-empirical method , AM1 model) employed to compute physical properties; heats of formation ( $\Delta H_f$ , kJ.mol<sup>-1</sup>)[24,25]. the results showed (Table:2) for the compound R-NH-Ph has lower heat of formation (more stability), Whereas the compound R-NHC<sub>6</sub>H<sub>5</sub> has a higher heat of formation (less stability), Perhaps due this result to the effect of the group substitutes for the stability the compound , as previously mentioned reason.

**Table 2: Calculated  $\Delta H_f$  (  $\text{kJ.mol}^{-1}$  ),  $\mu$  (in Debye) ,orbital energies ( $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ ,  $\Delta E$  in eV) ,  $IP$ (in eV) ,  $E_A$  (in eV) , and  $\eta$ (in eV) for the derivatives of 4 (1,3,4- thiadiazol-2-yl) benzene-1, 3- diol.**

Comp.	R- NH <sub>2</sub>	R- NH PH	R- NHPHF	R- NH PHCL
$\Delta H_f^0$	-0.5009	6.8153	-2.0260	5.8275
$\mu$	2. .5914	1.9902	1.0796	1.2132
HOMO	-8.3053	-5 .8573	-5. 8385	-6 . 0750
LUMO	2 .9231	5 . 3792	5 . 3327	5 . 15606
$\Delta E$	10.5976	11 .2365	11 . 1712	11. 2310
IP	8. 3053	6 .0750	5 . 8385	6 .07498
$E_A$	-8. 9231	-5 .1561	-5 . 3327	-5 . 1561
$\eta$	-4 . 1526	-3 .0375	-2 . 9193	-3 .0375

**Thermodynamics functions**

The fundamental vibration frequencies for the (R-NH<sub>2</sub> , R-NHC<sub>6</sub>H<sub>5</sub>, R-NHC<sub>6</sub>H<sub>4</sub>-Cl , R-NHC<sub>6</sub>H<sub>4</sub>-F) molecules along with the rotational constants, obtained in this study, where used to calculate the vibration and rotation contributions to the thermodynamic functions according to the statistical thermodynamic equations.

$$U_{vib}^0 = \sum_{i=1}^{3N-6} \frac{R T X_i}{e^{X_i} - 1}$$

$$S_{vib}^0 = R \sum_{i=1}^{3N-6} \left[ \frac{X_i}{e^{X_i} - 1} - \ln(1 - e^{-X_i}) \right]$$

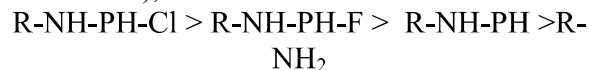
$$S_{rot}^0 = R \left[ \frac{3}{2} + \ln \frac{8\pi^2 (8\pi^2 I_X I_Y I_Z)^{\frac{1}{2}} (KT)^{\frac{3}{2}}}{\sigma h^3} \right]$$

These two contributions along with the others contributions, for the translation, electronic, and nuclear motions, where used to calculate

$E^0$ ,  $H^0$ ,  $S^0$ ,  $A^0$ , and  $G^0$  thermodynamic functions .Thermodynamics functions standard and heat capacity for the studied molecules listed **Table: 3** looking at the calculation results show that each of the thermodynamic functions ( $G^0$ ,  $A^0$ ,  $E^0$ ,  $H^0$ ) have the same gradient values (different the group substitutes),



While the functions ( $C_V$ ,  $C_P$ ,  $S^0$ ) have the same gradient values (different the group substitutes),



The deferent thermodynamics functions values due to deferent substituted groups(X), viz, the nitrogen atom that has Ion pair and a high electro-negative in addition to its high size which makes restricted movement. (X: -PH-Cl , -PH-F , -PH , -H<sub>2</sub>).

**Table 3: The calculated standard thermodynamics functions at 298.15oK of the derivatives of 4- (1,3,4- thiadiazol-2-yl) benzene– 1, 3- diol**

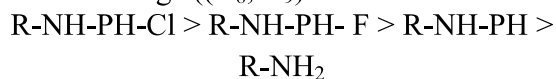
Comp.	R- NH2	R-NHPH	R-NH-PHF	R-NH-PHCL
E <sup>0</sup> KJ/mol	107.890	173.682	108.005	167.241
S <sup>0</sup> KJ/mol..K	0.105211	0.1146	0.1188	0.1213
C <sub>v</sub> KJ/mol..K	0.0428	0.05311	0.0568	0.0570
H <sup>0</sup> KJ/mol	108.4824	174.2744	168.0974	167.8364
C <sub>p</sub> KJ/mol..K	0.0448	0.0551	0.05817	0.05902
A <sup>0</sup> KJ/mol	76.5213	139.5027	132.5902	131.0739
G <sup>0</sup> KJ/mol	77.1138	140.0951	132.6826	131.6693

**The Charges**

The Calculated for all charges atoms of the molecules studied according to the method (RHF), have shown calculation results of the charges (**Table: 4**), are each of the (N<sub>8</sub>, N<sub>9</sub>) has lower value of charge (the highest density electronic ) in the case of compound ( R-NH<sub>2</sub>) while it has the highest value of charge (less density electronic ) in compound (R-NH-PH-Cl ) Perhaps the reason for this difference in electrical negative of electron with drawing .This scientific fact indicates that the compound (

R-NH<sub>2</sub>) can be strong legend , when it linked to metal complex formation , as a result of higher giving electronic to nitrogen atoms(N<sub>8</sub>, N<sub>9</sub>) compared to other compounds ,and on the contrary, the compound (R-NH-PH-Cl ) .

It also found that the amount of charge of the atom(C<sub>10</sub>) has gradient opposite to the value of charge ((N<sub>8</sub>, N<sub>9</sub>).



**Table:4** Calculated charge for the derivative of 4- (1,3,4- thiadiazol-2-yl) benzene- 1, 3- diol.

R-NH2		R-NH-ph		R-NH-CL		R-NH-PH-F	
Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
C1	3.6031	C1	3.8397	C 1	3.8384	C 1	.8394
C2	4.2171	C2	4.1094	C 2	4.1089	C 2	4.1092
C 3	3.6526	C 3	3.8429	C 3	3.8472	C 3	3.8479
C4	4.0262	C4	4.0526	C 4	4.0592	C 4	4.0587
C5	4.1475	C5	4.0212	C 5	4.0205	C 5	4.0211
C 6	4.2389	C 6	4.1121	C 6	4.1126	C 6	4.1129
C7	4.0788	C7	4.1275	C 7	4.1245	C 7	4.1269
N 8	5.3263	N 8	5.1621	N 8	5.1606	N 8	5.1614
N9	5.3395	N9	5.2456	N 9	5.2421	N 9	5.2455
C10	3.7285	C10	3.9681	C 10	3.9693	C 10	3.9681
S11	5.5197	S11	5.4857	S 11	5.4862	S 11	5.4874
O12	6.8041	O12	6.3546	O 12	6.3534	O 12	6.3543
O13	6.7858	O13	6.3097	O 13	6.3089	O 13	6.3095
N14	5.9402	N14	5.3367	N 14	5.3355	N 14	5.3368
H 15	0.7460	C15	3.8839	C 15	3.8782	C 15	3.8906
H 16	0.7213	C16	4.0834	C 16	4.0778	C 16	4.6739
H 17	0.7908	C17	4.0494	C 17	4.0407	C 17	4.0752
H 18	0.5538	C18	4.0815	C 18	3.9904	C 18	3.8703
H 19	0.5788	C19	4.0482	C 19	4.0390	C 19	4.0742
H 20	0.6078	C20	4.1408	C 20	4.1351	C 20	4.1313
H 21	0.5924	H21	0.9175	C 21	4.1414	F 21	5.1432
		H22	0.9072	H 22	0.9162	H 22	0.9171
		H23	0.9402	H 23	0.9066	H 23	0.9070
		H24	0.7576	H 24	0.9441	H 24	0.9449
		H25	0.7776	H 25	0.7592	H 25	0.7585
		H26	0.7802	H 26	0.7765	H 26	0.7773
		H27	0.9461	H 27	0.7469	H 27	0.7502
		H28	0.9346	H 28	0.9367	H 28	0.9408
		H29	0.9423	H 29	0.9154	H 29	0.9250

**References**

1. Elzahany E. A, Hegab K. H., Khalil S. K. H. and Youssef N .S.,( 2008)” **Synthesis, characterization and biological activity of some transition metal complexes with Schiff bases derived from 2 formylindole, salicylaldehyde, and Namino rhodanine**’. Aust. J. Basic Appl. Sci.; 2(2):pp. 210- 220.
2. Hadizadeh F.and .Vosoogh, ,( 2008)” **Synthesis of a-[5-(5-Amino-1, 3, 4-thiadiazol-2-yl)-2 imidazolylthio]acetic acids**’. J. Heterocyclic Chem. ,45: pp.1-3.
3. Lu S. M., and Chen R. Y. ,( 2000)” **Facial and efficient synthesis aminophosphate derivatives of 1, 3, 4 oxadiazole and 1, 3, 4 thiadizaole. Organic Preparations and Procedures International**’, 32(3): pp.302-306.



4. S. Jalhan , A. Jindal , A. Gupt , Hemraj (2012),” **Synthesis, biological activities and chemistry of thiadiazole derivatives and Schiff bases**” Asian J Pharm Clin Res., 5( 3) , pp 199-208.
5. Cramer C. J., (2004) **"Essentials of Computational Chemistry:Theories and Models"**, 2<sup>nd</sup> Ed., John Wiley & Sons Ltd, England.
6. .Heher W.J and .Shusterman A .J, (2000)**"Molecular Modeling in Undergraduate Chemistry Education,"** Wavefunction, Inc., USA;.
7. Young D. C., (2001)**"Computational Chemistry:A Practical Guide for Applying Techniques to RealWorld Problems"**,John Wiley & Sons, Inc., New York.
8. C.Trindle and D. Shillady, (2008) **"ElectronicStructureModeling:Connections Between Theory and Software"**, CRC press, Taylor & Francise Group, LLC, USA.
9. Bultinck P., Winter H. D., Langenaeker W. and Tollenaere J. P., (2008) , **"Computational Medicinal Chemistry for Drug Discovery"**, Taylor & Francise Group, LLC, USA.
10. F.Jensen, (2007) ;**"Introduction to Computational Chemistry"**, 2<sup>nd</sup> Ed., John Wiley & Sons Ltd., England.
11. E. G.Lewars, , (2004) ;**"Computational Chemistry: Introduction to the Theory and ApplicationsofMolecular and Quantum Mechanics"**, Kluwer Academic Puplishers, USA.
12. Z. R Zhou., L. X. Hong and Z. X.Zhou, (2012), **Indian Journal of Pure & Applied Physics** 50,pp. 719-726.
13. M. V.Putz, (2010) ;**"Communications in Mathematicaland in Computer Chemistry"**,64, pp.391-418.
14. J.Kobus, (2012).**"AFinite Difference Hartree-Fock Program for Atoms and Diatomic Molecules"**,Computer Physics Communications,Poland.
15. C. E. Dykstra, (1988) **"AB Initio Calculation of the Structures and Properties of Molecules"**, Elsevier, Netherlands;.
16. R. M Martin., ; (2004) **"Electronic Structure Basic Thøry and Practical Methods"**, Cambridge University Press, UK.
17. H.Adachi, T.Mukoyama and J.Kawai, **"Hartree-Fock-Slater Method for Materials Science"** Springer, Germany; (2006) .
18. Lawley K. P., (1987) ,**"Ab Initio Methods in Quantum Chemistry,"** Part 1, John Wiley & Sons Inc., UK.
19. Ivanov S., (2006) **"Theoretical and Quantum Mechanics: Fundamentals for Chemists"**,Springer, Netherlands;.
20. Moore C. E. , (1970) ,**"Ionization Potentials and Ionization Limits Derived from The Analyses of Optical Spectra"**, NSRDS-NBS, USA.
21. Vanfleteren D., Neck D. V., Ayers P. W., Morrison R. C. and Bultinck P, (2009) , *J.of Chemical Physics*,130, pp.194104(1)-194104(10).
22. Hotop H.and Lineberger W. C., (1975) , *Journal of Physical Chemistry*, 4, pp.539-576;.
23. C. G.Zhan, J. A. Nicholsand ,D. A. Dixon,(2003),*J. of Physical Chemistry A*, 107,pp. 4184-4195.
24. Pearson R.G., (1997),**"Chemical Hardness"**, wiley-VCH, Germany.
25. R.G., (1986) ,” *Pearson Proceedings of the National Academy of Sciences of the United States of America*, 83, pp.8440-8441..

دراسة التركيب الإلكتروني، الدوال الترموديناميكية والخصائص الفيزيائية لبعض المشتقات حلقة  $\text{C}_6\text{H}_4\text{N}_2$  باستخدام حسابات الطريقة التامة (RHF).

تاريخ القبول: 2015/5/31

شذى عبد الأمير جواد

تاريخ الاستلام 2015/3/5

منال عبد محمد

جامعة كربلاء – كلية التربية للعلوم الصرفة –  $\text{C}_6\text{H}_4\text{N}_2$

**ملخص:**

تضمنت هذه الدراسة اعتماد برنامج كاس (Gaussian 03) لاستخدام طريقة الحساب التام على وفق طريقة هارترى فوك (RHF)، وذلك لغرض حساب الأبعاد الهندسية (أطوال و زوايا التاصر) عند الشكل الهندسي المتوازن، الدوال الترموديناميكية ( $G^0, H^0, S^0, A^0, E^0$ ) وكذلك تم حساب السعة الحرارية ( $C_p, C_v$ )، بعض الخصائص الفيزيائية وكذلك الشحنات لمشتقات حلقة (R-NH<sub>2</sub>, R-NHC<sub>6</sub>H<sub>5</sub>, R-NHC<sub>6</sub>H<sub>4</sub>- (4-(1,3,4-thiadiazol-2-yl)benzene-1,3-diol) والتي يرمز لها اختصارًا (R-NHC<sub>6</sub>H<sub>5</sub>) يمتلك أعلى قيمة من قيم الدوال الترموديناميكية (R-NHC<sub>6</sub>H<sub>4</sub>-F), Cl, وقد أظهرت نتائج الحساب أن المركب (R-NHC<sub>6</sub>H<sub>4</sub>-Cl) يمتلك أعلى قيمة سعة حرارية ( $S^0, C_p, C_v$ )، كما أظهرت نتائج الحساب بان لكل من ذرات النتروجين ( $N_8, N_9$ ) قيمة شحنة سالبة عالية في المركب (R-NH<sub>2</sub>) مما يجعله ليكاند قوي عند ارتباطه بالفلز وتكوين المعقد.

كما تم حساب بعض الخصائص الفيزيائية عزم ثنائي القطب ( $\mu$  in Debye), طاقة المدارات ( $E_{\text{HOMO}}, E_{\text{LUMO}}$ ), طاقة التأين (IP in eV), فجوة الطاقة ( $\Delta E$  in eV), الألفة الإلكترونية و الصلابة ( $E_A, \eta$  in eV) وكذلك تم اعتماد برنامج MOPAC لاستخدام الطريقة الشبه تجريبية AM1 لحساب حرارة التكوين للمركبات ( $\Delta H_f^0$  in kJ/mole). وقد أظهرت النتائج الحساب أن المركب (R-NHC<sub>6</sub>H<sub>4</sub>-F) أكثر استقرارا لكونه يمتلك أقل قيمة في حرارة التكوين كذلك يمتلك أقل قيمة لطاقة التأين والمركب (R-NH<sub>2</sub>) يمتلك أقل قيمة لفرق الطاقة بين المدارات ( $E_{\text{HOMO}}, E_{\text{LUMO}}$ ) وهذا يعني أن هذا المركب هو أكثر المركبات فعالية لكونه يمتلك أقل قيمة لفجوة الطاقة. أن هذا التباين بالنتائج يعزى بصورة عامة لتأثير اختلاف المجموعة المعوضة على المركبات المدروسة في هذا البحث.

**الكلمات المفتاحية:** زوايا التاصر عزم ثنائي القطب الدوال الترموديناميكية