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Electronic Structure, Thermodynamics functions and Physical properties for thiadiazol derivatives ring by using Ab Intio calculations(RHF-Model).

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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($R-NO_2$) has less value of thermodynamic functions (E^0 , H^0 , G^0 , A^0) but the compound ($R-OCH_3$)) has highest value of heat capacity and Entropy (C_V , C_P,S^0) .The results showed that both nitrogen atoms (N_9 , N_8) had the highest negative charge when the compound($R-NO_2$) which makes it a strong legend when Linked to metal and the formation of the complex.
For ($R-CH_3$, $R-NO_2$, $R-OCH_3$, R-OH) molecules the calculated some of physical properties (dipole moment μ in Debye), orbital energies (E_{HOMO} , E_{LUMO} in e V), IP (in e V) , (measurement stability Δ) , hardness η and Electron Affinity E_A).Also For these molecules the calculated (ΔH_f^0 (in kJ/mole)by using (semi-empirical method AM1 model in MOPAC program). Calculation results have shown that the compound (R-OH) the lower value of the heat of formation (the more Stability)as well as has high value of the (ΔE , η , E_A),While the compound $R-NO_2$ has less ΔE 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.

Introduction

The term **theoretical chemistry** may be defined as the mathematical description of Chemistry[1, 2]. 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[3]. 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[4,5,6].

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[7,8]. For atoms of higher

atomic number, the best approach to finding agood wave function lies in first calculating an approximate wave function using the Hartree-Fock procedure , which we shall outline in this research [9]. The Hartree-Fock method is the basis for the use of atomic and molecular orbitals in many –electron systems.

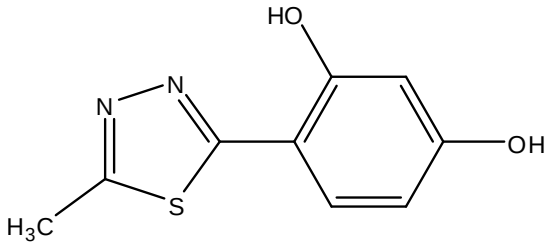
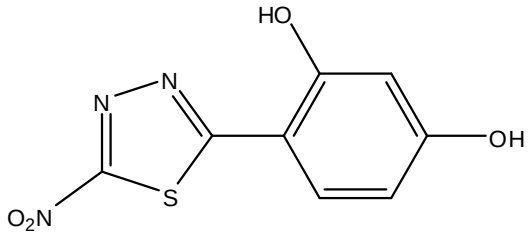
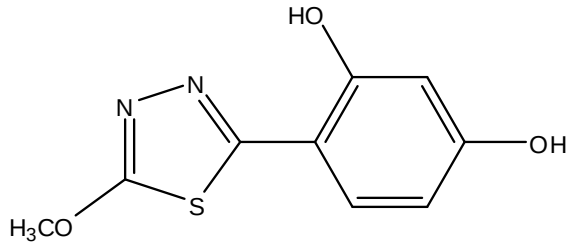
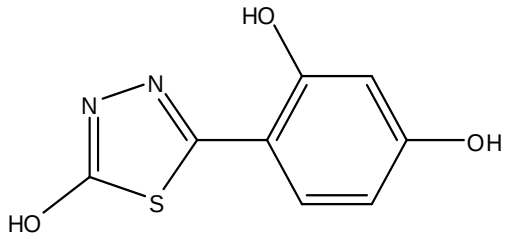
$$\underline{\underline{\mathrm{H}}} = -\frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\frac{Ze^2}{r_1} + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{e^2}{r_{ij}}$$

The firstsum 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})[10,11,12]. The Hartree-Fock SCF Method. Because of inter electronic repulsions terms (e^2/r_{ii}) the Schrödinger equation for an atom is not separable. The zeroth – order wave function would be a product of n hydrogen like (one – electron)orbitals:

$$\psi = f_1(r_1,\theta_1,\phi_1)f_2(r_2,\theta_2,\phi_2)...\mathrm{f}_n(r_n,\theta_n,\phi_n)$$

where the hydrogen like orbitals are $f = R_n(r)Y_i^m(\theta,\phi)$ then the Schrödinger equation for Hartree - Fock SCF : $\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 + V_1(\mathrm{r}_1)\right]t_1(1) = \varepsilon_1 t_1(1)$

V: potential energy , ε is the energy of the orbital of electron 1. Also this equation used for molecules which contain many electrons[13,14,15] .

 4-(5-methyl-1,3,4-thiadiazol-2-yl)benzene-1,3-diol	 4-(5-nitro-1,3,4-thiadiazol-2-yl)benzene-1,3-diol
R-CH_3	**R-NO_2**
 4-(5-methoxy-1,3,4-thiadiazol-2-yl)benzene-1,3-diol	 4-(5-hydroxy-1,3,4-thiadiazol-2-yl)benzene-1,3-diol
R-OCH_3	**R-OH**

Results and Discussion.

Geometrical parameter.

In this research calculated the geometry (bond lengths and bond angels) of the four molecules of derivatives 4-(1,3,4-thiadiazol-2-yl) benzene-1,3-diol(R-CH_3 , R-NO_2 , R-OCH_3, R-OH), 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 eachof the bonds (**C_{10}-N_9),(C_{10}-X_{14}),[X: C_{14} , O_{14},N_{14})** in compound R-NO_2 has less value compared to other compounds studies this value may be return to the electro-negative the

substituted groups. While the results showed the bond (**C_{10}-S_{11})** in compound R-OCH_3longer than the other compounds this caused by electron pair on **S** atom in this bond length.

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 ($\angle$ **$S_{11}C_{10}N_9$**) the compound R-OH has high value than other compounds is due to the differ of inductive effect of the substituted groups.the angle ($\angle$ **$C_7S_{11}C_{10}$**) the result showed that in compound R-CH_3has the high value when the compound R-OCH_3 ,Also the angle ($\angle$ **$C_{10}N_9N_8$**)in compound R-CH_3has the high value while the compound R-OH because the Ion pair on the (N ,S) and this rearrangement return to difference in molecular weight of substituted groups on **C_{10}** with the difference of electro-negative of the substituted groups.

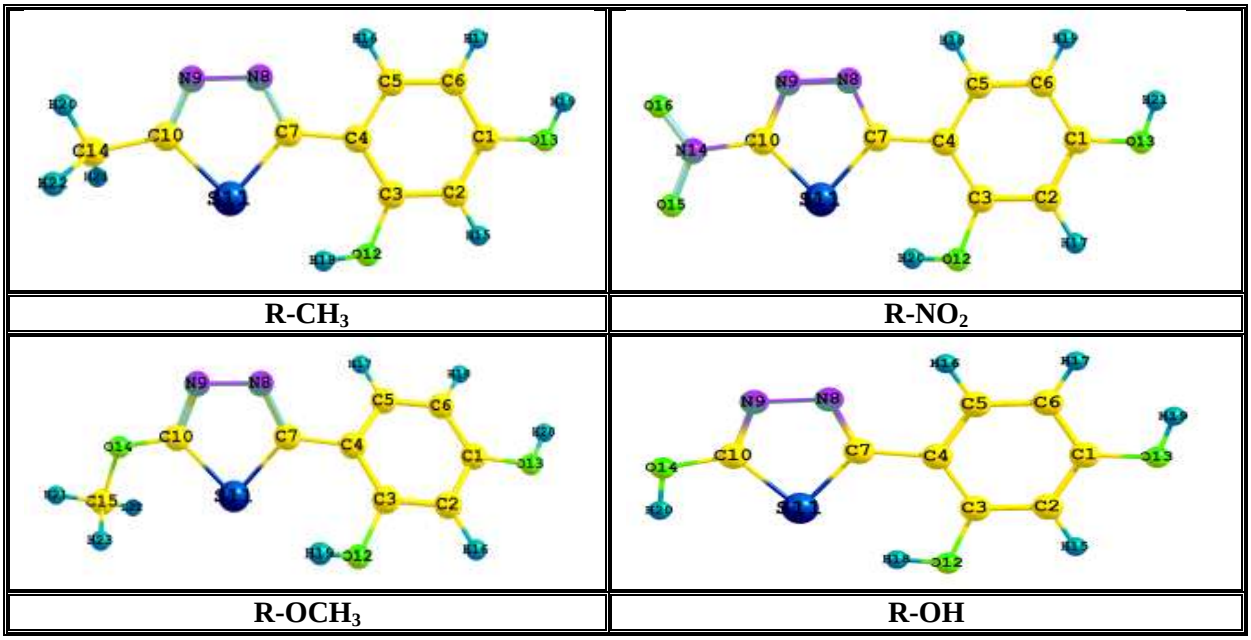


Fig.(1): The geometric equilibrium for the derivatives of 4- (1,3,4- thiadiazol-2-yl) benzene – 1, 3- diol.

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-CH3		R-NO2		R-OCH3		R-OH	
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(3-4)	1.402	R(3-4)	1.406	R(3-4)	1.398	R(3-4)	1.409
R(4-5)	1.405	R(4-7)	1.451	R(3-12)	1.375	R(3-12)	1.392
R(4-7)	1.463	R(7-8)	1.302	R(5-6)	1.379	R(4-5)	1.402
R(5-6)	1.374	R(7-11)	1.810	R(5-17)	1.071	R(4-7)	1.497
R(5-16)	1.070	R(8-9)	1.363	R(6-18)	1.073	R(5-6)	1.374
R(7-8)	1.286	R(9-10)	1.268	R(7-8)	1.278	R(5-16)	1.084
R(7-11)	1.817	R(10-11)	1.778	R(7-11)	1.829	R(7-8)	1.310
R(8-9)	1.382	R(10-14)	1.427	R(8-9)	1.384	R(8-9)	1.424
R(9-10)	1.275	A(2-1-6)	120.6	R(9-10)	1.274	R(9-10)	1.305
R(10-11)	1.807	A(1-6-5)	118.9	R(10-11)	1.815	R(10-11)	1.749
R(10-14)	1.486	A(1-6-19)	120.8	R(10-14)	1.330	R(10-14)	1.386
A(1-6-5)	118.9	A(3-4-5)	117.3	R(14-15)	1.444	R(12-18)	0.985
A(2-3-4)	120.8	A(3-4-7)	126.5	R(15-21)	1.074	R(14-20)	0.990
A(2-3-12)	113.1	A(3-12-20)	120.4	R(15-22)	1.080	A(1-2-3)	121.0
A(4-3-12)	126.1	A(5-4-7)	116.2	R(15-23)	1.080	A(1-2-15)	120.2
A(3-4-5)	117.2	A(4-5-6)	122.2	A(2-1-6)	120.7	A(6-1-13)	123.0

A(3-4-7)	126.5	A(4-7-8)	121.8	A(1-6-5)	119.1	A(1-6-5)	119.3
A(5-4-7)	116.3	A(4-7-11)	126.5	A(1-6-18)	120.7	A(3-2-15)	118.9
A(4-5-6)	122.3	A(7-8-9)	114.7	A(2-3-4)	121.2	A(2-3-4)	120.1
A(4-5-16)	117.6	A(7-11-10)	84.9	A(2-3-12)	115.5	A(2-3-12)	113.6
A(5-6-17)	120.3	A(8-9-10)	114.0	A(4-3-12)	123.3	A(4-3-12)	126.3
A(7-11-10)	86.2	A(9-10-11)	114.7	A(3-4-5)	117.8	A(3-12-18)	107.4
A(8-9-10)	115.2	A(9-10-14)	123.8	A(3-4-7)	124.2	A(4-7-8)	120.3
A(9-10-11)	112.0	A(11-10-14)	121.4	A(4-7-8)	123.9	A(4-7-11)	125.7
A(9-10-14)	125.2	A(10-14-15)	115.6	A(4-7-11)	124.2	A(5-6-17)	120.6
				A(6-5-17)	120.1	A(8-7-11)	114.0
				A(5-6-18)	120.2	A(7-8-9)	113.0
				A(8-7-11)	111.8	A(8-9-10)	110.9
				A(7-8-9)	116.1	A(9-10-11)	115.5
				A(8-9-10)	113.6	A(9-10-4)	120.1
				A(9-10-11)	113.8	A(11-10-14)	124.4
				A(9-10-14)	122.7		
				A(11-10-14)	123.5		

Physical properties.

Depending on the Ab initio of method of calculation according to the Hartree – Fock method (RHF) , is calculate some physical properties of the molecules studied in this research; Dipole moments (μ 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 (e V) , Also calculated the energy difference (ΔE , e V), And finally calculated (Molecular Hardness)Hardness(η) = ½(E_{HOMO} -E_{LUMO}), (Electron Affinity) EA = -E_{LUMO} according Koopmans theorem for N system of electrons**[16 ,17]**Electronegativity(χ) according to Mullikan1934 **[18]** and Electrophilicity (Ꞷ) according to Parr and co-workers 1999**[19]**.

This results shown**(table :2)** that compound R-NO_2has less value for each of (E_{LOMO}, E_{LUMO}, ΔE, η)that's means the activity of this compound is high , also this compound has high value of (χ,Ꞷ) .When the compound (R-OH) has less value for each (IP,EA)this means that this compound hasmore ability to lose electrons and be easier ionization compared to other compounds. Where the compound (R-CH_3) has less value of Dipole moment has less ability to gain electrons compared to other compounds.

Also ,The MOPAC computational packages (semi-empirical method , AM1 model) employed to compute physical properties; heats of formation (ΔHf, kJ.mol-1),the results showed **(Table:2)** for each of compounds (R-OCH3 , R-OH) have lower heat of formation (more stability), Whereas the compound (R-NO_2) 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 ΔHf (kJ.mol^{-1}), μ (in Debye) ,orbital energies (E_{HOMO}, E_{LUOM}, ΔE in eV) , IP(in eV) , E_A (in eV) , η(in eV), Electronegativity(χ) and Electrophilicity (ɷ) for the derivatives of 4- (1,3,4-thiadiazol-2-yl) benzene – 1, 3- diol.

Comp.	ΔHf KJ/Mol	Debye	$E_H$omo	$E_L$omo	ΔE	IP	EA	η	ɷ	χ
R-CH_3	-2.025	1.275	-8.668	1.894	10.562	8.668	1.894	-4.334	16.950	5.281
R-NO_2	2.788	6.364	-9.635	-2.522	7.112	9.635	2.522	-8.481	20.645	5.317
R-OCH_3	-8.602	2.664	-8.746	2.154	10.901	8.746	-2.154	-4.373	0.993	3.296
R-OH	-9.772	2.531	-6.475	5.237	11.711	6.474	-5.237	-3.237	0.001	0.618

Thermodynamics functions

The fundamental vibration frequencies for the (R-CH3, R-NO_2, R-OCH_3, ROH) molecules alongwith the rotational constants, obtained in this study, where used to calculate the vibration androtation contributions to the thermodynamic functions according to the statistical thermodynamic equations.

$$U_{vib}^{0} = \sum_{i=1}^{3N-6} \frac{RTX_i}{e^{X_i}-1} \qquad X_i = \frac{1.44\bar{\nu}}{T}$$

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

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

,,,

These two contributions along with the others contributions, for the translation, electronic, and nuclear motions, where used to calculate E^o, H^o, S^o, A^o, and G^o 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),

R-OCH_3>R-CH_3>R-OH >R-NO_2

Where , compound (R-OCH_3) has the highest value for each of the above functions, while compound (R-NO_2) has the lowest value .

In addition , compound (R-OH) has the lowest value for each of the functions (C_p, C_v,S^0) , while the compound (R-OCH_3) has the highest value for the same functions last,

R-OCH_3>……. >R-OH

The deferent thermodynamics functions values due to deferent substituted groups(X), viz, the sulfur atom a high electro-negative in addition to its high size which makes restricted movement.

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.	E^0	H^0	G^0	A^0	S^0	CP	Cv
R-CH3	119.513	120.105	85.408	84.816	0.116	0.049	0.047
R-NO2	98.408	99.000	65.502	64.909	0.112	0.047	0.045
R-OCH3	115.213	115.805	84.189	83.597	0.106	0.044	0.043
R-OH	104.521	105.113	73.414	73.414	0.104	0.042	0.040

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_8, N_9) has lower value of charge (the highest density electronic) in the case of compound (R-NO_2 , R-OCH_3) have the highest value of charges (less density electronic) when the compound (R-OH) has less value of charges (high density electronic)Perhaps the reason for this difference in electrical negative and molecular weight which increase the electronic density on nitrogen atom (N_8, N_9) As in the case of compound (R-OH , R-CH_3) This scientific fact indicates that the compound (R-NO_2 , R-OCH_3) can be strong legend when it linked to metal complex formation , as a result of higher giving electronic to nitrogen atoms(N_8, N_9) compared to other compounds, the compound (R-OH).

It also found that the amount of charge of the atom(S_{11}, C_{10}) has gradient opposite to the value of charge ((N_8, N_9).

R-NO_2>R-CH_3>R-OCH_3>R-OH

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

R-CH3			R-NO2			R-OCH3			R-OH		
Atom	**charge**	**density**	**Atom**	**charge**	**density**	**Atom**	**charge**	**density**	**Atom**	**charge**	**density**
C_1	0.401	3.801	C_1	0.412	3.587	C_1	0.392	4.607	C_1	0.141	3.858
C_2	-0.219	4.219	C_2	-0.222	4.222	C_2	-0.202	4.202	C_2	-0.105	4.105
C_3	0.356	3.790	C_3	0.375	3.624	C_3	0.354	4.645	C_3	0.135	3.864
C_4	-0.037	4.037	C_4	-0.051	4.051	C_4	-0.025	4.025	C_4	-0.050	4.050
C_5	-0.141	4.141	C_5	-0.125	4.125	C_5	-0.137	4.137	C_5	-0.029	4.029
C_6	-0.240	4.240	C_6	-0.241	4.241	C_6	-0.241	4.241	C_6	-0.112	4.112
C_7	-0.084	4.084	C_7	-0.092	4.092	C_7	-0.147	4.147	C_7	-0.008	4.008
N_8	-0.342	5.342	N_8	-0.348	5.348	N_8	-0.283	5.283	N_8	-0.174	5.174
N_9	-0.249	5.249	N_9	-0.163	5.163	N_9	-0.282	5.282	N_9	-0.189	5.189
C_{10}	-0.084	4.084	C_{10}	0.138	3.861	C_{10}	0.343	4.343	C_{10}	0.112	3.787
S_{11}	0.483	3.362	S_{11}	0.686	3.313	S_{11}	0.476	3.523	S_{11}	0.212	3.687
O_{12}	-0.802	6.802	O_{12}	-0.797	6.797	O_{12}	-0.790	6.790	O_{12}	-0.275	6.275
O_{13}	-0.784	6.784	O_{13}	-0.777	6.777	O_{13}	-0.784	6.784	O_{13}	-0.270	6.270
C_{14}	-0.492	4.492	N_{14}	0.267	4.732	O_{14}	-0.701	6.701	O_{14}	-0.244	6.244
H_{15}	0.255	0.859	O_{15}	-0.387	6.387	C_{15}	-0.152	4.152	H_{15}	0.083	0.916
H_{16}	0.281	0.870	O_{16}	-0.332	6.332	H_{16}	0.255	0.744	H_{16}	0.099	0.900
H_{17}	0.211	0.883	H_{17}	0.265	0.734	H_{17}	0.266	0.734	H_{17}	0.060	0.939
H_{18}	0.449	0.736	H_{18}	0.291	0.709	H_{18}	0.211	0.788	H_{18}	0.196	0.803
H_{19}	0.422	0.781	H_{19}	0.221	0.778	H_{19}	0.434	0.565	H_{19}	0.203	0.796
H_{20}	0.227	0.927	H_{20}	0.452	0.548	H_{20}	0.422	0.577	H_{20}	0.214	0.786
H_{21}	0.196	0.944	H_{21}	0.428	0.571	H_{21}	0.218	0.781			
H_{22}	0.196	0.944				H_{22}	0.188	0.811			

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