

Investigations study of structural Chemical properties for Some Thiazol Derivatives using Quantum calculations methods

دراسة ميكانيكا الكم للخصائص التركيبية والكيميائية لبعض مشتقات الثيادايازول باستخدام حسابات ميكانيكا الكم

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Abstract:-

DFT Ab-Intio quantum mechanical method within **Gaussian 09** (RB3LYP/6-311G) for calculating the geometry optimization of some Thiazol derivatives [$C_{13}H_6BrN_5O_5S(A)$, $C_{13}H_8N_6O_5S(B)$, $C_{15}H_{11}N_5O_5S(C)$]. The geometry parameter (bond length and bond angles), physical properties and thermodynamic functions. As a result showed that the compound $C_{15}H_{11}N_5O_5S(C)$ has high value of thermodynamic functions ($E^0, A^0, S^0, H^0, G^0, C_V, C_p$).

The results found Heat formation (ΔH_f^0 in KJ / mol) by using PM3 model in MOPAC program, the compound $C_{15}H_{11}N_5O_5S(C)$ has less value which means high stability than other 's and has high value in all thermodynamic functions.

Calculations' results showed the compound $C_{13}H_8N_6O_5S(B)$ has less value in energy gap ($\Delta E=2.616$) that means this compound more activity than other 's.

Key words: Thiazol, energy gap ΔE , Quantum calculations method , physical properties .

الخلاصة :

تم اعتماد برنامج كاو سين (2009) ودوال القاعدة (RB3LYP/6-311G) باستخدام طريقة الحساب التام طريقة نظرية الكثافة (DFT) لحساب الأبعاد الهندسية (أطوال وزوايا التاصر) الفيزيائية والدوال الترموديناميكية بعض الخصائص لبعض مشتقات الثيادايازول

[$C_{13}H_6BrN_5O_5S(A)$, $C_{13}H_8N_6O_5S(B)$, $C_{15}H_{11}N_5O_5S(C)$]

نتيجة لهذه الحسابات أظهرت أن المركب $C_{15}H_{11}N_5O_5S(C)$ يمتلك أعلى مقدار لهذه الدوال الترموديناميكية المتمثلة ($E^0, A^0, S^0, H^0, G^0, C_V, C_p$)

استخدم برنامج MOPAC باستخدام الطريقة شبه التامة طريقة PM3 لحساب استقرارية هذه المركبات من خلال حساب حرارة التكوين (ΔH_f^0 in KJ / mol) وتبين من الحسابات أن المركب $C_{15}H_{11}N_5O_5S(C)$ أكثر المركبات استقرارا لكونه يمتلك أقل مقدار من حرارة التكوين . أما الخصائص الفيزيائية فإن المركب $C_{13}H_8N_6O_5S(B)$ يمتلك أقل مقدار (ΔE) وهذا يدل على أنه أكثر فعالية من باقي المركبات.

Introductions:

Thiadiazole contains the five – membered di- unsaturated ring structure having molecular structure formula $C_2H_3N_3S$ containing a two carbon atom, three hydrogen, three nitrogen and one sulphur[1], thiadiazol and its derivatives are used for biological activities such as antiviral, antibacterial, antifungal and antitubercular[2-3].

Heterocyclic moieties can be found in a large number of compounds which display biological activity. The biological activity of the compounds mainly dependent on their molecular structures [4].

Carboxamide is a type of important herbicides widely used in the world. However, due to there stable physical and chemical properties, persistent used of Carboxamide herbicides can result in some extent of damage to crops environment and drug – fast weeds growth [5,6]. So it is important to find novel Carboxamide herbicides with high activity and low toxicity. In the study of new pharmaceuticals and agrochemicals, the application of heterocyclic like pyridine is warranted to improve the properties and biological activities and many pyridyl- containing compound have shown awide range of biological and pharmacological activities[7-9], for example an anti mycobacterial activity [10-12], as well as low toxicity towards mammals.

Density function theory (DFT) approaches, especially those using hybrid functional, have evolved to a powerful and very reliable tool, being routinely used for the determination of various molecular properties. B3LYP function has been previously shown to provide an excellent compromise between accuracy and computational efficiency of vibrational spectra for large and medium size molecules[13]. It is well known that vibrational frequencies obtained by quantum chemical calculations are typically larger than their experimental counterparts, and thus, empirical scaling factors are usually used to study the experimental vibrational frequencies [14]. These scaling factors depended both on the method and basis sets used is calculations and they are determined from the mean deviation between the calculated and experimental frequencies[15]. On the other hand, B exchange functional have the advantage of standard frequency scaling factor very close to unity so the B- based procedures can often be used without scaling [16]. For this reason by using the DFT (B3LYP) method with 6-311 basis set, we have calculated the geometric parameters and the vibrational spectrum of the title compound in the ground state and compared with the experimental frequencies[17].

Results and discussions:-

This results calculated (bonds lengths and bonds angels) of three molecules of derivatives [$C_{13}H_6BrN_5O_5S(A)$, $C_{13}H_8N_6O_5S(B)$, $C_{15}H_{11}N_5O_5S(C)$] . The results found in the (table 1 and fig. 1) the bond ($C_{19}-C_{25}$) in compound $C_{13}H_6BrN_5O_5S(A)$ has high value (1.929)compare with the other's this value caused by Br atom ,also the bond ($C_{19}-C_{20}$) in compound $C_{13}H_8N_6O_5S(B)$ the larger value(1.409) because the $-NH_2$ group in this compound .

The bond angles that study in this compounds which showed in the (table 1 and fig. 1) the angles $\angle C_{18}C_{19}C_{20}$ as high value(120.6) in compound $C_{13}H_6BrN_5O_5S(A)$ caused by $-Br$ atom which is electron with drawing electron where the angle $\angle C_{19}C_{18}C_{23}$ in compound $C_{15}H_{11}N_5O_5S(C)$ has high value(120.6) because of substituted group $-C_2H_5$.

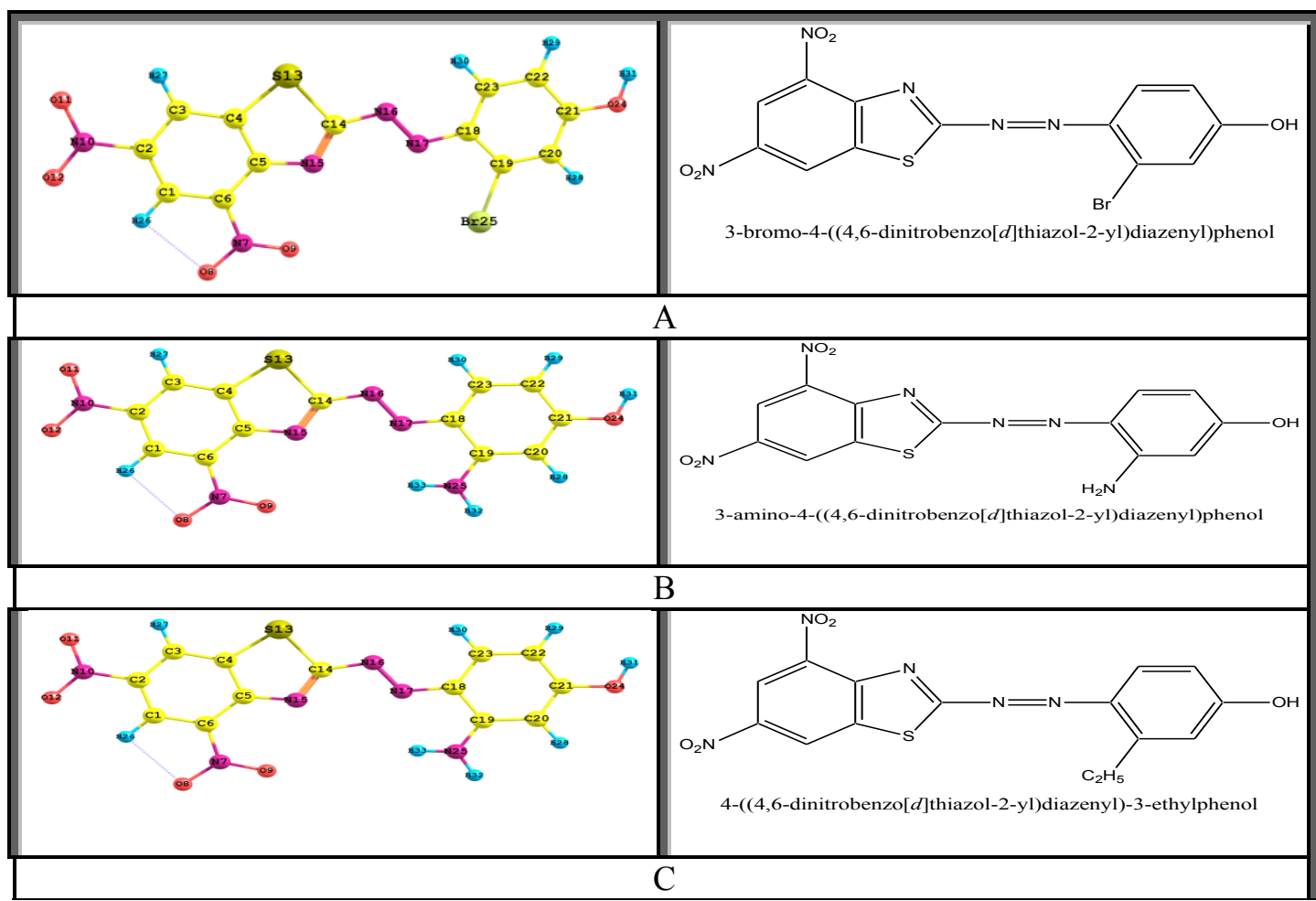


Fig.(1): The geometric equilibrium for the derivatives of **Some Thiazol** Derivatives.

Table 1 : Calculated geometric parameters (bond lengths in Angstrom length angles in degree) of Some *Thiazol* Derivatives.

C₁₃H₆BrN₅O₅S(A)		C₁₃H₈N₆O₅S(B)		C₁₅H₁₁N₅O₅S(C)	
Para. Geo.	Bond length and Angle	Para. Geo.	Bond length and Angle	Para. Geo.	Bond length and Angle.
R(7-9)	1.258	R(7-9)	1.261	R(7-9)	1.260
R(10-11)	1.267	R(10-11)	1.268	R(10-11)	1.267
R(10-12)	1.264	R(10-12)	1.266	R(10-12)	1.265
R(13-14)	1.851	R(13-14)	1.854	R(13-14)	1.854
R(14-15)	1.303	R(14-15)	1.310	R(14-15)	1.305
R(14-16)	1.389	R(14-16)	1.376	R(14-16)	1.385
R(16-17)	1.292	R(16-17)	1.308	R(16-17)	1.296
R(17-18)	1.396	R(17-18)	1.364	R(17-18)	1.392
R(18-19)	1.415	R(18-19)	1.444	R(18-19)	1.429
R(18-23)	1.413	R(18-23)	1.419	R(18-23)	1.412
R(19-20)	1.385	R(19-20)	1.409	R(19-20)	1.392
R(19-25)	1.929	R(19-25)	1.353	R(19-26)	1.517
R(20-21)	1.399	R(20-21)	1.383	R(20-21)	1.399
R(20-28)	1.078	R(20-28)	1.080	R(20-29)	1.078
R(21-22)	1.406	R(21-22)	1.423	R(21-22)	1.406
R(21-24)	1.378	R(21-24)	1.380	R(21-24)	1.380
R(22-23)	1.381	R(22-23)	1.372	R(22-23)	1.381
R(22-29)	1.082	R(22-29)	1.082	R(22-30)	1.083
R(23-30)	1.079	R(23-30)	1.079	R(23-31)	1.079
R(24-31)	0.972	R(24-31)	0.972	R(24-32)	0.972
R(8-26)	2.304	R(25-32)	1.003	R(25-26)	1.533
A(2-1-6)	119.6	R(25-33)	1.009	R(25-33)	1.091
A(2-1-26)	120.6	R(8-26)	2.308	R(25-34)	1.092
A(1-2-3)	122.6	A(2-1-6)	119.6	R(25-35)	1.092
A(1-2-10)	118.8	A(2-1-26)	120.6	R(26-36)	1.092
A(6-1-26)	119.8	A(1-2-3)	122.5	R(26-37)	1.094
A(6-7-9)	119.2	A(5-15-14)	113.0	A(6-5-15)	126.5
A(8-7-9)	123.9	A(6-7-8)	117.2	A(5-6-7)	121.8
A(7-8-26)	88.9	A(6-7-9)	119.4	A(5-15-14)	112.6
A(11-10-12)	124.1	A(8-7-9)	123.5	A(6-7-8)	116.9
A(13-14-15)	115.4	A(7-8-26)	88.7	A(6-7-9)	118.6
A(13-14-16)	113.8	A(11-10-12)	123.9	A(8-7-9)	124.5
A(15-14-16)	130.8	A(13-14-15)	115.0	A(11-10-12)	124.0
A(14-16-17)	115.4	A(13-14-16)	114.8	A(13-14-15)	115.2
A(16-17-18)	115.9	A(15-14-16)	130.1	A(13-14-16)	114.3
A(17-18-19)	117.9	A(14-16-17)	113.8	A(15-14-16)	130.4
A(17-18-23)	123.5	A(16-17-18)	118.5	A(14-16-17)	115.0
A(19-18-23)	118.6	A(17-18-19)	114.4	A(16-17-18)	116.8
A(18-19-20)	120.6	A(17-18-23)	125.7	A(17-18-19)	115.8
A(18-19-25)	120.9	A(19-18-23)	119.8	A(17-18-23)	123.4
A(18-23-22)	121.2	A(18-19-20)	118.5	A(19-18-23)	120.7
A(18-23-30)	117.6	A(18-19-25)	119.1	A(18-19-20)	117.7
A(20-19-25)	118.5	A(18-23-22)	120.7	A(18-19-26)	120.1
A(19-20-21)	119.6	A(18-23-30)	117.7	A(18-23-22)	120.5
A(19-20-28)	121.4	A(20-19-25)	122.4	A(18-23-31)	118.3
A(21-20-28)	119.0	A(19-20-21)	119.8	A(20-19-26)	122.1
A(20-21-22)	120.9	A(19-20-28)	121.2	A(19-20-21)	120.9
A(20-21-24)	116.3	A(19-25-32)	121.9	A(19-20-29)	121.4
A(22-21-24)	122.8	A(19-25-33)	118.4	A(19-26-25)	115.9
A(21-22-23)	119.1	A(21-20-28)	119.0	A(19-26-36)	108.4
A(21-22-29)	120.4	A(20-21-22)	122.1	A(19-26-37)	108.2
A(21-24-31)	113.1	A(20-21-24)	116.7	A(21-20-29)	117.7

Physical properties:

Depending on the Ab-initio of method of calculation using density function theory calculated some physical properties of the molecules are studied in this research, dipole moment (μ in Debye) , E_{HOMO} , E_{LUMO} energies (in e V) and IP(in e V) according to Koopmans's theorem[18,19] also calculated Molecular hardness η , Electron Affinity E_A according to the Koopmans theorems for N system of electrons , energy difference ΔE and Electronegativity (χ)in (e V)according to Mullikan 1934 [20-25] . And Electrophilicity (ω) according to Parr and co- workers 1999[26] . According to the results in (table 2) the compound $C_{13}H_6BrN_5O_5S(A)$ has high value in (μ Dipole moment, (ω) Electrophilicity, (χ) Electronegativity, η Molecular hardness and E_A Electron Affinity) .

MOPAC computational packages (Semi-empirical method , PM3 model) was used to compute physical properties, heat of formation (ΔH_f° in $KJ.mol^{-1}$) [27] . As a results in table 2 the compound $C_{15}H_{11}N_5O_5S(C)$ the most stability because it has less value of heat formation .

Table 2 : Energetic properties (ΔH_f° in $KJ.mol^{-1}$), (μ in Debye), Orbital energies (E_{HOMO} , E_{LUMO} , in e V) , [IP, ΔE , E_A , η , ω , χ in eV] for Some Thiazol Derivatives by using DFT/ B3LYP(3-211G) method.

Comp.	ΔH_f° in $KJ.mol^{-1}$	μ in Debye	E_{HOMO}	E_{LUMO}	IP	ΔE	E_A	η	ω	χ
$C_{13}H_6BrN_5O_5S(A)$	1008.05	11.059	-7.198	-4.204	7.198	2.9881	4.204	819.78	117.86	5.701
$C_{13}H_8N_6O_5S(B)$	995.19	11.119	-6.512	-3.896	6.512	2.616	3.896	811.56	107.16	5.204
$C_{15}H_{11}N_5O_5S(C)$	984.72	10.174	-4.029	-3.296	4.029	2.908	3.296	-226.9	336.54	3.662

(ΔH_f° in $KJ.mol^{-1}$), (μ in Debye), Orbital energies (E_{HOMO} , E_{LUMO} , in e V) , [IP, ΔE , E_A , η , ω , χ in eV]

Thermodynamic functions:

The fundamental vibration frequencies for molecules along with rotational constants, obtained in this study where used to calculate the vibration and rotation contributions to the thermodynamic function according to the statistical thermodynamic equations. Were listed in Table 3 . Calculation showed that each of thermodynamic functions [E° , H° , G° , S° , C_v] have a same gradient value (different group substitutes),



Table 3: thermodynamic functions for Thiazol derivative using DFT model.

<i>Comp.</i>	E° <i>KJ.mol⁻¹</i>	H° <i>KJ.mol⁻¹</i>	G° <i>KJ.mol⁻¹</i>	S° <i>KJ.mol.deg⁻¹</i>	A° <i>KJ.mol⁻¹</i>	C_p <i>KJ.mol.deg⁻¹</i>	C_v <i>KJ.mol.deg⁻¹</i>
C₁₃H₆BrN₅O₅S(A)	547.59	550.067	352.711	0.662	155.355	-0.309	0.317
C₁₃H₈N₆O₅S(B)	620.37	622.84	435.060	0.630	434.430	-0.313	0.322
C₁₅H₁₁N₅O₅S(C)	730.05	732.527	512.597	0.699	304.067	-0.344	0.353

The Charge:-

According to the Density function theory used for investigated the charge of the atoms in three molecules of some Thiazol derivatives [C₁₃H₆BrN₅O₅S(A), C₁₃H₈N₆O₅S(B), C₁₅H₁₁N₅O₅S(C)] .

As a results in table 4 the charge of Carbon atoms of phenyl molecules Which has a substituted found C₁₉ in C₁₃H₆BrN₅O₅S(A) has the substituted the most negativity than other's because Br atom, and C₂₀ in C₁₃H₈N₆O₅S(B) has more negativity because of -NO₂ substituted.

Table 4: Charge for some Thiazol derivatives using DFT model.

C₁₃H₆BrN₅O₅S(A)		C₁₃H₈N₆O₅S(B)		C₁₅H₁₁N₅O₅S(C)	
Atom	Charge	Atom	Charge	Atom	Charge
C1	-0.1519	C1	-0.1525	C1	-0.0933
C2	0.2761	C2	0.2741	C2	0.2643
C3	-0.0589	C3	-0.0647	C3	-0.0656
C4	-0.3840	C4	-0.3827	C4	-0.3846
C5	0.1743	C5	0.1777	C5	0.1953
C6	0.4283	C6	0.4239	C6	0.3697
N7	-0.0177	N7	-0.0185	N7	-0.0134
O8	-0.2624	O8	-0.2667	O8	-0.2528
O9	-0.2192	O9	-0.2387	O9	-0.2217
N10	0.0110	N10	0.0088	N10	0.0108
O11	-0.2608	O11	-0.2658	O11	-0.2621
O12	-0.2504	O12	-0.2571	O12	-0.2543
S13	0.4082	S13	0.3947	S13	0.4059
C14	0.0760	C14	0.0736	C14	0.0709
N15	-0.2271	N15	-0.2588	N15	-0.2518
N16	-0.2087	N16	-0.2176	N16	-0.2094
N17	-0.1934	N17	-0.2491	N17	-0.2033
C18	0.0870	C18	-0.0219	C18	-0.0222
C19	-0.3820	C19	0.4545	C19	0.1287
C20	-0.1083	C20	-0.1639	C20	-0.1629
C21	0.2754	C21	0.2574	C21	0.2633
C22	-0.1449	C22	-0.1573	C22	-0.1431
C23	-0.0152	C23	-0.0106	C23	-0.0155
O24	-0.5917	O24	-0.6003	O24	-0.5929
Br25	0.2886	N25	-0.8708	C25	-0.5411
H26	0.2550	H26	0.2514	C26	-0.4323
H27	0.2270	H27	0.2240	H27	0.2462
H28	0.2053	H28	0.1893	H28	0.2258
H29	0.1777	H29	0.1706	H29	0.1920
H30	0.1998	H30	0.1933	H30	0.1699
H31	0.3872	H31	0.3851	H31	0.1949
		H32	0.3378	H32	0.3840
		H33	-0.1526	H33	0.1900

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