Electronic Structure, Thermodynamics functions and Physical properties for oxazolo[4,5-b]pyridine Derivatives by Ab Initio calculation (RHF Method)

Khidhir Abdu Hussein Khidhir
*Dep. Of chemistry, college of Education, university of kerbala, Iraq
khbb@ymail.com

الخلاصـــة

تضمنت هذه الدراسة اعتماد برنامج كاوس (Gaussian 03) لاستخدام طريقة الحساب التام على وفق طريقة هارتري - فـوك (RHF) ، وذلـك لغـرض حسـاب الأبعـاد الهندسـية (أطـوال وزوايـا التآصـر) عند الشـكل الهندسـي المتـوازن، الـدوال الثرمودينـاميكية (E^o, H^o, S^o, A^o, G^o)، بعض الخصـائص الفيزيائية وكذلك الشـحنات لمشتقات حلقـة إلـى(oxazolo[4,5-b]pyridine)) والتي يرمز لها اختصاراً ($R-Cl, R-F, R-CH_3, R-NH_2, R-NO_2$). كــما وتم اعتمـاد برنامج الموباك (MOPAC) لاستخدام طريقة الحساب التقريبية شبه التجريبية ألـــ(MINDO/3) لحساب بعض الخصـائص الفيزيائية ؛ حرارة التكوين (ΔH_f in kcal/mole) ، عزم ثنائي القطب (μ in Debye) ، طاقة المدارات (E_{HOMO}, E_{LUMO}) وطاقة التأين (IP in eV) بالاضافة الى حساب مقياس الاستقرارية (Δ). وقد اظهرت نتائج الحساب ان المركب (R-F) يمتلك اقل قيمة انتروبي وسعة حرارية وكذلك اقل قيمة حرارة تكوين (اعلى استقرارية) واعلى قيمة (Δ) ، بينما اتضح من خلال نتائج الحساب بان المركب (R-Cl) يمتلك اقل قيمة (E_{HOMO}) وايضا (Δ) وأعلى قيمة لطاقة التأين (IP) وكذلك لحرارة التكوين مما يعني ان المركب (R-Cl) يكون اقل استقرارا واسهل تاينا مقارنة بالمركبات الاخرى . كما اظهرت النتائج بان لكل من ذرات النتروجين (N_3, N_7) قيمة شحنة عالية عند المركب ($R-NH_2$) مما يجعله ليكاند قوي عند ارتباطه بالفلز وتكوين المعقد، ان هذا التغاير بالنتائج يعزى بصورة عامة لتاثير اختلاف المجموعة المعوضة على المركبات المدروسة في هذا البحث .

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.

Also, For (R-Cl, R-F, R-CH$_3$, R-NH$_2$, R-NO$_2$) molecules the calculated some physical properties (ΔH_f (in kcal/mole), μ (in Debye) ,orbital energies (E_{HOMO}, E_{LUMO}, in eV), IP (in eV) and measurement stability Δ) by using (semi-empirical method, MINDO/3 model). Have shown calculation results that the compound (R-F) has the lowest value entropy (S^0) and heat capacity (C_v, C_p), as well as the lower value of the heat of formation (the more Stability) and the highest value (Δ), as shown by the results of the account that the compound (R-Cl) has the lowest value (E_{HOMO}, Δ) and the highest value for the ionization energy (IP) as well as to the heat of formation , which means that the compound (R-Cl) is less stability and easier ionization compared to other compound. The results showed that both nitrogen atoms (N_3, N_7) Had the highest value when the compound (R-NH$_2$),which makes it a strong legend when Linked to metal and the formation of the complex.

Keywords: RHF study, Oxazole Derivatives, Thermodynamics function.

Introduction

Benzoxazole, oxazolo[4,5-b]pyridine and benzimidazole moieties have attracted special attention in chemistry [1] and biochemistry [2-8]. Oxazoles and isoxazoles have an important role in the synthesis of potential medicines including antitumor, antimicrobial, anti-infective, cardiovascular, and nervous system agents [9]. These heterocycles show various pharmaceutical properties such as antiviral [2], antibiotic [3], antibacterial [4], antifungal [5], anticancer [6], antitumor [7] and anti-inflammatory [8] activities. Furthermore, some of them have found applications as fluorescent whitening agents, in dye laser and as dye releaser in instant color chromatography [10]. They have been also used as ligands in asymmetric synthesis [11]. The extensive applications of these heterocycles have prompted wide studies for their synthesis. There are various experimental methods developed for the synthesis of oxazole and isoxazole derivatives [12, 13]. But there are few relatively theoretical works on oxazoles and isoxazoles [14–16]. A number of methods have been reported for the preparation of these heterocycles including the condensation of carboxylic acids [17], orthoesters [18], acid chlorides [19], nitriles [20], amides [21], aldehydes [22] and esters [23] with o-substituted amino aromatics. However, most of these procedures have some drawbacks such as long reaction times, low yields of products, the use of expensive, toxic or non-reusable catalysts, high temperatures, harsh reaction conditions and use of toxic solvents and/or co-occurrence of several side reactions. In some cases more than one step is required for the synthesis of these heterocycles. Therefore, Quantum chemistry methods play an important role in obtaining molecular geometries and predicting various properties. To obtain highly accurate geometries and physical properties for molecules that are built from electronegative elements, expensive ab initio/HF electron correlation methods are required [24]. Density functional theory methods offer an alternative use of inexpensive computational methods which could handle relatively large molecules [25].
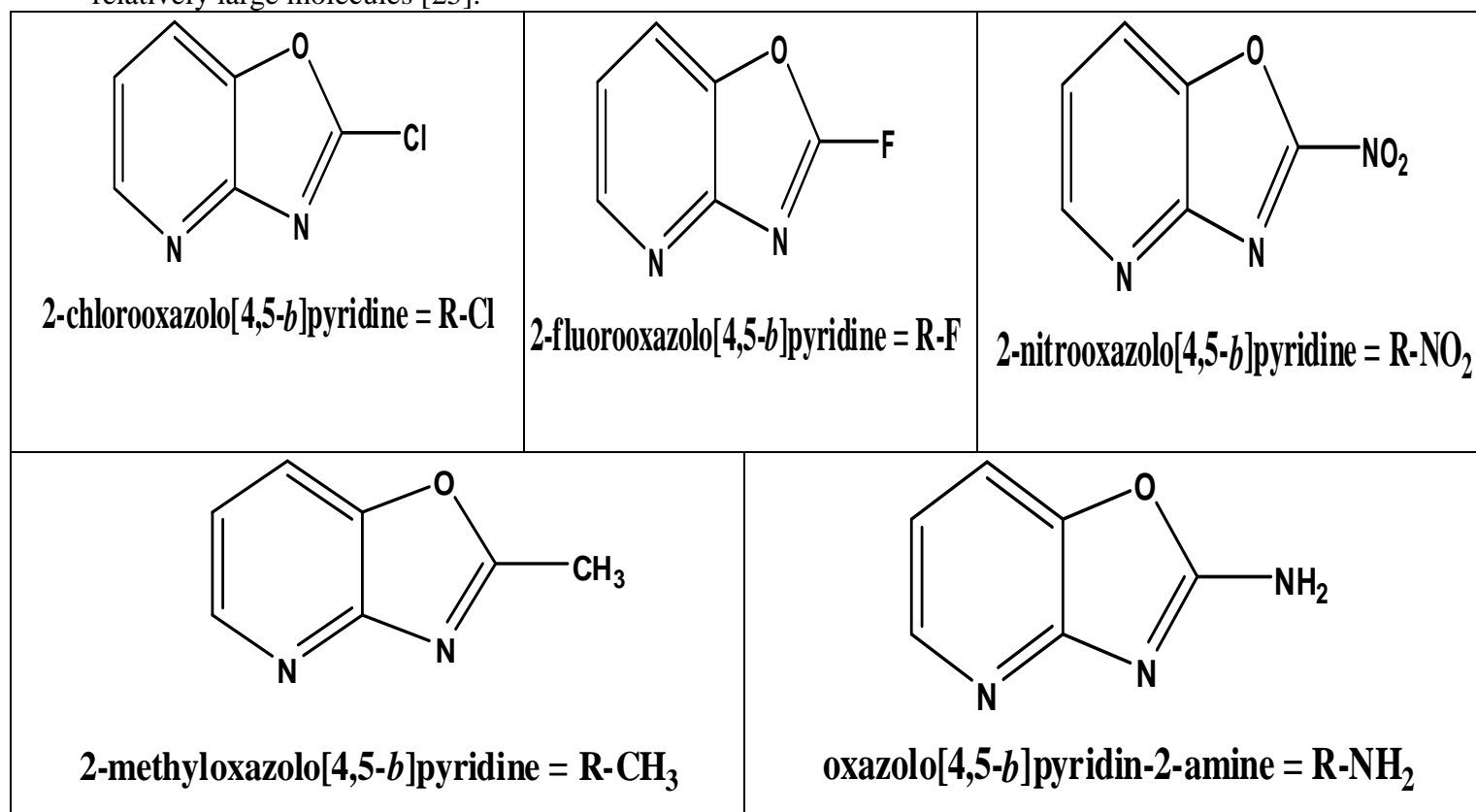

2-chlorooxazolo[4,5-*b*]pyridine = R-Cl

2-fluorooxazolo[4,5-*b*]pyridine = R-F

2-nitrooxazolo[4,5-*b*]pyridine = R-NO$_2$

2-methyloxazolo[4,5-*b*]pyridine = R-CH$_3$

oxazolo[4,5-*b*]pyridin-2-amine = R-NH$_2$

Fig. 1: compounds (R-Cl, R-F, R-CH$_3$, R-NH$_2$ and R-NO$_2$)

Results and Discussion

Geometrical parameter

In this research calculated the geometry (bond lengths and bond angels) of the five molecules of derivatives oxazolo[4,5-b]pyridine (R-F, R-Cl, R-CH$_3$, R-NH$_2$, R-NO$_2$), using the ab initio method of calculation according to the Hartree - Fock method (RHF). According to the results calculated and recorded in the (Fig. 2), show that bond length (C$_8$–X$_{10}$, X= -F, -Cl, -CH$_3$, -NH$_2$, -NO$_2$), Have less value when the compound (R-F) compared to other compounds studied, It may be due to the high electro-negative, Whereas for the same bond length for each of the compound (R-Cl, R-CH$_3$) have highest value , May be caused by the large size group substitutes (-CH$_3$, -Cl), And also electronic donor higher for these two groups. The results showed that the bond length (C$_8$=N$_7$) has less value when the compound (R-Cl), Results also showed the compound (R-CH$_3$) has the highest value of the bond length (C$_8$-O$_9$), while the less valuable to them when compound (R-NO$_2$).

Also had to change the group substitutes for the effect on the values of the angles of the compounds studied in this research, have shown calculation results of the geometric form of this change in the values of angles, where, have shown calculation results (Fig. 3), that the angle (<N$_7$C$_8$X$_{10}$) have the highest value when compound (R-CH$_3$) while have less value when compound (R-NO2), the reason for the large size methyl group (-CH$_3$), and also electronic donor higher for this group(-CH$_3$), on the contrary, Nitro group (-NO$_2$) where the group drawer the electrons. Also for each of the angle (<C$_8$N$_7$C$_9$ and <C$_8$O$_9$C$_5$) have the same the previous case, it may be for the same reason above. and the bond angle value which is located the group substituted X, (X= -F, -Cl, -CH$_3$, -NH$_2$, -NO$_2$), (<N$_7$C$_8$O$_9$), have less value when compound (R-CH$_3$) and the highest value when compound (R-NO$_2$).
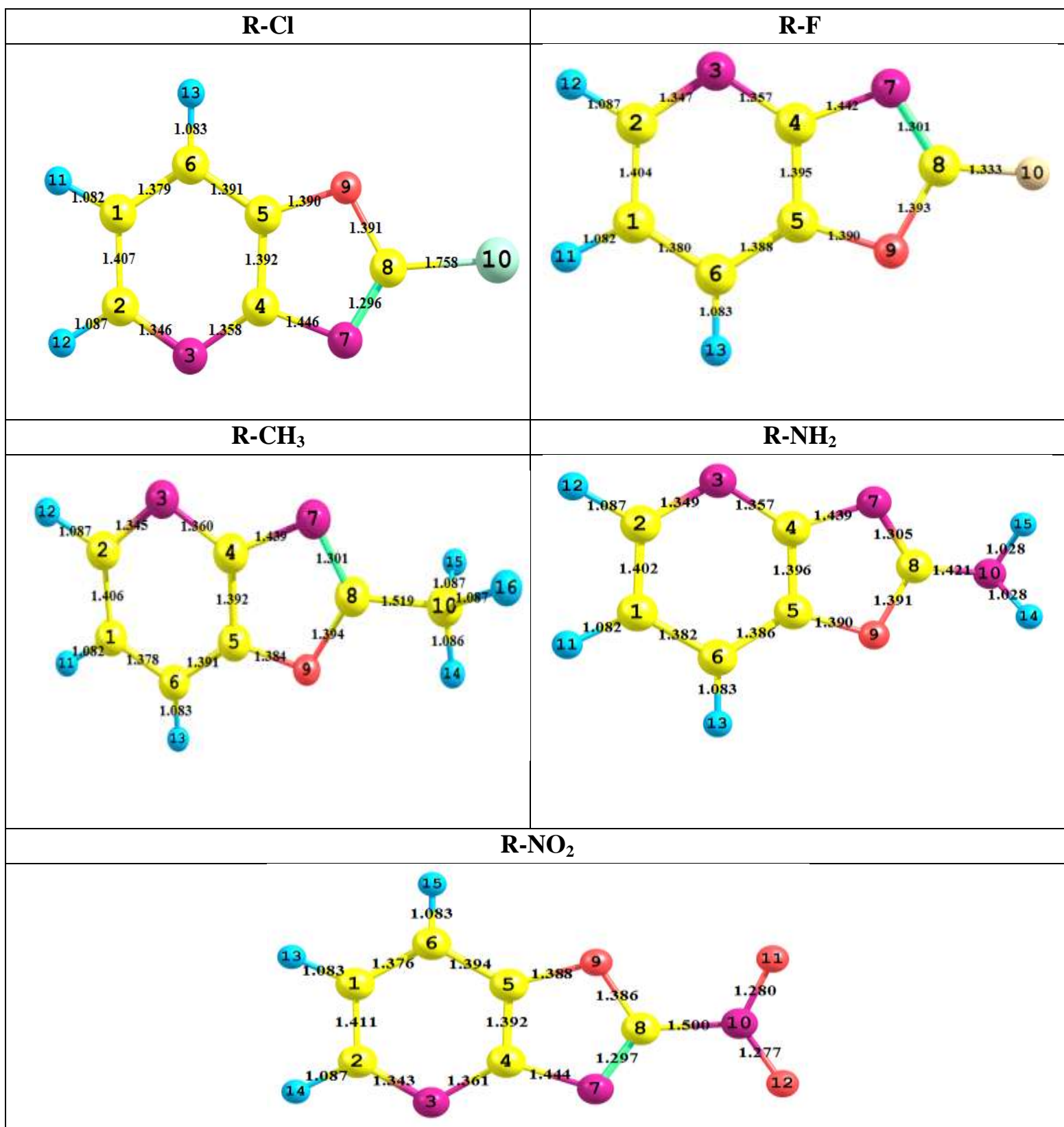
Fig. 2: Calculated geometric parameters (bond lengths in Angstrom) of the derivatives oxazolo[4,5-b]pyridine.
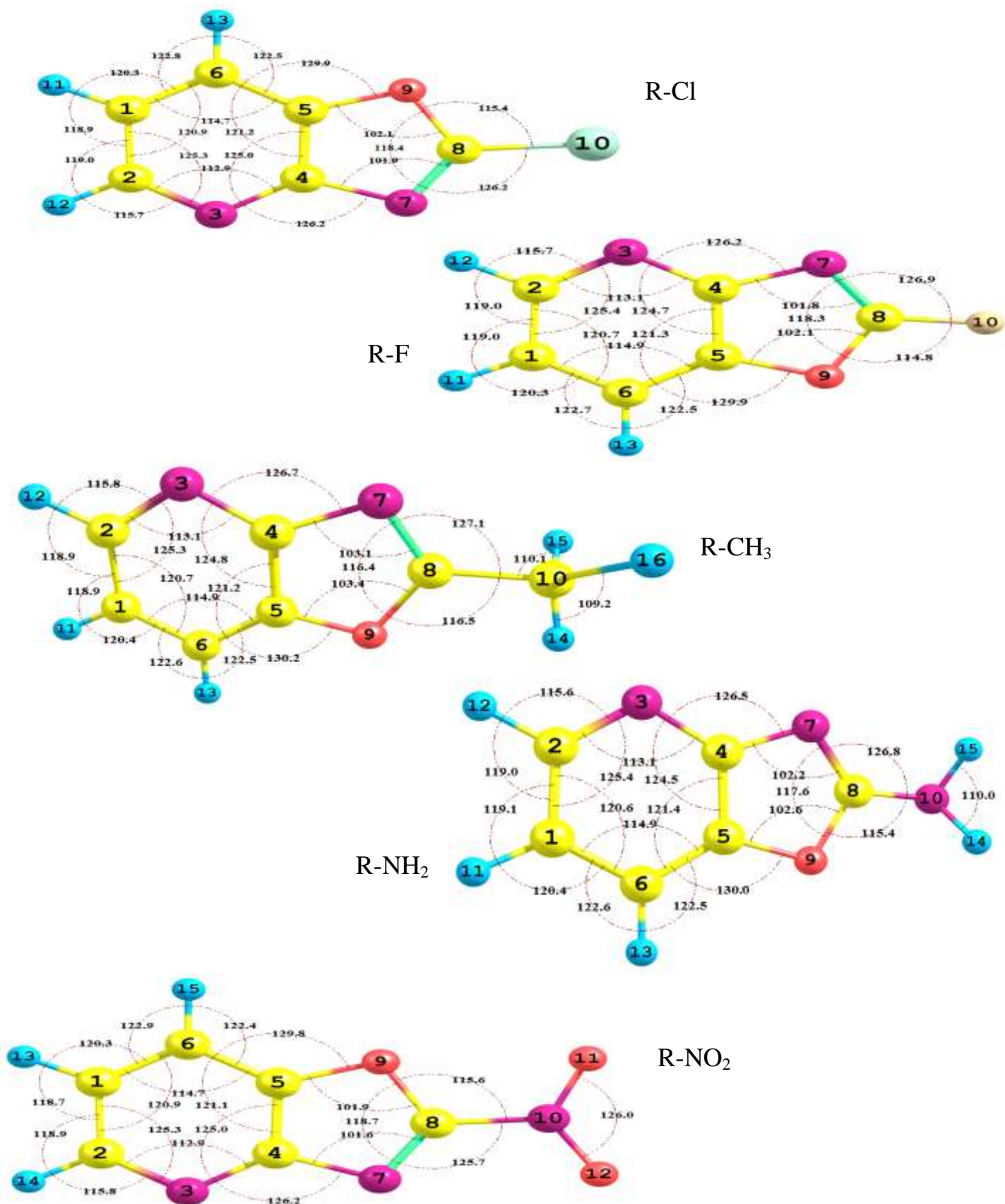
Fig. 3: Calculated geometric parameters (bond angles in degrees) of the derivatives oxazolo[4,5-b]pyridine

Thermodynamics functions

The fundamental vibration frequencies for the (R-F, R-Cl, R-CH$_3$, R-NH$_2$, R-NO$_2$) 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.

$$U_{vib}^0 = \sum_{i=1}^{3N-6} \frac{RTX_i}{e^{X_i}-1} \quad,,, \quad X_i = \frac{hc\bar{\nu}}{kT} = \frac{1.44\bar{\nu}}{T} \quad,,, \quad U_{rot}^0 = 1.5RT$$

$$S_{vib}^0 = R\sum_{i=1}^{3N-6}\left[\frac{X_i}{e^{X_i}-1} - \ln\left(1-e^{-X_i}\right)\right] \quad,,, \quad S_{rot}^0 = R\left[\frac{3}{2} + \ln\frac{8\pi^2\left(8\pi^2 I_X I_Y I_Z\right)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{\sigma\hbar^3}\right]$$

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 in Table.1. 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),

<div align="center">R-CH$_3$ > R-NH$_2$ > R-NO$_2$ > R-F > R-Cl</div>
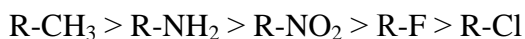
where, compound (R-CH$_3$) has the highest value for each of the above functions, while compound (R-Cl) has the lowest value. In addition, compound (R-NO$_2$) has the highest value for each of the functions (S^0, C$_v$, C$_p$), while compound (R-F) has the lowest value for the same functions mentioned last,

<div align="center">R-NO$_2$ > R-NH$_2$ ≈ R-Cl > R-CH$_3$ > R-F</div>

the deferent Thermodynamics functions values due to deferent substituted groups (X), viz, the pair electrons in nitrogen atom for nitro group (-NO$_2$) are less bounded consequently have the more freely motion. Therefore, the (R-NO$_2$) molecules has the higher S^o, While the fluorine atom has a high electro-negative in addition to its small size which makes it restricted movement and a few that we find the compound (R-F) has the lowest value (S^o).

Table 1: The calculated standard thermodynamics functions at 298.15^{o}K of the derivatives oxazolo[4,5-b]pyridine.

Molecule	E^0 (kcal. mol^{-1})	S^0 (cal. mol^{-1}K^{-1})	H^0 (kcal. mol^{-1})	G^0 (kcal. mol^{-1})	A^0 (kcal. mol^{-1})	C_V (cal. mol^{-1}K^{-1})	C_P (cal. mol^{-1}K^{-1})
R-Cl	64.128	82.222	64.720	40.205	39.613	23.774	25.761
R-F	64.979	79.505	65.571	41.867	41.274	22.820	24.807
R-CH$_3$	91.684	80.088	92.276	68.398	67.805	23.589	25.576
R-NH$_2$	83.166	81.413	83.758	59.485	58.892	25.362	27.349
R-NO$_2$	72.274	91.432	72.866	45.605	45.013	29.255	31.242

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 (eV) of the High Occupied Molecular Orbital (E_{HOMO}) and the Lower Unoccupied Molecular Orbital (E_{LUMO}) and according to Koopmans' theorem (the negative E_{HOMO} is equal to the ionization potential) the calculation has been ionization energies (eV), And also calculated the energy difference (ΔE, eV).

The shown this results (Table.2) that compound (R-N0$_2$) has highest dipole moments, And less value for each of the (E_{LUMO}, ΔE), and this indicates that the compound (R-N0$_2$) has more ability to gain electrons compared to other compounds. While we note the compound (R-NH$_2$) has the highest value (E_{HOMO}), (less the value of a negative energy), and has a lower value for the ionization potential (IP), and this means that the compound (R-NH$_2$) has a more ability to lose electrons and be easier ionization compared to other compounds. While we find the compound (R-Cl) be contrary to the above words. Results also showed that each of the compound (R-Cl, R-CH$_3$) has the highest value (ΔE), the sense of activity of these compounds are few.

Also, The MOPAC computational packages (semi-empirical method , MINDO/3 model) employed to compute the some physical properties; heats of formation (ΔH_f, kcal.mol^{-1}), Dipole moments (μ in Debye), energies (eV) of (E_{HOMO}, E_{LUMO}) and ionization energies (eV). The results showed (Table.3) for each of the compound (R-F, R-NO$_2$) has lower heat of formation ΔH_f, (kcal/mol), (More Stability), Whereas the compound (R-Cl) 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 μ (in Debye) ,orbital energies (E_{HOMO}, E_{LUOM}, ΔE in eV) and IP
(in eV) for the derivatives oxazolo[4,5-b]pyridine by using Hartree - Fock method (RHF).

Molecule	Dipole moment, μ (in Debye)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	IP (eV)
R-Cl	4.277	-8.244	4.979	13.224	8.244
R-F	3.631	-7.854	5.363	13.218	7.854
R-CH$_3$	3.235	-7.622	5.603	13.226	7.622
R-NH$_2$	3.450	-7.144	5.757	12.902	7.144
R-NO$_2$	5.372	-7.929	3.484	11.414	7.929

Table 3: Calculated ΔH_f (in kcal/mole), μ (in Debye) , orbital energies (E_{HOMO}, E_{LUOM}, in eV) and
IP (in eV) for the derivatives oxazolo[4,5-b]pyridine by using MINDO/3 model.

Molecule	ΔH_f (kcal. mol^{-1})	Dipole moment, μ (in Debye)	E_{HOMO} (eV)	E_{LUMO} (eV)	IP (eV)
R-Cl	50.555	4.189	-7.918	-1.385	7.918
R-F	-68.850	2.952	-8.541	-0.396	8.540
R-CH$_3$	-22.671	2.447	-8.088	0.859	8.088
R-NH$_2$	-2.932	6.606	-7.064	-0.034	7.063
R-NO$_2$	-29.709	4.451	-8.822	-0.360	8.822

substitutes effect on stability

Been studying the effect of a group substitutes on stability (a measure of stationary, Δ) depending on the heats of formation reactive material and the product, according to Isodesmic Reaction [26]. Isodesmic reactions represent a subclass of isogyric reactions, the latter of which are defined as transformations in which reactants and products have the same number of electron pairs. These reactions can, in principle, be purely hypothetical and can also be used to quantify the stability of reactive intermediates in a thermochemical sense, in the sense, it is a chemical reaction in which the type of chemical bonds broken in the reactant are the same as the type of bonds formed in the reaction product. This type of reaction is often used as a hypothetical reaction in thermochemistry. Where,

$$\Delta = (\Delta H_f)_{product} - (\Delta H_f)_{react}$$

The results showed (Table 4) that each of (R-F, R-NO$_2$) has the highest value (Δ), and this shows the effect of substitutes group on the stability, where, that both groups (-F, -NO$_2$) increase the Stability compound. While we find the compound (R-Cl) has the lowest value (Δ), i.e. the substitute group (-Cl) reduces the Stability compound. This may be due to the

same reason stated previously. And this can be conclude, where the calculation results indicate that the sequence of values (Δ) be the exact opposite of the sequence of values of heats of formation of all molecules studied, and this shows the role of the substitutes group in Stability the compound.

Table 4: Evaluation of substituted effects by using mindo/3 model calculations (energies Δ , in kcal/mol).

Isodesmic Reaction					Δ (kcal. mol^{-1})
R$-$Cl	+ CH$_3$CH$_3$ $\longrightarrow$	R$-$H	+ CH$_3$CH$_2$Cl		-61.171942
R$-$F	+ CH$_3$CH$_3$ $\longrightarrow$	R$-$H	+ CH$_3$CH$_2$Cl		18.357819
R$-$CH$_3$	+ CH$_3$CH$_3$ $\longrightarrow$	R$-$H	+ CH$_3$CH$_2$Cl		13.291012
R$-$NH$_2$	+ CH$_3$CH$_3$ $\longrightarrow$	R$-$H	+ CH$_3$CH$_2$Cl		4.337293
R$-$NO$_2$	+ CH$_3$CH$_3$ $\longrightarrow$	R$-$H	+ CH$_3$CH$_2$Cl		25.483544

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. 5), are each of the (N_3, N_7) has a lower value of charge (the highest density electronic) in the case of compound (R-NH$_2$), while it has the highest value of the charge (less density electronic) When the compound (R-NO$_2$), may be due of donor higher of its electrons to a (-NH$_2$) which increases the electronic density on the nitrogen atoms (N_3, N_7) As in the case of compound (R-NO$_2$), the reason may be due to the impact of electronic drawing of the group (-NO$_2$), which reduces the electronic density of nitrogen atoms of the above.

This scientific fact indicates that the compound (R-NH$_2$) can be a strong legend when it linked to metal complex formation, as a result of higher giving electronic to nitrogen atoms (N_3, N_7) compared to other compounds, and on the contrary, the compound (R-NO$_2$).

Above that this result agreed exactly with the amount of the charge on the oxygen atom (O_9) and perhaps due to the same reason above. While noting the amount of the charge on the carbon atom (C_8) had the highest value (less electronic density) when the compound (R-F), and the reason for this is electro-negative high fluorine. While the lowest value for the charge carbon atom (C_8) when the compound (R-CH$_3$), and may be the cause to the induction of higher motivation of the electrons of the group (-CH$_3$), causing a decrease in the value of the charge (an increase in the electronic density).

Table 5: Calculated charge for the derivatives oxazolo[4,5-b]pyridine.

Atom Symbol	R-Cl	R-F	R-CH$_3$	R-NH$_2$	R-NO$_2$
C$_1$	-0.060	-0.064	-0.066	-0.069	-0.056
C$_2$	0.037	0.036	0.032	0.033	0.040
N$_3$	-0.215	-0.221	-0.224	-0.228	-0.210
C$_4$	0.145	0.145	0.137	0.144	0.143
C$_5$	0.103	0.097	0.095	0.092	0.110
C$_6$	-0.055	-0.057	-0.060	-0.059	-0.054
N$_7$	-0.227	-0.266	-0.263	-0.287	-0.208
C$_8$	0.261	0.374	0.238	0.330	0.309
O$_9$	-0.188	-0.208	-0.211	-0.212	-0.183
X$_{10}$	-0.064	-0.089	-0.190	-0.385	0.135
H$_{11}$(O$_{11}$)	0.084	0.080	0.077	0.076	-0.158
H$_{12}$(O$_{12}$)	0.084	0.081	0.077	0.076	-0.140
H$_{13}$	0.095	0.091	0.087	0.087	0.087
H$_{14}$			0.087	0.196	0.087
H$_{15}$			0.091	0.206	0.098
H$_{16}$			0.091		

X= Cl, F, C, N, N

References

[1] a) S. Lin, L. Yang, Tetrahedron Lett. 46 (2005) 4315; b) C. Chen, Y.-J. Chen, Tetrahedron Lett. 45 (2004) 113; c) G. Frachy, C. Crestini, R. Berini, R. Salidino and E. Micione, Heterocycles 38 (1994) 2621.

[2] a) X. Song, B.S. Vig, P.L. Lorenzi, J.C. Drach, L.B. Townsend and G.L. Amidon, J. Med. Chem. 48 (2005) 1274; b) I. Mohammadpoor-Baltorka, , M. Moghadama, S. Tangestaninejada, V. Mirkhania, M.A. Zolfigolb and S.F. Hojatia, J. Iran. Chem. Soc., 5, (2008) 65.

[3] I. Yildiz-Oren, I. Yalcin, E. Aki-Sener and N. Ucarturk, Eur. J. Med. Chem. 39 (2004) 291.

[4] D.A. Evans, C.E. Sacks, W.A. Kleschick and T.R. Taber, J. Am. Chem. Soc. 101 (1979) 6789.

[5] M. Yamato, J. Pharm. Sci. Jpn. 112 (1992) 81.

[6] D. Kumar, M.R. Jacob, M.B. Reynolds and S.M. Kerwin, Bioorg. Med. Chem. 10 (2002) 3997.

[7] C.G. Mortimer, G. Wells, J.-P. Crochard, E.L. Stone, T.D. Bradshaw, M.F.G. Stevens and A.D. Westwell, J. Med. Chem. 49 (2006) 179.

[8] N. Terzioglu, R. van Rijn, R.A. Bakker, I.J.P. De Esch and R. Leurs, Bioorg. Med. Chem. Lett. 14 (2004) 5251.

[9] E. G. Robertson, Journal of Molecular Spectroscopy, vol. 231(2005) 50.

[10] a) A. Reiser, L.J. Leyshon, D. Saunders, M.V. Mijovic, A. Bright and J. Bogie, J. Am. Chem. Soc. 94 (1972) 2414; b) C.-W. Ko, Y.-T. Tao, Chem. Matter. 13 (2001) 2441.

[11] A. Figge, H.J. Altenbach, D.J. Braauer and P. Tielmann, Tetrahedron: Asymmetry 13 (2002) 137.

[12] H. Agirbas, S. Guner, F. Budak et al., Bioorganic and Medicinal Chemistry, vol. 15(2007) 2322.

[13] O. V. Shablykin, V. S. Brovarets, and B. S. Drach, Russian Journal of General Chemistry, vol. 77 (2007) 1308.

[14] M. H. Palmer, R. Wugt Larsen, and F. Hegelund, Journal of Molecular Spectroscopy, vol. 252 (2008) 60.

[15] S. Belaidi, M. Mellaoui, M. Lemchounchi, and O. Youcef, in Proceedings of the 8th Congress of the Algerian Society of Chemistry, Bejaia, Algeria, May 2009.

[16] O. Abdelmalek, S. Belaidi, M. Mellaoui, and R. Mazri, Asian Journal of Chemistry, vol. 23 (2011) 1183.

[17] a) E. Alcalde, I. Dinarés, L. Pérez-García and T. Roca, Synthesis (1992) 395; b) Y.-H. So, J.P. Heeschen, J. Org. Chem. 62 (1997) 3552; c) S. Heuser, M. Keenan and A.G. Weichert, Tetrahedron Lett. 46 (2005) 9001.

[18] a) D. Villemin, M. Hammadi and B. Martin, Synth. Commun. 26 (1996) 2895; b) M. Doise, F. Dennin, D. Blondeau and H. Sliwa, Tetrahedron Lett. 31 (1990) 1155; c) G.L. Jenkins, A.M. Knevel & C.S. Davis, J. Org. Chem. 26 (1961) 274.

[19] a) R.S. Pottorf, N.K. Chadha, M. Katkevics, V. Ozola, E. Suna, H. Ghane, T. Regberg and M.R. Player, Tetrahedron Lett. 44 (2003) 175; b) R.N. Nadaf, S.A. Siddiqui, T. Daniel, R.J. Lahoti and K.V. Srinivasan, J. Mol. Catal. A: Chem. 214 (2004) 155.

[20] D.W. Hein, R.J. Alheim and J.J. Leavitt, J. Am. Chem. Soc. 79 (1957) 427.

[21] M. Terashima, M. Ishii, Synthesis (1982) 484.

[22] a) A. Hari, C. Karan, W.C. Rodrigues and B.L. Miller, J. Org. Chem. 66 (2001) 991; b) P.L. Beaulieu, B. Haché and E. von Moos, Synthesis (2003) 1683; c) M. Curini, F.Epifano, F. Montanari, O. Rosati and S. Taccone, Synlett (2004) 1832; d) P. Gogoi, D. Konwar, Tetrahedron Lett. 47 (2006) 79; e) R. Trivedi, S.K. De & R.A. Gibbs, J. Mol. Catal. A: Chem. 245 (2006) 8; f) C.L. Lee, Y. Lam and S.-Y. Lee, Tetrahedron Lett. 42 (2001) 109.

[23] a) A.K. Chakraborti, S. Rudrawar, G. Kaur and L. Sharma, Synlett (2004) 1533; b) W.R. Dolbier Jr., C.R. Burkholder and M. Médebielle, J. Fluorine Chem. 95 (1999) 127.

[24] W. J. Hehre, Practical Strategies for Electronic Structure Calculations, Wavefunctions, Irvine, Calif, USA, 1995.

[25] E. R. Davidson, "Quantum theory of matter: introduction," Chemical Reviews, vol. 91 (1991) 649.

[26] M. H. Lien and A.C. Hopkinson; J. Phys. Chem., 88 (1984) 1513.