

THEORETICAL INVESTIGATIONS OF STRUCTUREAL AND THERMAL PROPERTIES FOR SOME ACRYLAMIDE DERIVATIVES

دراسة نظرية للخصائص التركيبية والحرارية لبعض مشتقات الأكريل أميد.

Mohanad J. Yasir

Manal A. Mohammed

Dep. Of chemistry , college of Education for pure Sciences , university of Karbala, Iraq.

Abstract:-

Theoretical calculation method that implemented into(Gaussian 03) have been used to investigate the structural properties (lengths and angles bond) and geometrical properties, thermodynamic functions, some physical properties, for A crylamide derivatives.

The results investigation Heat formation(ΔH_f^0 (in kJ/mole) by using (semi-empirical method PM3 model in MOPAC) for these molecules and the results showed that the compound (**R-PH-O-CH₃**)has less value which means high stability than the other's.

Calculation results have shown that the compound (R – pyridine) is less activity because it has the high Energy gap and shown that this compound has high value in (E_A, IP, η).

The results have shown that the compound (R–PH–O–CH₃) has highest value of thermodynamic functions ($E^0, H^0, G^0, A^0, C_V, C_P, S^0$).

This difference in results come according to the difference of substituted groups.

Key words: DFT-Model , Acryl amide , Hardness, thermodynamics functions.

الخلاصة:-

تضمنت هذه الدراسة اعتماد برنامج كاوس (Gaussian 03) باستخدام طريقة الحساب التام وفق نظرية دالة الكثافة (DFT)، وذلك لغرض حساب الأبعاد الهندسية (أطوال و زوايا التاصر) عند الشكل الهندسي المتوازن ، الدوال الترموديناميكية (E^0, H^0, A^0, G^0) ، حساب السعة الحرارية الانتروبي (S^0, C_P, C_V)، وكذلك بعض الخصائص الفيزيائية لمشتقات الأكريل أميد.

تم اعتماد برنامج **MOPAC** لاستخدام الطريقة الشبه تجريبية **PM3** لحساب حرارة التكوين للمركبات (ΔH_f^0 in kJ/mole) وقد أظهرت النتائج الحساب أن المركب (**R-PH-O-CH₃**) أكثر استقرارا لكونه يمتلك اقل قيمة في حرارة التكوين.

حيث أظهرت نتائج الحساب أن المركب (R – pyridine) اقل المركبات فعالية لكونه يمتلك أعلى قيمة ΔE . وكذلك بينت الحسابات إن هذا المركب يمتلك أعلى مقدار في (E_A, IP, η).

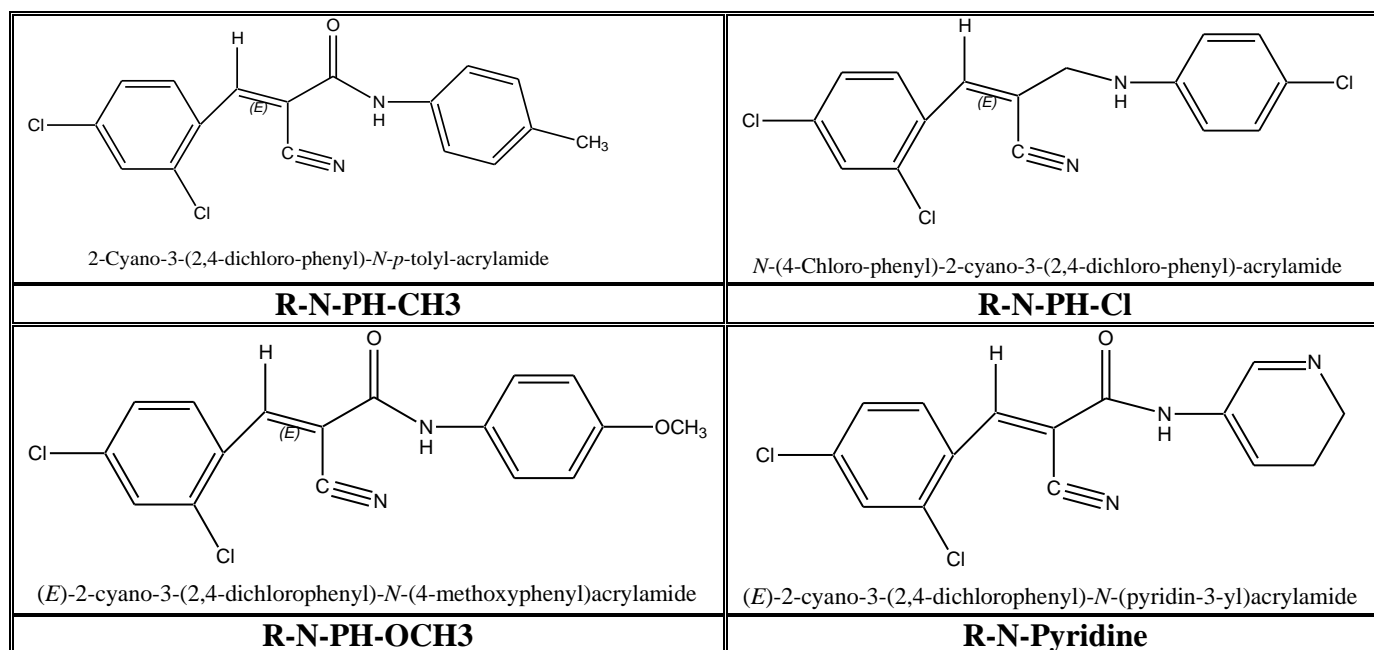
كما تم حساب الدوال الترموديناميكية حيث تبين أن المركب (**R–PH–O–CH₃**) يمتلك أعلى قيمة للدوال ($E^0, H^0, S^0, C_P, C_V, A^0, G^0$) وأن هذا التباير بالنتائج يعزى بصورة عامة لتأثير اختلاف المجموعة المعوضة على المركبات المدروسة في هذا البحث

Introduction.

The recent wide importance of 2-propenoylamides [1,2], 2-propenoates [3-6], besides, the interesting biological and pharmacological activities of many heterocyclic systems, like, benzoxazoles [7], pyrimidines [8], pyridopyrimidines [9] and pyrazoles encourage the authors to gather these moieties hoping to produce a valuable new compounds of expected antibacterial and antifungal activity [10].

In this work, investigated theoretically using the Density Functional Theory (DFT) calculation [9] at the B3LYP/6-311G(p,d) level of theory to get the optimised geometry . DFT calculations were carried out with Becke's three-parameter hybrid model using the Lee–Yang–Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny's optimisation algorithm using redundant internal coordinates. All optimized structures were confirmed to be minimum energy conformations [11]. Harmonic vibrational wave numbers were

calculated using analytic second derivatives to confirm the convergence to minima in the potential surface. At the optimized structure of the examined species, proving that a true minimum on the potential surface was found. The optimum geometry was determined by minimizing the energy with respect to all geometrical parameters without imposing molecular symmetry constraints [12, 13].



Results and Discussion.

Geometrical parameter.

In this research calculated the geometry (bond lengths and bond angles) of the five molecules of Some Acrylamide derivatives.

According to the results calculated and recorded in the (table 1 and fig. 1). Show that the bond ($C_{16}-N_{15}$) in the compound (R-N-Pyridine) has less value compared to other compounds studies when in each compound (R-N-PH-CH₃), (R-N-PH-OCH₃) it may be due to the Ion pair in nitrogen atom and electron with drawing of substituted groups of the other compound.

The bond ($C_{12}-N_{15}$) for carbonyl group the result showed the compound R-N-PH-Cl has high value compare to other compounds studies it may be due to high electro – with drawing electron of substituted group.

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 angles $\angle C_{17}C_{16}C_{21}$ in compound R-N-PH-Cl has high value may be to the electro – with drawing electron of substituted group. The angle $\angle C_{12}N_{15}C_{21}$ the results showed that in compound R-N-PH-CH₃ has high value .

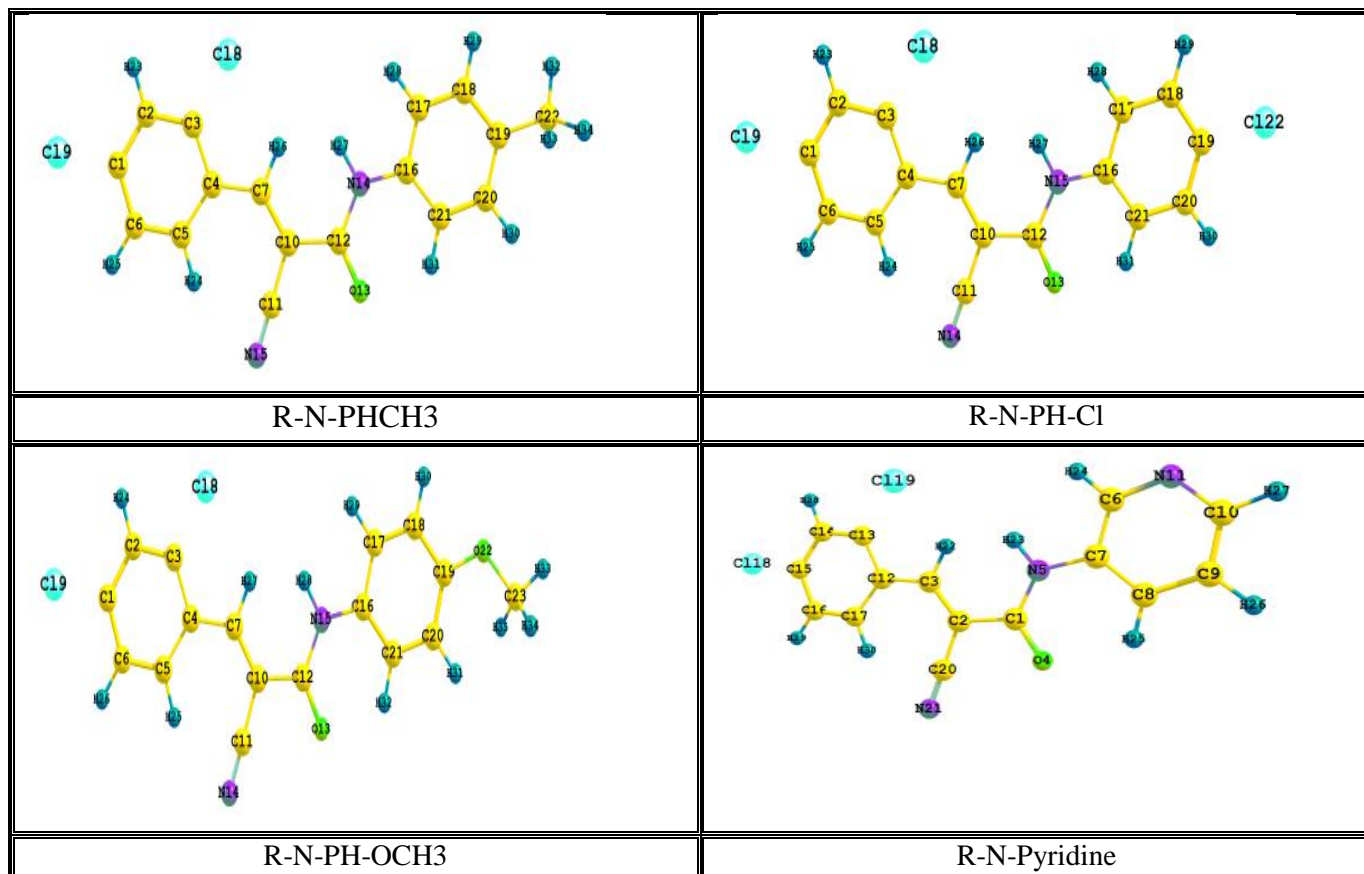


Fig.(1): The geometry Optimized of the derivatives for Acryl amide Derivatives.

Table 1 : Geometric parameters (bond lengths in Angstrom length angles in degree) of Acryl amide derivatives Calculated by DFT B3LYP/6-311G(p,d).

R-N-PH-CH3		R-N-PH-Cl		R-N-PH-OCH3		R-N-Pyridine	
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(1-2)	1.393	R(1-2)	1.393	R(1-2)	1.393	R(1-2)	1.510
R(1-6)	1.393	R(1-6)	1.393	R(1-6)	1.393	R(1-4)	1.252
R(7-10)	1.363	R(7-10)	1.363	R(7-10)	1.363	R(6-11)	1.342
R(7-26)	1.082	R(7-26)	1.082	R(7-27)	1.082	R(6-24)	1.089
R(10-11)	1.431	R(10-11)	1.431	R(10-11)	1.431	R(7-8)	1.406
R(10-12)	1.513	R(10-12)	1.511	R(10-12)	1.512	R(8-9)	1.398
R(11-15)	1.174	R(11-14)	1.174	R(11-14)	1.174	R(8-25)	1.079
R(12-13)	1.253	R(12-13)	1.252	R(12-13)	1.254	R(9-10)	1.397
R(12-14)	1.372	R(12-15)	1.375	R(12-15)	1.371	R(9-26)	1.084
R(14-16)	1.422	R(15-16)	1.419	R(15-16)	1.422	R(10-11)	1.353
R(14-27)	1.009	R(15-27)	1.009	R(15-28)	1.009	R(10-27)	1.084
R(16-17)	1.405	R(16-17)	1.408	R(16-17)	1.410	R(12-13)	1.417
R(16-21)	1.407	R(16-21)	1.407	R(16-21)	1.403	R(12-17)	1.417
R(17-18)	1.395	R(17-18)	1.395	R(17-18)	1.389	R(13-14)	1.390
R(17-28)	1.088	R(17-28)	1.087	R(17-29)	1.087	R(14-15)	1.393
R(18-19)	1.404	R(18-19)	1.393	R(18-19)	1.404	R(14-28)	1.081
R(18-29)	1.086	R(18-29)	1.083	R(18-30)	1.083	R(15-16)	1.393

A(1-6-25)	120.6	A(3-4-7)	119.9	A(1-6-5)	119.1	A(2-3-12)	131.9
A(3-2-23)	120.7	A(5-4-7)	124.3	A(1-6-26)	120.6	A(2-3-22)	116.3
A(2-3-4)	123.3	A(4-5-6)	122.1	A(3-2-24)	120.7	A(2-20-21)	179.0
A(3-4-5)	115.8	A(4-5-24)	119.7	A(2-3-4)	123.3	A(12-3-22)	111.8
A(11-10-12)	112.0	A(13-12-15)	123.4	A(7-10-12)	124.5	A(7-8-25)	120.1
A(10-11-15)	178.9	A(12-15-16)	127.9	A(11-10-12)	112.0	A(9-8-25)	121.9
A(10-12-13)	118.6	A(12-15-27)	118.2	A(10-11-14)	178.9	A(8-9-10)	120.0
A(10-12-14)	117.8	A(16-15-27)	113.9	A(10-12-13)	118.6	A(8-9-26)	119.9
A(13-12-14)	123.6	A(15-16-17)	116.7	A(10-12-15)	117.9	A(10-9-26)	120.1
A(12-14-16)	128.1	A(15-16-21)	123.7	A(13-12-15)	123.5	A(9-10-11)	122.1
A(12-14-27)	118.2	A(17-16-21)	119.5	A(12-15-16)	128.0	A(9-10-27)	121.6
A(16-14-27)	113.6	A(16-17-18)	120.8	A(12-15-28)	118.3	A(11-10-27)	116.3
A(14-16-17)	116.8	A(16-17-28)	120.0	A(16-15-28)	113.7	A(13-12-17)	115.9
A(14-16-21)	123.9	A(16-21-20)	119.6	A(15-16-17)	116.8	A(12-13-14)	123.2
A(17-16-21)	119.3	A(16-21-31)	119.8	A(15-16-21)	124.0	A(12-17-16)	122.1
A(16-17-18)	120.5	A(18-17-28)	119.2	A(17-16-21)	119.2	A(12-17-30)	119.7

Physical properties.

Depending on the Ab initio of the DFT calculation model is calculate some physical properties for Acryl amide molecules; 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 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) = $\frac{1}{2}(E_{HOMO} - E_{LUMO})$, (Electron Affinity) $E_A = - E_{LUMO}$ according Koopmans theorem for N system of electrons[14-17].

The results shown that compound (**R – pyridine**)is less activity because it has the higher value of ΔE , E_A , IP and η . This means that this compound has more ability to lose electrons and be easier ionization compared to other compounds.

The MOPAC computational packages (semi-empirical method , PM3 model) employed to compute physical properties; heats of formation (ΔH_f , kJ.mol⁻¹)[18,19]. the results showed (**Table 2**) for the compound (**R-PH-O-CH3**) has less value which means high stability than the other's.

Table 2: Energetic properties of Acryl amide ΔH_f (kJ.mol⁻¹), μ (in Debye) ,orbital energies (E_{HOMO} , E_{LUOM} , ΔE in eV) , IP(in eV) , E_A (in eV) , and η (in eV) for Acryl amide derivatives Calculated by DFT method.

Comp	R-N-PH-CH3	R-N-PH-Cl	R-PH-O-CH3	R-pyridine
ΔH_F^o	199.4221	201.8126	75.2634	281.5493
μ	5.1785	5.5388	3.8906	3.2100
E_{HOMO}	-6.1128	-6.5011	-5.7715	-6.7419
E_{LUMO}	-3.0572	-3.241	-3.03790	-3.2419
ΔE	3.0555	3.2569	2.7336	3.4999
IP	6.1128	6.5011	5.7715	6.7419
E_A	3.0572	3.2414	3.0379	3.2419
η	1.5277	1.6298	1.3668	1.7499

Thermodynamics functions

The fundamental vibration frequencies for five compound of **Acryl amide** 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.

Thermodynamics functions standard and heat capacity for the studied molecules listed **Table: 3** Showed the calculation results show that each of the thermodynamic functions (E^0 , H^0 , G^0 , A^0 , C_V , C_P , S^0).



Table 3: *standard thermodynamics functions for Acryl amide molecules calculated by DFT model at 298.15oK of.*

Comp.	E^0 KJ/Mol	H^0 KJ/mol	G^0 KJ/mol	S KJ/mol.deg	A^0 KJ/mol	Cp KJ/mol.deg	Cv KJ/mol.deg
R-N-PH-CH3	708.5101	710.9889	526.4937	0.6188	341.9985	0.3011	0.2928
R-N-PH-Cl	610.9895	613.4647	428.9695	0.6334	244.4743	0.3008	0.2925
R-PH-O-CH3	725.5181	727.9976	543.5024	0.6511	359.0072	0.3236	0.3153
R-pyridine	601.504	603.9828	419.4876	0.5905	234.9924	0.2802	0.2719

References

- [1]. Santos, S. A.; Pereira, N. Jr.; Da Silva, I. M.; Sarquis, M. I. M; Antunes, O.A. C. *Process Biochem.* **2004**, 39, 2269-2275.
- [2]. Li, Y. L.; Xu, W. F. *Bioorg. Med. Chem.* **2004**, 13, 5171-5180.
- [3]. Sousa, J. B.; Calheiros, R.; Rio, V.; Borges, F.; Marques, M. P. M. *J. Mol. Struct.* **2006**, 783, 122-128.
- [4]. Schwaiger, S.; Cervellati, R.; Seger, C.; Ellmerer, E. P.; About, N.; Renimel, I.; Godenir, C.; Andre, P.; Gafner, F.; Stuppner, H.; *Tetrahedron* **2005**, 61(19), 4621-4630.
- [5]. Rehman, S. U.; Shahid, K.; Ali, S.; Bhatti, M. H.; Parvez, M. J. *Organomet.Chem.* **2005**, 690(5), 1396-1408.
- [6]. Grayer, R. J.; Eckert, M. R.; Veitch, N. C.; Kite, G. C.; Marin, P. D.; Kokubun, T.; Simmonds, M. S. J.; Paton, A. J. *Phytochemistry* **2003**, 64(2), 519-528.
- [7]. Sondhi, S. M.; Singh, N.; Kumar, A.; Lozach, O.; Meijer L. *Bioorg. Med.Chem.* **2006**, 14(11), 3758-3765.
- [8]. Zhao, L.; Tao, K.; Li, H.; Zhang, J. *Tetrahedron* **2011**, 67(15), 2803-2806.
- [9]. ric, A.; Alexander, Y.; Kots, B.; Ferid, M.; Scott, R. *Bioorg. Med. Chem. Lett.* **2009**, 19(11), 3067-3071.
- [10]. Musad, E. A.; Mohamed, R.; Saeed, B. A.; Vishwanath, B. S.; Rai, K. M. L. *Bioorg. Med. Chem. Lett.* **2011**, 21(12), 3536-3540.
- [11] MJ Frisch, GW Trucks, HB Schlegel, GE Scuseria, MA Robb, JR Cheeseman, JA Montgomery, T Vreven, KN Kudin, JC Burant, et al. Gaussian, Inc., Pittsburgh, PA 2003.
- [12] Ali J.H.; *J. of Pharm., Bio. and Chem. Sciences* , **2013** ; 4(1), 624- 634.
- [13] Flukiger, HP Luthi, S Portmann, J Weber. *MOLEKEL 4.3*. Swiss Center for Scientific Computing: Manno, Switzerland **2000-2002**.
- [14] C. E. Moore , "Ionization Potentials and Ionization Limits Derived from The Analyses of Optical Spectra", NSRDS-NBS, USA, **1970** .
- [15] D. Vanfleteren, Neck D. V., Ayers P. W., Morrison R. C. and Bultinck P. , *The Journal of Chemical Physics*, **130**, **2009**, 194104(1)-194104(10).
- [16] H. Hotop and Lineberger W. C., *Journal of Physical Chemistry*, 4, 1975, 539-576.
- [17] C.G.Zhan, J.A.Nichols and, D.A.Dixon, *Journal of Physical Chemistry A*, 107, **2003**. 4184-4195.
- [18] R.G. Pearson , "Chemical Hardness", wiley-VCH, Germany; **1997**.
- [19] R. G. Pearson, *Proceedings of the National Academy of Sciences of the United States of America*, 83, **1986**. 8440-8441.