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Electronic Structure, Thermodynamics functions and Physical properties for [(E)-2-cyano-3-(2,4-dichlorophenyl) acrylic acid]derivatives by using Ab Intio calculations(DFT-Model)

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Abstract:

This study involved the adoption of the program (Gaussian 03) to use the method of calculating the total (Ab initio of method) according to the DFT method, for the purpose of the expense of dimensional geometry (lengths and bond angles) when the geometry of a balanced, functions thermodynamic, some physical properties, charges for[(E)-2-cyano-3-(2,4-dichlorophenyl)acrylic acid]derivatives .

Have shown calculation results that the compound (R-N-pyridine) has the highest value of thermodynamic functions (E^0,H^0,G^0,A^0) but the compound (R-Cl) has the highest value of heat capacity (C_V,C_P,S^0). The results showed that both nitrogen atoms (N_{15},N_{21}) had the highest negative charge in the compound (R-O-PH) and (R- N-pyridine), which makes it a strong legend when Linked to metal and the formation of the complex.

For (R-Cl , R-O-PH , R-S-PH-Cl , R-N-pyridine) molecules the calculated some of physical properties (dipole moment μ in Debye), orbital energies (E_{HOMO}, E_{LUMO} in eV), IP (in e V), (measurement stability ΔE), hardness η and Electron Affinity E_A). Also for these molecules the calculated (ΔHf^0 (in KJ/mole) by using (semi-empirical method AM1 model in MOPAC program). Calculation results have shown that the compound (R-O-PH) the lower value of the heat of

formation (the more Stability) as well as the compound (R-Cl) has the highest value of ΔE and IP that means it's the less active between the compounds. This difference in the results comes according to the difference of substituted groups.

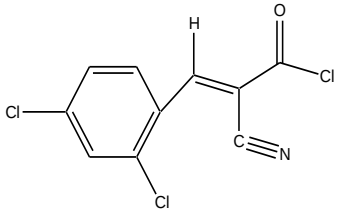
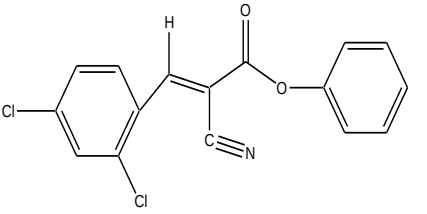
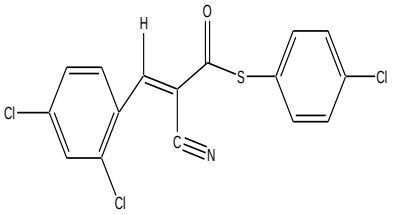
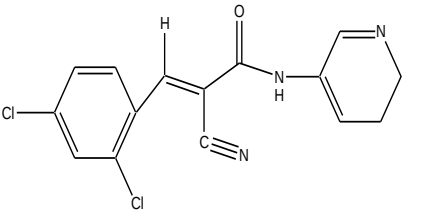
Key words: DFT-Model, thermodynamics functions, acrylic derivatives.

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. We report here the physical properties of the hetrocyclic acrylic derivatives by using DFT method. Also this modified method is fast, more accuracy for this field [10].

In this work were 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, no imaginary wavenumber modes were obtained,

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].**

 (*E*)-2-cyano-3-(2,4-dichlorophenyl)acryloyl chloride	 (*E*)-phenyl 2-cyano-3-(2,4-dichlorophenyl)acrylate
R-Cl	**R-O-PH**
 (*E*)-*S*-4-chlorophenyl 2-cyano-3-(2,4-dichlorophenyl)prop-2-enethioate	 (*E*)-2-cyano-3-(2,4-dichlorophenyl)-*N*-(pyridin-3-yl)acrylamide
R-S-PH-Cl	**R-N-Pyridine**

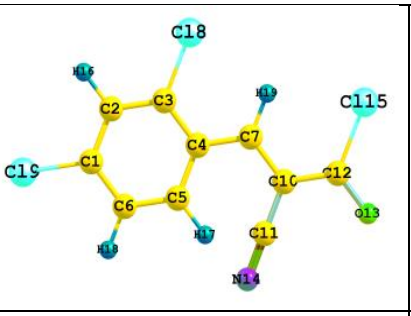
RESULTS AND DISCUSSION

Geometrical parameter

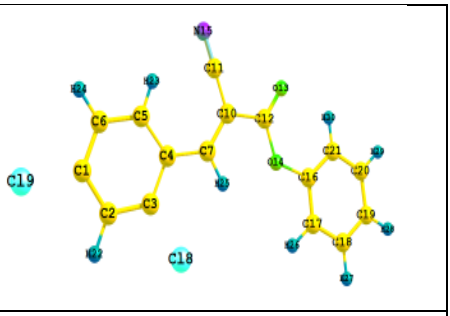
In this research calculated the geometry (bond lengths and bond angels) of the four molecules of **(E)-2-cyano-3-(2,4-dichlorophenyl)acrylic acid** derivatives (R-Cl , R-O-PH , R-S-PH- Cl , R- N - pyridine) , using the Ab initio method of according to DFT method). According to the results calculated and recorded in the (**table 1**and **fig. 1)** . Show that each the bonds **($C_{(1,12)}$-X)** (**X** = Cl_{15} , O_{14} , S_{15} , N_5) in compound R-S-PH-Cl has high value compared to other compounds studies it may be due to high electro – negative of S_{15} atom with substituted

group, whereas for the same bond length for the compound (R-N - pyridine) have less value , may be caused by the less electro – negative of (N) with substituted groups.

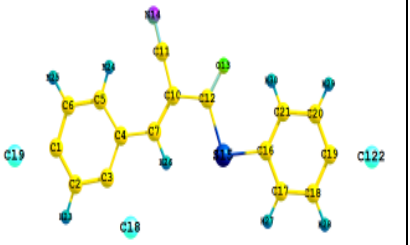
Also the change of the group substituted had effect on the value of the angles of the compounds studied in this research , have shown calculation in the (**table 1**and **fig. 1).** That the angles which have the same position in all compounds have the same value that means this atom with substituted groups have no effect on acrylic angles and these compounds have stable geometry.



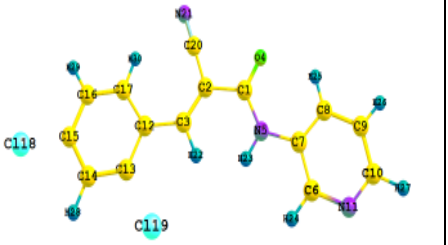
R-Cl



R-O-PH



R-S-PH-Cl



R-N-Pyridine

Fig.(1): The geometric equilibrium for the derivatives of ***(E)-2-cyano-3-(2,4-dichlorophenyl)acrylic acid.***

Table 1: Calculated geometric parameters (bond lengths in Angstrom length angles in degree) of the derivatives (E)-2-cyano-3-(2,4-dichlorophenyl)acrylic acid.

R-Cl		R-O-PH		R-S-PH-Cl		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)	1.337	R(1-2)	1.337	R(1-2)	1.337	R(1-2)	1.351
R(1-6)	1.337	R(1-6)	1.337	R(1-6)	1.337	R(1-4)	1.208
R(1-9)	1.719	R(1-9)	1.719	R(1-9)	1.719	R(1-5)	1.266
R(2-3)	1.337	R(2-3)	1.337	R(2-3)	1.337	R(2-3)	1.337
R(2-16)	1.100	R(2-22)	1.100	R(2-23)	1.100	R(2-20)	1.313
R(3-4)	1.337	R(3-4)	1.337	R(3-4)	1.337	R(3-12)	1.337
R(3-8)	1.719	R(3-8)	1.719	R(3-8)	1.719	R(3-22)	1.100
R(4-5)	1.337	R(4-5)	1.337	R(4-5)	1.337	R(5-7)	1.266
R(4-7)	1.337	R(4-7)	1.337	R(4-7)	1.337	R(6-7)	1.337
R(5-6)	1.337	R(5-6)	1.337	R(5-6)	1.337	R(6-11)	1.260
R(5-17)	1.100	R(5-23)	1.100	R(5-24)	1.100	R(6-24)	1.100
R(6-18)	1.100	R(6-24)	1.100	R(6-25)	1.100	R(7-8)	1.337
R(7-10)	1.337	R(7-10)	1.337	R(7-10)	1.337	R(8-9)	1.337
R(7-19)	1.100	R(7-25)	1.100	R(7-26)	1.100	R(8-25)	1.100
R(10-11)	1.313	R(10-11)	1.313	R(10-11)	1.313	R(9-10)	1.259
R(10-12)	1.351	R(10-12)	1.351	R(10-12)	1.351	R(9-26)	1.100
R(11-14)	1.158	R(11-15)	1.158	R(11-14)	1.158	R(10-11)	1.260
R(12-13)	1.208	R(12-13)	1.208	R(12-13)	1.208	R(10-27)	1.100
R(12-15)	1.795	R(12-14)	1.338	R(12-15)	1.815	R(12-13)	1.337
A(2-1-6)	120.0	R(14-16)	1.355	R(15-16)	1.815	R(12-17)	1.337
A(2-1-9)	120.0	R(16-17)	1.337	R(16-17)	1.337	R(13-14)	1.337
A(1-2-3)	120.0	R(16-21)	1.337	R(16-21)	1.337	R(13-19)	1.719
A(1-2-16)	120.0	R(17-18)	1.337	R(17-18)	1.337	R(14-15)	1.337
A(6-1-9)	120.0	R(17-26)	1.100	R(17-27)	1.100	R(14-28)	1.100
A(1-6-5)	120.0	R(18-19)	1.337	R(18-19)	1.337	R(15-16)	1.337
A(1-6-18)	120.0	R(18-27)	1.100	R(18-28)	1.100	R(15-18)	1.719
A(3-2-16)	120.0	R(19-20)	1.337	R(19-20)	1.337	R(16-17)	1.337
A(2-3-4)	120.0	R(19-28)	1.100	R(19-22)	1.719	R(16-29)	1.100
A(2-3-8)	120.0	R(20-21)	1.337	R(20-21)	1.337	R(17-30)	1.100
A(4-3-8)	120.0	R(20-29)	1.100	R(20-29)	1.100	R(20-21)	1.158
A(3-4-5)	120.0	R(21-30)	1.100	R(21-30)	1.100	R(4-25)	1.414
A(3-4-7)	120.0	R(13-30)	1.541	A(2-1-6)	120.0	A(2-1-4)	120.0
A(5-4-7)	120.0	A(2-1-6)	120.0	A(2-1-9)	120.0	A(2-1-5)	120.0
A(4-5-6)	120.0	A(2-1-9)	120.0	A(1-2-3)	120.0	A(1-2-3)	120.0
A(4-5-17)	120.0	A(1-2-3)	120.0	A(1-2-23)	120.0	A(1-2-20)	120.0
A(4-7-10)	120.0	A(1-2-22)	120.0	A(6-1-9)	120.0	A(4-1-5)	120.0
A(4-7-19)	120.0	A(6-1-9)	120.0	A(1-6-5)	120.0	A(1-4-25)	118.7
A(6-5-17)	120.0	A(1-6-5)	120.0	A(1-6-25)	120.0	A(1-5-7)	120.0
A(5-6-18)	120.0	A(1-6-24)	120.0	A(3-2-23)	120.0	A(3-2-20)	120.0
A(10-7-19)	120.0	A(3-2-22)	120.0	A(2-3-4)	120.0	A(2-3-12)	120.0
A(7-10-11)	120.0	A(2-3-4)	120.0	A(2-3-8)	120.0	A(2-3-22)	120.0
A(7-10-12)	120.0	A(2-3-8)	120.0	A(4-3-8)	120.0	A(2-20-21)	180.0
A(11-10-12)	120.0	A(4-3-8)	120.0	A(3-4-5)	120.0	A(12-3-22)	120.0
A(10-11-14)	180.0	A(3-4-5)	120.0	A(3-4-7)	120.0	A(3-12-13)	120.0
A(10-12-13)	120.0	A(3-4-7)	120.0	A(5-4-7)	120.0	A(3-12-17)	120.0
A(10-12-15)	120.0	A(5-4-7)	120.0	A(4-5-6)	120.0	A(5-7-6)	120.0
A(13-12-15)	120.0	A(4-5-6)	120.0	A(4-5-24)	120.0	A(5-7-8)	120.0
		A(4-5-23)	120.0	A(4-7-10)	120.0	A(7-6-11)	120.0
		A(4-7-10)	120.0	A(4-7-26)	120.0	A(7-6-24)	120.0
		A(4-7-25)	120.0	A(6-5-24)	120.0	A(6-7-8)	120.0
		A(6-5-23)	120.0	A(5-6-25)	120.0	A(11-6-24)	120.0
		A(5-6-24)	120.0	A(10-7-26)	120.0	A(6-11-10)	115.0
		A(10-7-25)	120.0	A(7-10-11)	120.0	A(7-8-9)	120.0
		A(7-10-11)	120.0	A(7-10-12)	120.0	A(7-8-25)	120.0
		A(7-10-12)	120.0	A(11-10-12)	120.0	A(9-8-25)	120.0
		A(11-10-12)	120.0	A(10-11-14)	180.0	A(8-9-10)	111.2
		A(10-11-15)	180.0	A(10-12-13)	120.0	A(8-9-26)	124.4
		A(10-12-13)	120.0	A(10-12-15)	120.0	A(8-25-4)	121.3
		A(10-12-14)	120.0	A(13-12-15)	120.0	A(10-9-26)	124.4
		A(13-12-14)	120.0	A(12-15-16)	120.0	A(9-10-11)	133.8

		A(12-13-30)	116.5	A(15-16-17)	120.0	A(9-10-27)	113.1
		A(12-14-16)	120.0	A(15-16-21)	120.0	A(11-10-27)	113.1
		A(14-16-17)	120.0	A(17-16-21)	120.0	A(13-12-17)	120.0
		A(14-16-21)	120.0	A(16-17-18)	120.0	A(12-13-14)	120.0
		A(17-16-21)	120.0	A(16-17-27)	120.0	A(12-13-19)	120.0

Physical properties

Depending on the Ab initio of method of calculation according to the density function theory (DFT) 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**[15-18].** that compound (R-Cl) has high value for each of (Dipole moments , IP, Electron Affinity E_A, ΔE),And less value E_{HOMO}(less the value of a negative energy), (E_{LUMO})this means that this compound has more ability to lose electrons and be easier ionization compared to other compounds ,And less value Hardness(η) .

Also, the MOPAC computational packages (semi-empirical method , AM1 model) employed to compute physical properties; heats of formation (ΔHf, kJ.mol-1)**[19,20]**. the results showed **(Table 2)** for the compound (R-O-Ph) has lower heat of formation (more stability), Whereas the compound (R-N-pyridine) 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) , and η(in eV) for the derivatives of (E)-2-cyano-3-(2,4-dichlorophenyl)acrylic acid.

Comp.	ΔH_f KJ/Mol	μDebye	E_{HOMO}	E_{LOMO}	ΔE	IP	EA	η
R-Cl	91.3133	4.8939	-7.67041	-3.7397	3.93072	7.67041	3.7397	-1.9653
R-O-PH	77.1333	4.1119	-6.82521	-3.1661	3.6591	6.82521	3.1661	-1.8296
R-S-PH-Cl	221.9334	4.5239	-6.6562	-3.4668	3.1895	6.6562	3.4668	-1.5947
R-N-Pyridine	273.1328	3.2100	-6.7419	-3.2419	3.4999	6.7419	3.2419	-1.7500

Thermodynamics functions

The fundamental vibration frequencies for the (R-Cl , R-O-PH , R-S-PH- Cl, R- N - pyridine) 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.

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

$$X_i = \frac{1.44\bar{\nu}}{T}$$

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

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

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 Go 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- N - pyridine > R-O-PH > R-S-PH-Cl > R-Cl

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

R-Cl > R-S-PH-Cl > R-O-PH > R- N – pyridine

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: - Cl , -S-PH-Cl , -O-PH , - N – pyridine).

Table 3: The calculated standard thermodynamics functions at 298.15oK of the derivatives of (E)-2-cyano-3-(2,4-dichlorophenyl)acrylic acid.

Comp.	E KJ/Mol	H KJ/mol	G KJ/mol	S KJ/mol.deg	A KJ/mol	Cp KJ/mol.deg	Cv KJ/mol.deg
R-Cl	337.239	2478.819	2323.900	0.5196	2168.982	8.5177	**0.2037**
R-O-PH	600.174	3078.993	3034.598	0.1484	2990.204	8.3809	**0.0669**
R-S-PH-Cl	565.9069	3044.726	3000.779	0.1474	2956.831	8.3831	**0.0691**
R-N-Pyridine	**601.5044**	**3080.324**	**3038.254**	**0.1411**	**2996.186**	**8.379**	**0.0650**

The Charges

The Calculated for all charges atoms of the molecules studied according to the method (DFT) have shown calculation results of the charges **(Table: 4)**, are each of the (C_{12} , O_{13}) atoms for carbonyl group has lower value of charge (the highest density electronic) in the case of compound (R- N – pyridine) while it has the highest value of charge (less density electronic) in compound (R-O-PH) Perhaps the reason for this difference in electrical negative of electron with drawing . when it linked to metal complex formation , as a result of higher giving electronic to nitrogen atoms(N) of cyanide bonds in the compound (R-O-PH) compared to other compounds , it can be strong legend , when it linked to metal complex formation.

R-O-PH > R- N – pyridine > R-S-PH-Cl > R-Cl

Table: 4 Calculated charge for the derivatives of(E)-2-cyano-3-(2,4-dichlorophenyl)acrylic acid using DFT model.

R-Cl		R-O-PH		R-S-PH-Cl		R-N-Pyridine	
Atom	charge	Atom	charge	Atom	charge	Atom	charge
C1	-0.2335	**C1**	-0.2325	**C1**	-0.2334	**C1**	0.536
C2	-0.0725	**C2**	-0.0743	**C2**	-0.0715	**C2**	0.1082
C3	-0.3059	**C3**	-0.3044	**C3**	0.3087	**C3**	-0.1430
C4	0.1417	**C4**	0.1482	**C4**	0.1469	**O4**	-0.433
C5	-0.1207	**C5**	-0.1279	**C5**	-0.1241	**N5**	-0.7939
C6	-0.0976	**C6**	-0.0980	**C6**	-0.0991	**C6**	-0.0591
C7	-0.1388	**C7**	-0.1252	**C7**	-0.1628	**C7**	0.3312
Cl8	0.1592	**Cl8**	0.1349	**Cl8**	0.1448	**C8**	-0.0709
Cl9	0.1317	**Cl9**	0.1170	**Cl9**	0.1237	**C9**	-0.1426
C10	0.1281	**C10**	0.0788	**C10**	0.1201	**C10**	0.0088
C11	0.0299	**C11**	0.0080	**C11**	0.0251	**N11**	-0.3616
C12	0.1053	**C12**	0.5280	**C12**	0.0536	**C12**	0.1571
O13	-0.2995	**O13**	-0.3912	**O13**	-0.3910	**C13**	-0.3117
N14	-0.2386	**O14**	-0.5916	**N14**	-0.2431	**C14**	-0.0705
Cl15	0.0282	**N15**	-0.2472	**S15**	0.4189	**C15**	-0.2346
H16	0.2008	**C16**	0.2673	**C16**	-0.2599	**C16**	-0.0983
H17	0.1902	**C17**	-0.1304	**C17**	-0.1314	**C17**	-0.1271
H18	0.1865	**C18**	-0.1357	**C18**	-0.0851	**Cl18**	0.1205
H19	-0.2335	**C19**	-0.1064	**C19**	-0.2380	**Cl19**	0.1266
		C20	-0.1536	**C20**	-0.0889	**C20**	0.0048
		C21	-0.0904	**C21**	-0.1391	**N21**	-0.2463
		H22	0.1960	**Cl22**	0.0739	**H22**	0.1374
		H23	0.1875	**H23**	0.1981	**H23**	0.3508
		H24	0.1821	**H24**	0.1885	**H24**	0.1403
		H25	0.2055	**H25**	0.1842	**H25**	0.2055
		H26	0.1496	**H26**	0.1989	**H26**	0.1455
		H27	0.1360	**H27**	0.1581	**H27**	0.1500
		H28	0.1335	**H28**	0.1653	**H28**	0.1975
		H29	0.1391	**H29**	0.1676	**H29**	0.1837
		H30	0.1971	**H30**	0.2084	**H30**	0.1894

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