Study of Some Physical Properties and thermodynamic functions for mercabtoacetamide derivatives by using calculations (DFT-Model).

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Abstract:-

A study of (2-mercaptoacetamide) novelty ligands were carried out theoretical study by DFT/B3LYP(3-211G)(d,p) method by using the program (Gaussian 09) .

The results have shown calculation that the compound ($C_{10}H_{12}N_2O_2S_2$) has the highest value of thermodynamic functions (E^0, H^0, G^0, A^0, C_V, C_P, S^0) but the compound ($C_4H_8N_2O_2S_2$) has the lowest value of these functions when The results showed that both nitrogen atoms ($N_{1(3)}, N_{6(12,4)}$) had the highest negative charge in the compound ($C_{10}H_{12}N_2O_2S_2$) which makes it a strong legend when Linked to metal and the formation of the complex.
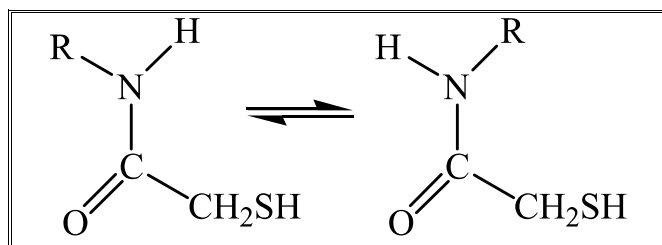
For($C_6H_{12}N_2O_2S_2, C_{10}H_{12}N_2O_2S_2$, $C_4H_8N_2O_2S_2$) molecules calculated someofphysical properties (dipole moment µ in Debye), orbital energies (E_{HOMO}, E_{LUMO} in eV),IP (in e V) , (measurement stability ΔE) , (hardness η),(Electron Affinity E_A),(χElectronegativity)and(Ġ Electrophilicity) in eV. Also For these molecules the calculated (ΔHf^0 (in KJ/mole)by using (semi-empirical methodPM3 model in MOPAC program). Calculation results have shown that the compound ($C_6H_{12}N_2O_2S_2$) the lower value of the heat of formation (the more Stability)as well asthe compound ($C_{10}H_{12}N_2O_2S_2$) has the lowest value of ΔE and IP.

Key words: DFT-Model , mercabtoacetamide ,Electrophilicity.

Chemistry classification : QD 450-801

Introduction

The analytical use mercabtoacetamide as suitable reagents in the determination of some metal ions is well-established[1]. Due to the presence of nitrogen, Sulphur and oxygen atoms at suitable positions, N-alkyl-2-mercaptoacetamides are reported to behave as monofunctional bidentate ligands and also show linkage isomerism in their complexes[2-5]. In most of the metal complexes these ligands are reported to behave as N,S bonded or O,S⁻ bonded ligands[6-9]. However ,some complexes have also been reported in which these ligands are bonded through N and O atoms with metals[10]. In addition to above , these ligands are reported to exist in following two conformational isomeric forms.

The field of computational chemistry use's computers to predict molecular structure and reactivity[11].The latter are now applied routinely to compute molecular properties in a wide variety of chemical applications, including pharmaceuticals and drug design, atmospheric and environmental chemistry , nanotechnology ,and materials science[12].

In this work,were investigated theoretically using the Density Functional Theory (DFT) calculation [13] at the B3LYP/6-311G(p,d) level of theory to get the optimized geometry . DFT calculations were carried out with Beck's three-parameter hybrid model using the Lee–Yang–Parr correlation functional (B3LYP) method. Molecular geometries were fully optimized by Berny'soptimization algorithm using redundant internal coordinates. All optimized structures were confirmed to be minimum energy conformations **[14,15].**

## Results and Discussion.

Geometrical parameter.

In this research calculated the geometry (bond lengths and bond angles) of the four molecules of ($C_6H_{12}N_2O_2S_2$, $C_{10}H_{12}N_2O_2S_2$, $C_4H_8N_2O_2S_2$). According to the results calculated and recorded in the (**table 1**and **fig 1**) . Show that each the bonds [bis($N_{1(3)}$-X) , X= (-CH_2-CH_2-) ,-Ph-, -NH-NH-] in compound ($C_6H_{12}N_2O_2S_2$) has high value compared to other compounds studies it may be due to low electro – negative of C atom with substituted group, whereas for the(HNCON-C) bond length for the compound ($C_6H_{12}N_2O_2S_2$) has less value , may be caused

by the less electro – negative of (N) with substituted groups .

For carbonyl bond length the results showed that in the compound ($C_6H_{12}N_2O_2S_2$) taller than the other's on two side of group substituted :

$C_6H_{12}N_2O_2S_2 > C_{10}H_{12}N_2O_2S_2 > C_4H_8N_2O_2S_2$
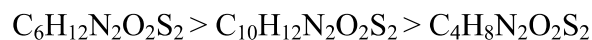
Also the change of the group substituted had effect on the value of the angles of the compounds studied in this research , have shown calculation in the (**table 1**and **fig 1**) That the angle ($\angle$ **C_2 N_1 C_6**) and [HNCOCH₃] showed that in compound ($C_{10}H_{12}N_2O_2S_2$)have

high value ,May be due to the big size of substitution groups of phenyl on the angles .

$C_{10}H_{12}N_2O_2S_2 > C_6H_{12}N_2O_2S_2 > C_4H_8N_2O_2S_2$

$C_6H_{12}N_2O_2S_2$
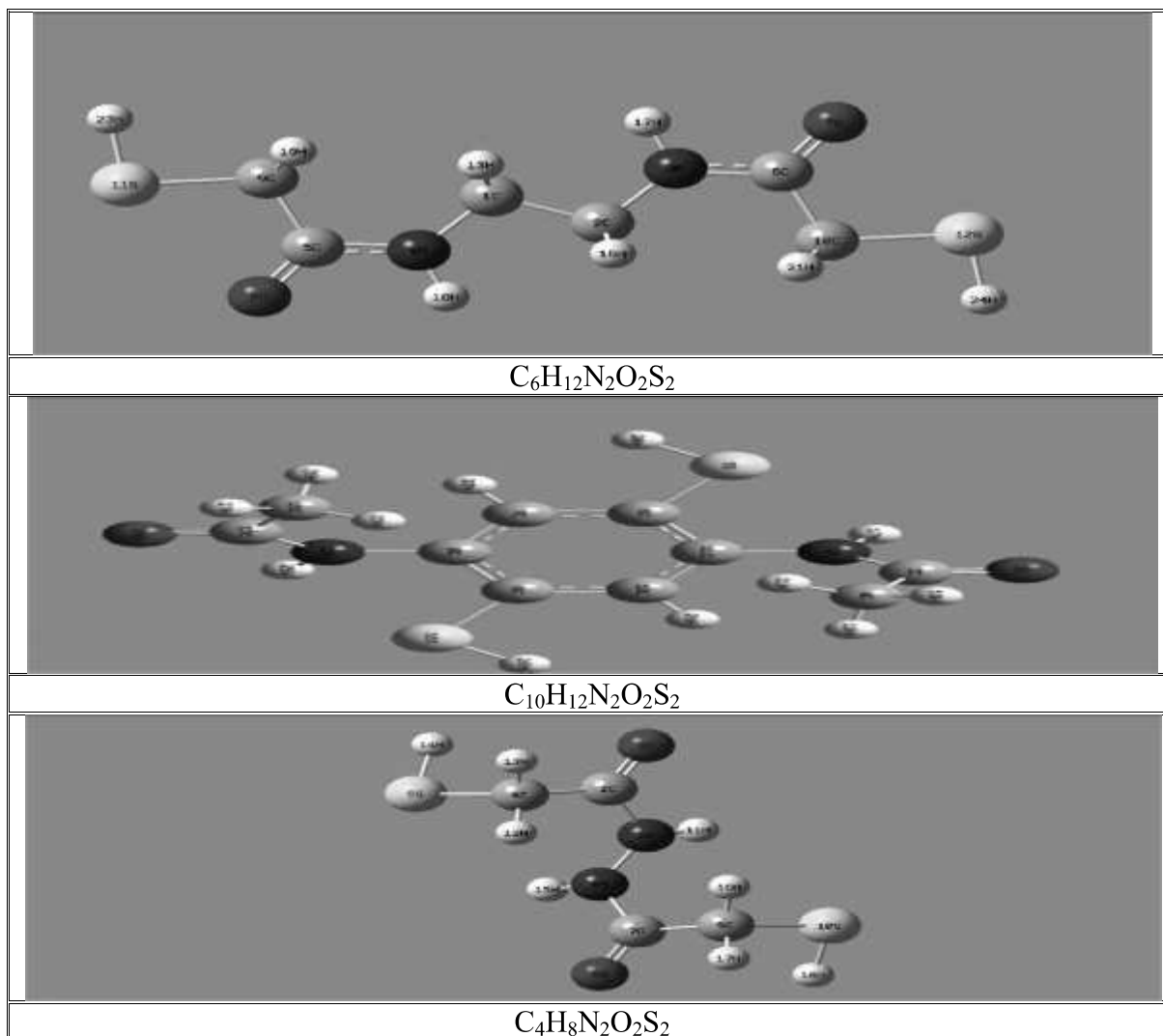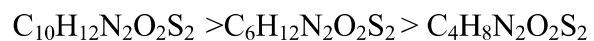
$C_{10}H_{12}N_2O_2S_2$

$C_4H_8N_2O_2S_2$

Fig.(1): The geometric equilibrium for the derivatives of mercabtoacetamide derivatives calculated by DFT/B3LYP(3-211G)(d ,p) method.

Table 1 : Calculated geometric parameters (bond lengths in Angstrom length angles in degree) of mercabtoacetamide derivatives calculated by DFT/B3LYP(3-211G)(d ,p) method.

C6H12N2O2S2		C10H12N2O2S2		C4H8N2O2S2	
Para. Geo.	Bond length and Angle	Para. Geo.	Bond length and Angle	Para. Geo.	Bond length and Angle
R(1,2)	1.5278	R(1,2)	1.389	R(1,2)	1.3844
R(1,4)	1.4543	R(1,11)	1.4139	R(1,6)	1.3802
R(1,13)	1.0968	R(1,17)	1.0139	R(1,11)	1.015
R(1,14)	1.0968	R(2,3)	1.2137	R(2,3)	1.2122
R(2,3)	1.4543	R(2,4)	1.5162	R(2,4)	1.5172
R(2,15)	1.0968	R(4,5)	4.8152	R(4,5)	1.8453
R(2,16)	1.0968	R(4,18)	1.0936	R(4,12)	1.0886
R(3,6)	1.3714	R(4,19)	1.0889	R(4,13)	1.0873
R(3,17)	1.0106	R(4,21)	1.0902	R(5,14)	1.3493
R(4,5)	1.3714	R(5,6)	1.7869	R(5,15)	3.1705
R(4,18)	1.0106	R(5,7)	2.801	R(6,7)	1.3844
R(5,8)	1.2144	R(5,11)	2.7414	R(6,15)	1.015
R(5,9)	1.5252	R(5,20)	1.3471	R(7,8)	1.2122
R(6,7)	1.2144	R(5,21)	4.4308	R(7,9)	1.5172
R(10,12)	1.8348	R(7,22)	1.0824	R(10,18)	1.3493
R(10,21)	1.0928	R(8,9)	1.4065	A(2,1,6)	123.3004
R(10,22)	1.0928	R(8,12)	1.4139	A(2,1,11)	115.7919
R(11,23)	1.3505	R(8,16)	2.7414	A(6,1,11)	117.9048
R(12,24)	1.3505	R(9,10)	1.3933	A(1,2,3)	120.4809
A(2,1,4)	109.7182	R(9,16)	1.7869	A(1,2,4)	116.9432
A(2,1,13)	108.7946	R(9,23)	3.5984	A(3,2,4)	122.5717
A(2,1,14)	108.7945	R(10,11)	1.3954	A(2,4,5)	110.9511
A(4,1,13)	110.9171	R(10,16)	2.801	A(2,4,12)	112.7281
A(4,1,14)	110.9154	R(10,24)	1.0824	A(2,4,13)	108.0677
A(13,1,14)	107.6334	R(12,13)	1.389	A(5,4,12)	105.1102
A(1,2,3)	109.7182	R(12,25)	1.0139	A(5,4,13)	109.8359
A(1,2,15)	108.7948	R(13,14)	1.2137	A(12,4,13)	110.1302
A(1,2,16)	108.7944	R(13,15)	1.5162	A(4,5,14)	95.6871
A(3,2,15)	110.9174	R(15,16)	4.8152	A(4,5,15)	71.8397
A(3,2,16)	110.9151	R(15,23)	1.0902	A(14,5,15)	117.4144
A(15,2,16)	107.6334	R(15,26)	1.0936	A(1,6,7)	123.3004
A(2,3,6)	127.6979	R(15,27)	1.0889	A(1,6,15)	117.9048
A(2,3,17)	118.881	R(16,23)	4.4308	A(7,6,15)	115.7919
A(6,3,17)	113.4211	R(16,28)	1.3471	A(6,7,8)	120.4809
A(1,4,5)	127.6979	A(2,1,11)	129.9321	A(6,7,9)	116.9432
A(1,4,18)	118.881	A(2,1,17)	112.5994	A(8,7,9)	122.5717
A(5,4,18)	113.4211	A(1,2,4)	117.8822	A(7,9,10)	110.9511
A(4,5,8)	121.6222	A(3,2,4)	122.3395	A(7,9,16)	112.7281
A(4,5,9)	115.5155	A(2,4,5)	50.5194	A(7,9,17)	108.0677
A(8,5,9)	122.8624	A(8,12,13)	129.9321	A(10,9,16)	105.1102
A(3,6,7)	121.6222	A(8,12,25)	117.4634	A(10,9,17)	109.8359
A(3,6,10)	115.5155	A(13,12,25)	112.5994		
A(7,6,10)	122.8624	A(12,13,14)	119.7717		
		A(12,13,15)	117.8822		

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),Andfinallycalculated(MolecularHardness)Hardness(η) = ½(E_{HOMO} - E_{LUMO}), (Electron Affinity) EA = - E_{LUMO} according Koopmans theorem for N system of electrons[16-19], Electronegativity(χ) according to

Mullikan1934 [20] and Electrophilicity (ᴕ) according to Parr and co-workers 1999[21].

That compound (**C6H12N2O2S2**) has less value for each of (Dipole moments μ , Electron Affinity EA and Electrophilicity (ᴕ),And high value [E_{LUMO}(high value of a negative energy) and ΔE that's means this compound less active than the other's], and less value Electronegativity(χ).

Also ,The MOPAC computational packages (semi-empirical method , PM3 model) employed to compute physical properties; heats of formation (ΔHf, kJ.mol-1)[22,23]. the results showed **(Table 2)** for the compound (**C6H12N2O2S2**) has lower heat of formation (more stability), Perhaps due this result to the effect of the group substitutes of ethyl for the stability the compound.Whereas the compound (**C4H8N2O2S2**) has a higher heat of formation (less stability).

Table 2:Calculated ΔHf (kJ.mol^{-1}), μ (in Debye) ,orbital energies (E_{HOMO}, E_{LUOM}, $ΔE_{HOMO-LUOM}$ in eV) , IP(in eV) , E_A (in eV) , η(in eV),Electronegativity(χ) andElectrophilicity (ᴕ) for themercabtoacetamide derivatives calculated by DFT/B3LYP(3-211G)(d ,p) method.

Comp.	ΔHf KJ/Mol	(μ)Debye	E_{HOMO}	E_{LUMO}	ΔE	IP	E_A	η	χ	ᴕ
C6H12N2O2S2	-295.8992	0.0006	-6.773	-0.067	-6.705	6.772	0.067	-3.352	3.420	3.043
C10H12N2O2S2	-180.3983	0.0865	-6.252	-1.378	-4.873	6.251	1.377	-2.436	3.814	8.915
C4H8N2O2S2	-173.4551	0.3128	-7.083	-1.023	-6.059	7.082	1.022	-3.541	4.052	7.346

Thermodynamics functions

The fundamental vibration frequencies for the($C_6H_{12}N_2O_2S_2$, $C_{10}H_{12}N_2O_2S_2$, $C_4H_8N_2O_2S_2$)were listed in Table 3. Showed that the phenyl group substituted in ($C_{10}H_{12}N_2O_2S_2$) caused increase in entropy S ,Due to high Electrophilicity .

Looking at the calculation results show that each of the thermodynamic functions (G^0, A^0, E^0, H^0 , S , Cp , Cv) have the same gradient values (different the group substitutes).

$C_{10}H_{12}N_2O_2S_2$ > $C_6H_{12}N_2O_2S_2$ > $C_4H_8N_2O_2S_2$

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.

$$[X= \text{-Ph-} , \text{-CH2-CH2-}]$$

Table 3: *The calculated standard thermodynamics functions at 298.15oK of themercabtoacetamide derivatives calculated by DFT/B3LYP(3-211G)(d ,p) method.*

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
$C_6H_{12}N_2O_2S_2$	519.5990	522.0778	372.2553	0.5025	222.4328	0.2070	0.1987
$C_{10}H_{12}N_2O_2S_2$	587.340	589.8188	412.9398	0.5932	236.0609	0.2741	0.2659
$C_4H_8N_2O_2S_2$	368.7637	371.2425	233.7879	0.4610	96.3335	0.1804	0.1721

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 ($N_{1(3)}$, $N_{4(6,12)}$) atoms have higher value of of negative charge in the case of compound ($C_{10}H_{12}N_2O_2S_2$) while it has the lowest value of charge in compound ($C_4H_8N_2O_2S_2$) Perhaps the reason for electrical negative of electron with drawing of phenyl group that

substituted,it can be strong legend when it linked to metal complex formation.

Also as a result of higher giving electronic to oxygen atoms(O) of carbonyl bonds in the same compound ($C_{10}H_{12}N_2O_2S_2$) compared to other compounds . From this result this compound ($C_{10}H_{12}N_2O_2S_2$) canbe strong tetradenit chelating legend.

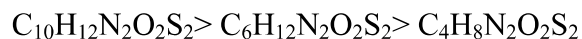$$C_{10}H_{12}N_2O_2S_2> C_6H_{12}N_2O_2S_2> C_4H_8N_2O_2S_2$$

Table 4 : Calculated charge for themercabtoacetamide derivatives calculated by DFT/B3LYP(3-211G)(d ,p) method.

C6H12N2O2S2		C10H12N2O2S2		C4H8N2O2S2	
Atom	charge	Atom	charge	Atom	charge
C1	-0.0567	N1	-0.4639	N1	-0.2945
C2	-0.0567	C2	0.3054	C2	0.3592
N3	-0.4347	O3	-0.3396	O3	-0.3316
N4	-0.4347	C4	-0.3474	C4	-0.4295
C5	0.3724	S5	0.0644	S5	-0.0165
C6	0.3723	C6	-0.2340	N6	-0.2945
O7	-0.3280	C7	0.0122	C7	0.3592
O8	-0.3280	C8	0.1645	O8	-0.3316
C9	-0.4567	C9	-0.2339	C9	-0.4295
C10	-0.4567	C10	0.0122	S10	-0.0165
S11	0.0287	C11	0.1645	H11	0.2626
S12	0.0287	N12	-0.4639	H12	0.1746
H13	0.1312	C13	0.3054	H13	0.1888
H14	0.1312	O14	-0.3396	H14	0.0869
H15	0.1312	C15	-0.3474	H15	0.2626
H16	0.1312	S16	0.0644	H16	0.1746
H17	0.2326	H17	0.2453	H17	0.1888
H18	0.2326	H18	0.1319	H18	0.0869
H19	0.1674	H19	0.1464		
H20	0.1674	H20	0.0759		
H21	0.1674	H21	0.1355		
H22	0.1674	H22	0.1034		
H23	0.0455	H23	0.1355		
H24	0.0455	H24	0.1034		
		H25	0.2453		
		H26	0.1319		
		H27	0.1464		
		H28	0.0759		

References:

[1]S.Kumar, D.N.Dhar&P.N.Saxena, ",(2009), Applications of metal Complexes of Sciff- bases – A Review ., "**J. of Sci. & Indus. Res.,** 68, pp:181- 187.

[2]Kuai,H.wei,X.Chun,X.Hong,Jiang,D.Yun,X. Hai,(2014),J.of coord.Chem.,68(1).

[3]J.AbdulGhani,A.Jaber,J.Mohamad;(2009) ;J.ofcoord.Chem.,62(16).

[4]Dixit S C , Sharan R &Kapoor R N, (1987); J.oforganometalalChem, 332,p:135.

[5]R.A.M.Al-Hasani, "Mannich base derived from 1,3,4- thiadiazole as chelating ligand Forsome transition metal complexes ",(2007), **M.Sc. Thesis**, Al-MustansiryaUniversity.

[6]Karra R, Singh Y P &Rai A K,(1987);J.ofMain Group Met Chem., 13,pp:295.

[7]Kaushik A, Singh Y P &Rai A K,(1996) ;J.of Indian J Chem.,35A,p:764.

[8] K.Jiril,H.Peter,K.Kamil,J.Daniel,,(2008);J.of coord.Chem.,61(22),pp3525-3533.

[9] Kaushik A, Singh Y P &Rai A K,,(1993);J.of Main Group Met Chem.,16,pp:71.

[10] Kaushik A, Singh Y P &Rai A K ,(2001).;J.ofIndian J Chem.,40A,pp.642-644.

[11] Atkins,P.,Depaula , J .and Fridman,R.(2009)," Quanta, Matter and Charge :A Molecullar Approach to Physical Chemists" , 1st ed. ,W.H. Freeman and company , New York, USA.

[12] Young C., (2001);J.ofComput. Chem. ;"A practical guide for applying techniques to red-world problems", st ed., John Wiley and Sons, USA.

[13]A.Ahmed,R.Yasser,M.Elmurssi,(2014);J.oft heort.and Comput.Chem.,13(08).

[14]M.Toy,H.Tank;J.of Theor.comput.Chem.,11(4), (2012).

[15] Landers J., GorG.Yu., V. Neimark,(2013);J.ofPhysicochem. Eng. Aspects, 437 , ,pp:3– 32,.

[16] Moore C. E. ,(1970),*"Ionization Potentials and Ionization Limits Derived from The Analyses of Optical Spectra"*, NSRDS-NBS, USA.

[17] Vanfleteren D., Neck D. V., Ayers P. W., Morrison R. C. and Bultinck P.,, (2009); *J. of Chemical Physics,***130**,194104(1)-194104(10).

[18] Hotop H. and Lineberger W. C., , (1975); *J. of Physical Chemistry,* 4,539-576.

[19] Zhan C. G., J. A. Nicholsand ,D. A. Dixon,, (2003);*J. of Physical Chemistry A,* 107,. 4184-4195 .

[20]Mulliken ,R. S. ; (1934) ;***J.of Chemical Physics,*** 2, pp782-793.

[21] R. G. Parr, L. V. Szentpály and S. Liu,; (1999) ***J. of the American Chemical Society,*** 121,pp 1922-1924.

[22]R.G.,Pearson ,**(1997)***"Chemical Hardness"*, wiley-VCH, Germany.

[23]R.G., Pearson,**(1986)***Proceedings of the National Academy of Sciences of the United States of America,*83,8440-8441.

دراسة بعض الخصائص الفيزيائية والدوال الثرموداينميكية لبعض مشتقات مركبتواسيتاماید باستخدام طريقة (DFT).

منال عبد محمد

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الخـــلاصــة:-

تضمنت هذه الدراسة اعتماد برنامج كاوس (Gaussian 09) لاستخدام طريقة الحساب التام على وفق طريقة نظرية دالة الكثافة (DFT) .

وقد أظهرت نتائج الحساب أن المركب (2$C_{10}H_{12}N_2O_2S_2$) يمتلك أعلى قيمةمن قيم الدوال الثرموديناميكية (G^0,H^0,A^0,E^0, S^0,C_p ,C_V). كما أظهرت نتائج الحساب بان لكل من ذرات النتروجين ($N_{1(3)},N_{6(12)}$) قيمة شحنة سالبة عالية في المركب ($C_{10}H_{12}N_2O_2S_2$)مما يجعله ليكاند قوي عند ارتباطه بالفلز وتكوين المعقد.

كما تم حساب بعض الخصائص الفيزيائية عزم ثنائي القطب (μ in Debye) , طاقة المدارات(E_{HOMO} E_{LUMO}),طاقة التأين (IP in eV) , فجوة الطاقة(Δ in eV)E,الألفة الالكترونية,الصلابة ,الكهروسالبية والالكتروفيلية (ω, χ , $E_A, \eta,$ in eV) على التوالي وكذلك تم اعتماد برنامج **MOPAC**لاستخدام الطريقة الشبه تجريبية **PM3**لحساب حرارة التكوين للمركبات (ΔHf^0 in kJ/mole).وقد أظهرت النتائج الحساب أن المركب (2$C_6H_{12}N_2O_2S_2$) اكثر استقرارا لكونه يمتلك اقل قيمة في حرارة التكوين كذلك يمتلكالمركب ($C_{10}H_{12}N_2O_2S_2$) يمتلك أقل قيمة لفرق الطاقة بين المدارات (E_{HOMO} , E_{LUMO}).

N,N'-(ethane-1,2-diyl)bis(2-mercaptoacetamide)
$C_6H_{12}N_2O_2S_2$
N,N'-(1,4-phenylene)bis(2-mercaptoacetamide)
$C_{10}H_{12}N_2O_2S_2$
2-mercapto-N'-(2-mercaptoacetyl)acetohydrazide
$C_4H_8N_2O_2S_2$