DFT Study of Some Benzo Thiazol Amine Derivatives.

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الخـــلاصـــــة:-

تضمنت هذه الدراسة اعتماد برنامج كاوس (Gaussian 09) لاستخدام طريقة الحساب التام على وفق طريقة نظرية دالة الكثافة (DFT), وذلك لغرض حساب الأبعاد الهندسية (أطوال و زوايا التاصر)عند الشكل الهندسي المتوازن , الدوال الثرموديناميكية (G^0,H^0,A^0,E^0) وكذلك تم حساب السعة الحرارية (C_V, C_p , S^0), بعض الخصائص الفيزيائية وكذلك الشحنات لمشتقات حلقة الثايايازول.

تم اعتماد برنامج **MOPAC** لاستخدام الطريقة الشبه تجريبية **PM3** لحساب حرارة التكوين للمركبات (ΔHf^0 in kJ/mole) وقد أظهرت النتائج الحساب أن المركب **R-COOH($C_8H_6N_2O_2S$)** اكثر استقرارا لكونه يمتلك اقل قيمة في حرارة التكوين.

أظهرت نتائج الحساب أن المركب **RpClNO$_2$($C_7H_4ClN_3O_2S$)** اكثر المركبات فعالية لكونه يمتلك اقل قيمة ΔE واقل قيمة للصلابة η وأعلى قيمة في الالكتروفيلية ω و الكهروسلبية χ .

كذلك تم حساب الدوال الثرموديناميكية حيث بينت الحسابات أن المركب **R-CH$_3$($C_8H_8N_2S$)** يمتلك أعلى قيمة للدوال (E^0 , H^0 , G^0 , A^0) بينما المركب **RpClNO$_2$($C_7H_4ClN_3O_2S$)** يمتلك أعلى قيمة للدوال (S^0, C_P , C_V) , أن هذا التغاير بالنتائج يعزى بصورة عامة لتأثير اختلاف المجموعة المعوضة على المركبات المدروسة في هذا البحث.

Abstract:-

In the present work , the adoption of the program (Gaussian 09) to use the method of calculation the total (Ab initio of method) according to the Density Function theory (DFT) , 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 for Some Benzo Thiazol Amine Derivatives .

Also the results investigation Heat formation(ΔHf^0 (in kJ/mole) by using (semi-empirical method PM3 model in MOPAC) for these molecules and the results showed that the compound **R-COOH($C_8H_6N_2O_2S$)** has less value which means high stability than the other's.

Calculation results have shown that the compound **RpClNO$_2$($C_7H_4ClN_3O_2S$)** is more activity because it has the lower value of ΔE and hardness η and has high value of (**Ɔ** Electrophilicity) and),(χ Electronegativity) .

Also the results have shown that the compound **R-CH$_3$($C_8H_8N_2S$)** has highest value of thermodynamic functions (E^0 , H^0 , G^0 , A^0) and the compound **RpClNO$_2$($C_7H_4ClN_3O_2S$)** has highest value of thermodynamic functions (C_V , C_P ,S^0) This difference in results come according to the difference of substituted groups.

Key words: Benzo Thiazol Amine , Electronegativity, DFT-Model.

Introduction.

Thiadiazole and its derivatives are used for biological activities such as antiviral, antibacterial, antifungal and antitubercular. The antileukemic action and host toxicity of the thiadiazoles were blocked by administration of nicotinamide. A large number of 4-thiazolidinones have been reported to be antifungal, antibacterial and antileukemic properties. These observations prompted us to synthesis the title compound with a presumption that incorporation thiadizole and thiazolidinones wound produce new compound with significant fungicidal properties[1].

The biological activity of the compounds is mainly dependent on their molecular structures [2].1, 3, 4-thiadiazoles are very interesting compounds due to their important applications in many pharmaceutical, biological and analytical field [3, 4].

In this work, were investigated theoretically computational chemistry using the Density Functional Theory (DFT) calculations .

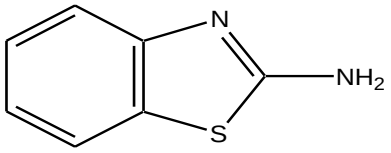
The field of computational chemistry used of computers to predict molecular structure and reactivity , has grown in the past few decades due to the tremendous advances in the computer hardware and the development of efficient software packages [5].

Density function theory , DFT ; It allows us to compute all properties of systems by electron density , $\rho(r)$ which is a function of three variables $\rho(r) = f(x, y, z)$ [6-9]. : is the "functional" part of name comes from the fact that the energy of the molecule is a function of the electron density (the square of wave function ,in fact , is a direct measure of electron density)[10].

In 1964 Hohenberg and Kohn [11] were able to prove that the exact ground – state energy of an electron molecule is uniquely determined by the " electron probability density

$$E[\rho]=E_{classical}[\rho]+E_{xc}[\rho]\ldots*$$

$E_{classical}[\rho]$ is the sum of contribution of kinetic energy, electron – nucleus interactions and the classical electron –electron potential energy and $E_{xc}[\rho]$ is the " exchange-correlation energy" .

 benzo[*d*]thiazol-2-amine
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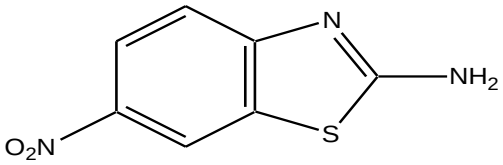 6-nitrobenzo[*d*]thiazol-2-amine
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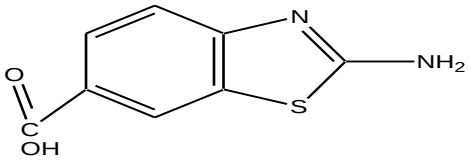 2-aminobenzo[*d*]thiazole-6-carboxylic acid
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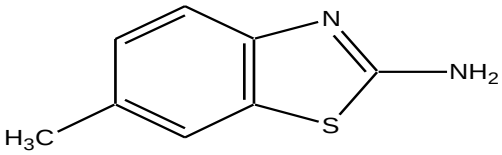
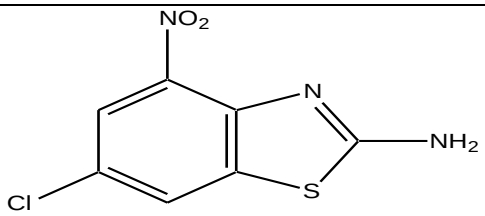
 6-methylbenzo[*d*]thiazol-2-amine
R-CH_3
 6-chloro-4-nitrobenzo[*d*]thiazol-2-amine
R-pCl-PNO_2

Computational details

Calculations of the title compound were carried out with(Gaussian09) software program using B3LYP /6-311G within DFT method, B3LYP basis sets to predict the molecular structure Calculations were carried out with Becke's three parameter hybrid model using

the Lee–Yang– Parr correlation functional (B3LYP) method. Molecular geometries and physical properties and used MOPAC (PM3model)for heat formation calculated.

Results and Discussion.

Geometrical parameter.

In this research calculated the geometry (bond lengths and bond angels) of the five molecules of Some Benzo Thiazol Amine derivatives .

According to the results calculated and recorded in the (**table 1**and **fig. 1)** . Show that the bond (C_1 –C_{11}) in compound **R-pCl-PNO2** has high value compared to other compounds studies it may be due to high electro – negative of Cl atom with substituted group. , Whereas for the same bond length for the compound **R** has less value. Also each bonds length (C_1 –C_2), (C_1 –C_6) in benzene ring the result showed the compound **RCOOH** has high value compare to other compounds studies it may be due to high electro – with drawing electron of carbonyl group.

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 $\angle C_2C_1C_6$ in compound **R-NO2** has high value may be to the electro – with drawing electron of substituted group. Also the angle $\angle C_2C_1C_6$ the results showed that in compound **R-NO2** has high value .

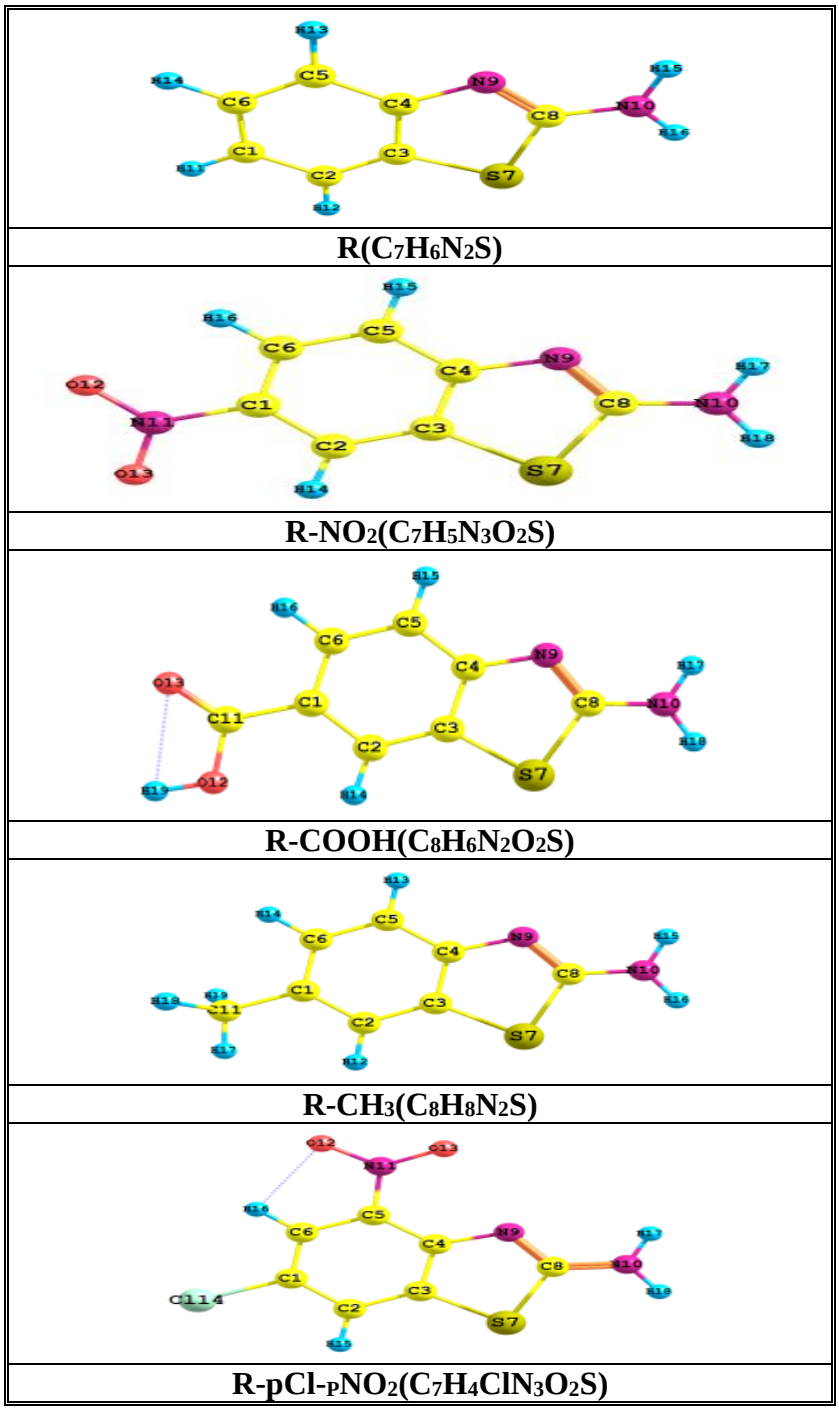


Fig.(1): The geometric equilibrium for the derivatives of Benzo Thiazol Amine Derivatives

Table 1 : Calculated geometric parameters (bond lengths in Angstrom length angles in degree) of Benzo Thiazol Amine Derivatives using Gaussian09

$R(C_7H_6N_2S)$		$R\text{-}NO_2(C_7H_5N_3O_2S)$		$R\text{-}COOH(C_8H_6N_2O_2S)$		$R\text{-}CH_3(C_8H_8N_2S)$		$RpClNO_2(C_7H_4ClN_3O_2S)$	
Para. Geo.	**Bond length and Angle**	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)	1.399	R(1-2)	1.399	R(1-2)	1.407	R(1-2)	1.403	R(1-2)	1.395
R(1-6)	1.403	R(1-6)	1.402	R(1-6)	1.410	R(1-6)	1.410	R(1-6)	1.384
R(1-11)	1.081	R(1-11)	1.457	R(1-11)	1.468	R(1-11)	1.513	R(2-3)	1.383
R(2-3)	1.389	R(2-3)	1.381	R(2-3)	1.382	R(2-3)	1.389	R(2-15)	1.079
R(2-12)	1.081	R(2-14)	1.078	R(2-14)	1.079	R(2-12)	1.082	R(3-4)	1.426
R(3-4)	1.415	R(3-4)	1.421	R(3-4)	1.418	R(3-4)	1.411	R(3-7)	1.823
R(3-7)	1.831	R(3-7)	1.827	R(3-7)	1.831	R(3-7)	1.832	R(4-5)	1.409
R(4-5)	1.398	R(4-5)	1.402	R(4-5)	1.401	R(4-5)	1.398	R(4-9)	1.386
R(4-9)	1.403	R(4-9)	1.392	R(4-9)	1.395	R(4-9)	1.403	R(5-6)	1.399
R(5-6)	1.395	R(5-6)	1.389	R(5-6)	1.388	R(5-6)	1.393	R(5-11)	1.465
R(5-13)	1.080	R(5-15)	1.079	R(5-15)	1.080	R(5-13)	1.080	R(6-16)	1.077
R(6-14)	1.082	R(6-16)	1.078	R(6-16)	1.080	R(6-14)	1.083	R(7-8)	1.871
R(7-8)	1.874	R(7-8)	1.869	R(7-8)	1.869	R(7-8)	1.876	R(8-9)	1.301
R(8-9)	1.296	R(8-9)	1.303	R(8-9)	1.301	R(8-9)	1.296	R(8-10)	1.348
R(8-10)	1.357	R(8-10)	1.351	R(8-10)	1.353	R(8-10)	1.358	R(10-17)	1.006
R(10-15)	1.005	R(10-17)	1.005	R(10-17)	1.005	R(10-15)	1.005	R(10-18)	1.002
R(10-16)	1.001	R(10-18)	1.002	R(10-18)	1.002	R(10-16)	1.001	R(11-12)	1.273
A(2-1-6)	120.6	R(11-12)	1.269	R(11-12)	1.387	R(11-17)	1.090	R(11-13)	1.261
A(2-1-11)	119.4	R(11-13)	1.270	R(11-13)	1.238	R(11-18)	1.093	R(12-16)	2.289
A(1-2-3)	118.2	A(2-1-6)	122.4	R(12-19)	0.976	R(11-19)	1.093	A(2-1-6)	122.3
A(1-2-12)	120.6	A(2-1-11)	118.4	R(13-19)	2.353	A(2-1-6)	118.8	A(1-2-3)	117.2
A(6-1-11)	120.0	A(1-2-3)	117.1	A(2-1-6)	120.4	A(2-1-11)	120.7	A(1-2-15)	120.8
A(1-6-5)	120.8	A(1-2-14)	119.6	A(2-1-11)	121.2	A(1-2-3)	119.2	A(1-6-5)	119.6
A(1-6-14)	119.6	A(6-1-11)	119.2	A(1-2-3)	118.1	A(1-2-12)	119.9	A(1-6-16)	121.8
A(3-2-12)	121.2	A(1-6-5)	119.6	A(1-2-14)	119.7	A(6-1-11)	120.4	A(3-2-15)	122.0
A(2-3-7)	128.1	A(1-11-12)	118.4	A(1-6-5)	120.9	A(1-6-14)	119.0	A(2-3-7)	126.5
A(4-3-7)	109.9	A(1-11-13)	118.3	A(1-6-16)	118.3	A(1-11-17)	111.4	A(4-3-7)	110.2
A(3-4-5)	119.1	A(3-2-14)	123.3	A(1-11-12)	113.3	A(1-11-18)	111.4	A(3-4-5)	116.8
A(3-4-9)	116.1	A(2-3-4)	122.1	A(1-11-13)	125.9	A(1-11-19)	111.4	A(3-4-9)	115.6
A(3-7-8)	86.0	A(2-3-7)	127.9	A(3-2-14)	122.2	A(3-2-12)	120.9	A(3-7-8)	85.8
A(5-4-9)	124.8	A(4-3-7)	110.0	A(2-3-4)	122.2	A(2-3-4)	122.1	A(5-4-9)	127.6
A(4-5-6)	119.3	A(3-4-5)	119.2	A(2-3-7)	128.0	A(2-3-7)	128.0	A(4-5-6)	120.8
A(4-5-13)	118.9	A(3-4-9)	116.1	A(4-3-7)	109.9	A(4-3-7)	109.9	A(4-5-11)	122.7
A(4-9-8)	112.8	A(3-7-8)	86.0	A(3-4-5)	119.1	A(3-4-5)	118.7	A(4-9-8)	113.1
A(6-5-13)	121.8	A(5-4-9)	124.7	A(3-4-9)	116.2	A(3-4-9)	116.2	A(6-5-11)	116.5
A(5-6-14)	119.6	A(4-5-6)	119.6	A(3-7-8)	86.0	A(3-7-8)	86.0	A(5-6-16)	118.6
A(7-8-9)	115.2	A(4-5-15)	119.0	A(5-4-9)	124.8	A(5-4-9)	125.1	A(5-11-12)	117.3
A(7-8-10)	119.4	A(4-9-8)	112.7	A(4-5-6)	119.4	A(4-5-6)	119.5	A(5-11-13)	119.4
A(9-8-10)	125.3	A(6-5-15)	121.4	A(4-5-15)	118.9	A(4-5-13)	118.9	A(6-16-12)	98.9
A(8-10-15)	118.2	A(5-6-16)	121.5	A(4-9-8)	112.7	A(4-9-8)	112.7	A(7-8-9)	115.2

Physical properties.

Depending on the Ab initio of method of calculation according to the DFT model 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($E_{HOMO} - {}_{LUMO}$) , (Electron Affinity) EA = $-_{LUMO}$ according Koopmans theorem for N system of electrons**[12-15].**

That compound **R-pCl-$_P$NO$_2$** is more activity because it has the lower value of ΔE and hardness η and has high value of (ꞤƆ Electrophilicity), E_A and IP, this means that this compound has more ability to lose electrons and be easier ionized compared to other compounds.

Also ,the MOPAC computational packages (semi-empirical method , PM3 model) employed to compute physical properties; heats of formation (ΔHf, kJ.mol-1**)[16,17]**. the results showed **(Table 2)** for the compound **RCOOH** has less value which means high stability than the other's.

Table 2:Calculated ΔHf (kJ.mol^{-1}) in (PM3model), μ (in Debye) ,orbital energies (E_{HOMO}, E_{LUOM}, ΔE in eV) , IP(in eV) , E_A (in eV) , and η(in eV)in (DFT model) for Benzo Thiazol Amine Derivatives

Comp.	ΔH_f KJ/Mol	μ Debye	E_{HOMO}	E_{LOMO}	ΔE	IP	EA	η	χ	ꞤƆ
R	221.6782	1.9192	-5.9830	-0.5532	5.4298	5.9830	0.5532	**2.7149**	**3.2681**	**1.4490**
R-NO$_2$	186.3895	8.0086	-6.7833	-2.9619	3.8213	6.7833	2.9619	**1.9107**	**4.8726**	**6.5034**
R-COOH	-160.3536	4.7909	-6.3773	-1.7733	4.6042	6.3773	1.7733	**2.3020**	**4.0753**	**3.1340**
R-CH$_3$	**182.5177**	**1.494**	**-5.8061**	**-0.4476**	**5.3585**	**5.8061**	**0.4476**	**2.6793**	**3.1268**	**1.3619**
R-pCl-PNO$_2$	**169.8637**	**7.2111**	**-6.8437**	**-3.1010**	**3.7426**	**6.8437**	**3.1010**	**1.8714**	**4.9723**	**7.0600**

Thermodynamics functions

The fundamental vibration frequencies for five compound of **Benzo Thiazol Amine** 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** looking at the calculation results show that each of the thermodynamic functions (G^0, A^0, E^0, H^0)

RCH_3 >RCOOH > RNO_2 > R > R-pCl-$_P$$NO_2$

and (C_V , C_P , S)have the same gradient values (different the group substitutes),

R-pCl-$_P$$NO_2$ >RCOOH > RNO_2 > R > RCH_3

Table 3: The calculated standard thermodynamics functions at 298.15oK of the Benzo Thiazol Amine molecules

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	334.1677	336.6465	227.4938	0.3661	118.3411	0.1419	0.1336
R-NO_2	345.3850	347.8638	221.3587	0.4243	94.8536	0.1781	0.1698
R-COOH	379.1373	381.6161	253.9185	0.4283	126.2208	0.1846	0.17633
R-CH_3	410.9525	413.4313	291.0224	0.4105	168.6319	0.1676	0.1593
R-pCl-PNO_2	319.3396	321.8184	191.7355	0.4363	61.6527	0.1874	0.1791

<u>The Charges</u>

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_9, N_{10}) has high negative charge (the lowest density electronic) in each compounds**(R-CH_3 ,R)** Perhaps the reason for this difference in electrical negative and molecular weight which increase the electronic density on nitrogen atom (N_9, N_{10}) As in the case

of compound **(R- CH_3 ,R)**. This scientific fact indicates that the compound **(R- CH_3 ,R)**. can be strong bi-donate legend when it linked to metal complex formation .

Table 4: Calculated charge for the derivatives of the Benzo Thiazol Amine molecules.

R		R-NO_2		R-COOH		R-CH_3		R-pCl-pNO$_2$	
Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
1 C	-0.1486	1 C	0.2572	1 C	-0.1837	1 C	0.0262	1 C	-0.3278
2 C	-0.1516	2 C	-0.1098	2 C	-0.0432	2 C	-0.1420	2 C	-0.0029
3 C	-0.3383	3 C	-0.3562	3 C	-0.3732	3 C	-0.3501	3 C	-0.3671
4 C	0.1685	4 C	0.1972	4 C	0.2107	4 C	0.1833	4 C	0.1972
5 C	-0.0485	5 C	-0.0552	5 C	-0.0721	5 C	-0.05769	5 C	0.39828
6 C	-0.1606	6 C	-0.1269	6 C	-0.0910	6 C	-0.13859	6 C	-0.04658
7 S	0.3035	7 S	0.3485	7 S	0.3275	7 S	0.2994	7 S	0.3505
8 C	0.2378	8 C	0.2454	8 C	0.2436	8 C	0.2384	8 C	0.2593
9 N	-0.4047	9 N	-0.3983	9 N	-0.4030	9 N	-0.4047	9 N	-0.3373
10 N	-0.7722	10 N	-0.7635	10 N	-0.7677	10 N	-0.7740	10 N	-0.7597
11 H	0.1497	11 N	0.00860	11 C	0.4672	11 C	-0.61363	11 N	-0.0163
12 H	0.1594	12 O	-0.2757	12 O	-0.5869	12 H	0.1605	12 O	-0.2752
13 H	0.1640	13 O	-0.2782	13 O	-0.3728	13 H	0.1610	13 O	-0.2394
		14 H	0.2139	14 H	0.1967	14 H	0.1470	14 Cl	0.0078
		15 H	0.1792	15 H	0.1713	15 H	0.3458	15 H	0.2050
		16 H	0.2046	16 H	0.1851	16 H	0.3447	16 H	0.2360
		17 H	0.3558	17 H	0.3517	17 H	0.1839	17 H	0.3639
		18 H	0.3535	18 H	0.3497	18 H	0.1950	18 H	0.3544

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