Quantum Chemical DFT Study of Some Saccharine Derivatives

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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 method (DFT) , for the purpose of the expense of the thermodynamic functions, some physical properties, charges for some Saccharine 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 ($R-CH_2-O-PH-CH_2$) has less value which means high stability than the other's.Also this result studied physical properties with thermodynamic function G^0, A^0, E^0, H^0 , C_p, C_v , S^0) which showed that the compound ($R-CH_2N(C_2H_5)_2$ more active than the other , more ability to lose electrons and be easier ionization compared to other compounds , less hardness and less Electronegativity because has less value of (ΔE,IP, η and χ).

Keywords: saccharine , DFT model , Electronegativity and hardness.

Introduction

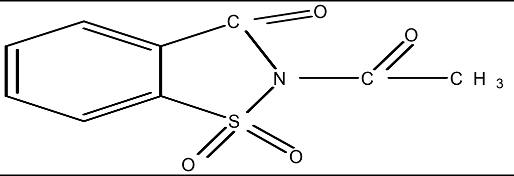
Saccharin is a synthetic organic compound has the chemical formula $C_7H_5NO_3S$, white crystalline powder [1-4] . Most of sulfur compounds have wide ranging pharmacological applications [5,6]. Saccharine used starting material in the chemical synthesis of a range of drugs & other chemical compounds[7- 13] . These properties of this type compound lead to chosen for theoretical study in this report.

In this work, were investigated theoretically using the Density Functional Theory (DFT) calculation [14] at the (B3LYP/6-31G)level of theory to get the optimized geometry .”A technique that has gained considerable ground in recent years to become one of the most widely used procedures for the calculation of molecular structure is “ density functional theory, DFT” .It allows us to compute all properties of systems by the electron density , ***p** (r)* which is a function of three variables, , *p (r)*=f(x ,y , z)”[15,16].

Kohn and Sham showed that ***p*** can be expressed as contribution from each electron present in the molecule, and written: $\rho(r) = \sum_{i=1}^{Ne} /\psi i(r)/^2$

ψi is called a Kohn – Sham orbital and is a solution of the Kohn – Sham equation , which closely resembles the form of Schrodinger equation. The Kohn – Sham equation is

$\left[\frac{h^2}{2m}\nabla^2 + V_{(r)} + V_{H(r)} + V_{XC(r)}\right]\psi i(r) = \varepsilon_i \, \psi_{i(r)}$ Thus ,the $V_{(r)}$, $V_{H(r)}$, $V_{XC(r)}$ are refers to the interaction between an electron and the collation of atomic unclei , the Hartree potential and exchange-correlation contributions to the single- electrons, respectively[17-20].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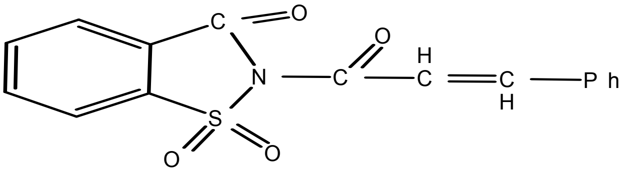
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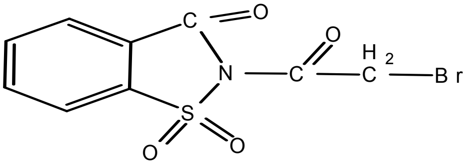
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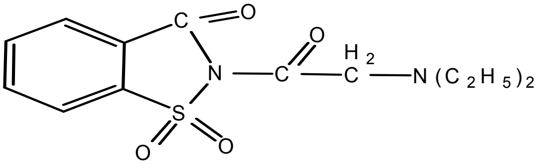
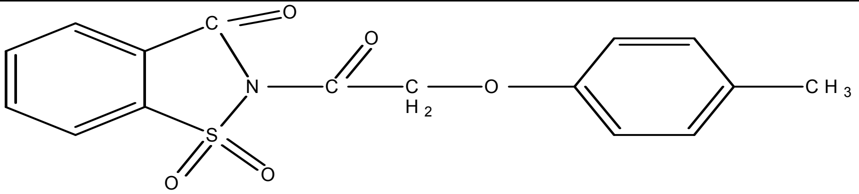
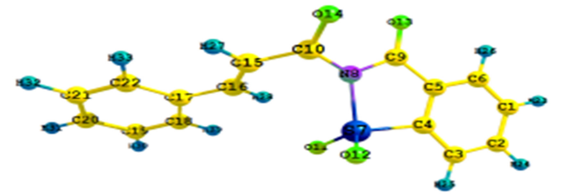

R-$CH_2N(C_2H_5)_2$

R-CH_2-O-PH-CH_3

Results and Discussion.

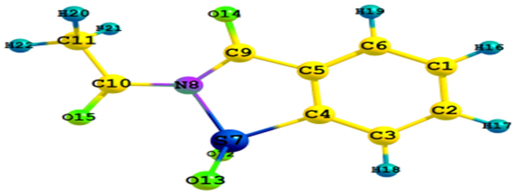
Geometrical parameter.

In this research calculated the geometry (bond lengths and bond angels) of the four molecules of derivatives [R-CH_3 , R-CH=CH-PH , R-CH_2-Br , R-$CH_2N(C_2H_5)_2$, R-CH_2-O-PH-CH_3]. According to the results calculated and recorded in the (**table 1**and **fig. 1)** . Show that the bond **(C_{10}-N_8)** in compound (R-CH=CH-PH) has high value compare with the other's this value caused by electron pair on **N** atom in this bond length that caused conjugated effect with substituted groups. Where the bond (N_8-C_7) in compound (R-CH_2-Br) has high value compare with the other's this value caused by Br atom.

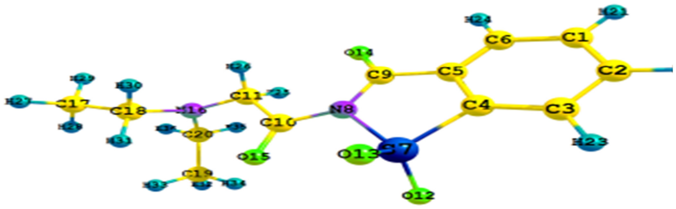
Also the change of the group substituted had effect on the value of the angles of the compounds studied in this research , have shown calculation in the (**table 1**and **fig.1).** The angles ($\angle$ **$C_9N_8S_7$**) and ($\angle$ **N_8S_7 C_4**) showed that in(R-$COCH_3$) has larger value than the other's because of the Ion pair on **S** with the electron with drawing group of the substituted groups.



R-CH=CH-PH

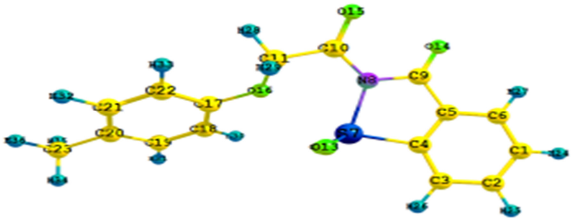


R-COCH$_3$



R-CH$_2$N(C$_2$H$_5$)$_2$

R-CH$_2$-Br



R-CH$_2$-O-PH-CH$_3$

Fig.(1): The geometric equilibrium for Saccharin derivatives .

Table (1) : Calculated geometric parameters (bond lengths in Angstrom length angles in degree) for Saccharin derivatives .

R-COCH3		R-COCH=CH-PH		R-CO-CH2-Br		R-COCH$_2$N(C$_2$H$_5$)$_2$		R-COCH2-O-PH-CH3	
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)	1.4033	R(1,2)	1.4036	R(1-2)	1.403	R(1,2)	1.4032	R(1-2)	1.404
R(1,6)	1.3996	R(1,6)	1.3999	R(1-6)	1.400	R(1,6)	1.3993	R(1-6)	1.399
R(1,16)	1.0842	R(1,23)	1.0843	R(1-17)	1.084	R(1,21)	1.0842	R(1-24)	1.084
R(2,3)	1.4044	R(2,3)	1.4043	R(2-3)	1.405	R(2,3)	1.4042	R(2-3)	1.404
R(2,17)	1.0842	R(2,24)	1.0843	R(2-18)	1.084	R(2,22)	1.0843	R(2-25)	1.084
R(3,4)	1.3841	R(3,4)	1.3842	R(3-4)	1.384	R(3,4)	1.3847	R(3-4)	1.385
R(3,18)	1.0834	R(3,25)	1.0832	R(3-19)	1.083	R(3,23)	1.0834	R(3-26)	1.083
R(4,5)	1.3911	R(4,5)	1.3887	R(4-5)	1.391	R(4,5)	1.3918	R(4-5)	1.388
R(4,7)	1.8708	R(4,7)	1.8654	R(4-7)	1.871	R(4,7)	1.8715	R(4-7)	1.862
R(5,6)	1.3983	R(5,6)	1.3977	R(5-6)	1.398	R(5,6)	1.3988	R(5-6)	1.399
R(5,9)	1.4848	R(5,9)	1.4883	R(5-9)	1.483	R(5,9)	1.485	R(5-9)	1.486
R(6,19)	1.0839	R(6,26)	1.0839	R(6-20)	1.084	R(6,24)	1.0838	R(6-27)	1.084
R(7,8)	1.9228	R(7,8)	1.9026	R(7-12)	1.624	R(7,8)	1.9642	R(7-12)	1.627
R(7,12)	1.626	R(7,11)	1.6338	R(7-13)	1.625	R(7,12)	1.6278	R(7-13)	1.630
R(7,13)	1.626	R(7,12)	1.629	R(8-9)	1.400	R(7,13)	1.628	R(8-9)	1.419
R(8,9)	1.3979	R(8,9)	1.408	R(8-10)	1.407	R(8,9)	1.3942	R(8-10)	1.414
R(8,10)	1.4173	R(8,10)	1.4596	R(9-14)	1.242	R(8,10)	1.406	R(9-14)	1.235
R(9,14)	1.2435	R(9,13)	1.2373	R(10-11)	1.506	R(9,14)	1.2457	R(10-11)	1.513
A(5,4,7)	124.6627	A(3,2,24)	119.3071	A(5-4-7)	111.6	R(19,34)	1.0927	R(23-34)	1.097
A(4,5,6)	111.5206	A(2,3,4)	116.5425	A(4-5-6)	118.9	R(20,35)	1.0972	R(23-35)	1.098
A(4,5,9)	118.9346	A(2,3,25)	121.4575	A(4-5-9)	117.2	R(20,36)	1.0978	R(23-36)	1.095
A(6,5,9)	117.1055	A(4,3,25)	122.0001	A(4-7-12)	111.7	A(2,1,6)	120.8131	A(2-1-6)	120.9
A(1,6,5)	123.9599	A(3,4,5)	124.2491	A(4-7-13)	111.1	A(2,1,21)	119.5711	A(2-1-24)	119.5
A(1,6,19)	118.8328	A(3,4,7)	125.2888	A(6-5-9)	123.9	A(6,1,21)	119.6158	A(1-2-3)	120.7
A(5,6,19)	121.8618	A(5,4,7)	110.4321	A(5-6-20)	119.3	A(1,2,3)	120.6948	A(1-2-25)	119.9
A(4,7,8)	119.3054	A(4,5,6)	118.7305	A(5-9-8)	110.9	A(1,2,22)	119.9634	A(6-1-24)	119.6
A(4,7,12)	87.3299	A(4,5,9)	117.0941	A(5-9-14)	124.4	A(3,2,22)	119.3418	A(1-6-5)	118.8
A(4,7,13)	110.9432	A(6,5,9)	124.174	A(12-7-13)	119.8	A(2,3,4)	116.975	A(1-6-27)	122.0
A(8,7,12)	110.9287	A(1,6,5)	118.8145	A(9-8-10)	131.2	A(3,2,22)	119.3418	A(3-2-25)	119.3
A(8,7,13)	111.5481	A(1,6,26)	121.9961	A(8-9-14)	124.7	A(2,3,4)	116.975	A(2-3-4)	116.7
A(12,7,13)	111.5654	A(5,6,26)	119.1889	A(8-10-11)	117.8	A(2,3,23)	121.3208	A(2-3-26)	121.4
A(7,8,9)	119.8687	A(4,7,8)	89.1116	A(8-10-15)	119.8	A(4,3,23)	121.7042	A(4-3-26)	121.9
A(7,8,10)	113.0843	A(4,7,11)	110.098	A(11-10-15)	122.4	A(3,4,5)	123.6697	A(3-4-5)	124.0
A(8,9,14)	124.3472	A(11,7,12)	117.737			A(4,5,9)	117.6061	A(4-5-9)	117.3
A(8,10,11)	124.6931	A(7,8,9)	111.535			A(6,5,9)	123.4761	A(4-7-12)	105.9
A(8,10,15)	117.6134	A(7,8,10)	120.6392			A(1,6,5)	118.9296	A(4-7-13)	113.4
A(11,10,15)	118.4064	A(9,8,10)	123.8535			A(1,6,24)	121.8636	A(6-5-9)	123.8
A(10,11,20)	123.9802	A(5,9,8)	111.7597			A(5,6,24)	119.2068	A(5-6-27)	119.2
A(10,11,21)	111.1233	A(5,9,13)	124.0863			A(4,7,8)	86.9251	A(5-9-8)	111.3
A(10,11,22)	111.132	A(8,9,13)	124.1366			A(4,7,12)	110.5775	A(5-9-14)	123.8
A(20,11,21)	107.4447	A(8,10,14)	118.5522			A(4,7,13)	110.8036	A(12-7-13)	119.9
A(20,11,22)	106.5814	A(8,10,15)	117.6728			A(8,7,12)	112.3532	A(9-8-10)	125.2
A(21,11,22)	110.2934	A(14,10,15)	123.775			A(8,7,13)	111.8934	A(8-9-14)	124.9
		A(10,15,16)	125.2355			A(12,7,13)	119.5887	A(8-10-11)	117.4
		A(10,15,27)	112.7574			A(7,8,9)	112.2783	A(8-10-15)	121.6
		A(16,15,27)	121.949			A(7,8,10)	116.3536	A(11-10-15)	120.9
		A(15,16,17)	126.6972			A(9,8,10)	131.3681	A(10-11-16)	108.2

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[21-24]**.** Electronegativity(χ) according to Mullikan1934 [25] and Electrophilicity (ω) according to Parr and co-workers 1999[26]·that compound (R-CH$_2$N(C$_2$H$_5$)$_2$) has less value for each of (Electronegativity(χ) , IP, Molecular Hardness, ΔE(more active than the other compounds),And the compound (R-CH3-Br) has high value (Dipole moment μ).

Also ,The MOPAC computational packages (semi-empirical method , PM3 model) employed to compute physical properties; heats of formation (ΔHf, kJ.mol-1)[27,28]. The results showed **(Table 2)** for the compound ($R-CH_2-O-PH-CH_3$) has lower heat of formation (more stability), Whereas the compound (($R-CH_2N(C_2H_5)_2$) 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}*,* $\Delta E_{HOMO-LUOM}$ *in eV) , IP(in eV) ,* E_A *(in eV) , η(in eV), Electronegativity(χ) and Electrophilicity (ω) for the* Saccharin *derivatives calculated by DFT/B3LYP(3-21G) method.*

Comp.	**ΔH$_f$ KJ/Mol**	**Debye**	**E_{HOMO}**	**E_{LOMO}**	**ΔE**	**IP**	**EA**	**η**	**χ**	**ω**
$R-CH_3$	**-472.2644**	**7.7208**	**-7.7765**	**-2.8321**	**4.9443**	**7.7765**	**2.8321**	**2.4722**	**5.3043**	**32.3787**
R-CH=CH-PH	**-251.0400**	**5.3260**	**-6.6192**	**-2.9372**	**3.6820**	**6.6192**	**2.9372**	**1.8412**	**4.7782**	**38.4494**
$R-CH_2-Br$	**-421.6552**	**7.8512**	**-7.7520**	**-3.1198**	**4.6322**	**7.7520**	**3.1198**	**2.3161**	**5.4359**	**40.6922**
$R-CH_2N(C_2H_5)_2$	**-484.4905**	**6.5376**	**-5.4730**	**-2.9595**	**2.5135**	**5.4730**	**2.9595**	**1.2567**	**4.2163**	**50.0189**
$R-CH_2O-PH-CH_3$	**-497.5801**	**5.2510**	**-5.9615**	**-3.1065**	**2.8550**	**5.9615**	**3.1065**	**1.4275**	**4.5339**	**51.8388**

Thermodynamics functions

The fundamental vibration frequencies for 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. Were listed in ***Table 3.*** 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),

$R-CH_2N(C_2H_5)_2 > R-CH_2-O-PH-CH_3 > R-CH=CH-PH > R-CH_3 > R-CH_2-Br$

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

$R-CH_2-O-PH-CH_3 > R-CH_2N(C_2H_5)_2 > R-CH=CH-PH > R-CH_2-Br > R-CH_3$

The deferent thermodynamics functions values due to deferent substituted groups. viz , the high size which makes restricted movement.

Table 3: The calculated standard thermodynamics functions at 298.15oK of the Saccharin derivatives calculated by DFT/B3LYP(3-21G) 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
$R-CH_3$	432.3536	434.8324	290.5875	0.4838	146.3426	0.2165	0.2082
R-CH=CH-PH	676.4565	678.9353	498.2057	0.6062	317.4762	0.3039	0.2956
$R-CH_2-Br$	411.0612	413.5400	257.7029	0.5227	101.8659	0.2288	0.2205
$R-CH_2N(C_2H_5)_2$	794.7173	797.1961	608.7056	0.6322	420.2152	0.3175	0.3092
$R-CH_2O-PH-CH_3$	751.2665	753.7453	561.7963	0.6438	369.8474	0.3303	0.3220

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)**, showed that the (N_8) atom in (**R-CH=CH-PH)** compound has more negative charge because of the electron with drawing of substituted group . This scientific fact indicates that this compound can be strong legend when it linked to metal complex formation ,Also in a comparison between every Oxygen atoms identical beteen compounds found that all the Oxygen atoms(O_{11}, O_{12}, O_{13}, O_{14}) in each compound(**$R-CH_3$, $R-CH_2N(C_2H_5)_2$)** have lower negative charge values (highest electronic density) than the other's. the reason of this due to the high pushing of electrons effect of the substituted groups.

Table 4 : Calculated charge for Saccharin derivatives calculated by DFT/B3LYP(3-21G) method**.**

R-COCH3		R-COCH=CH-PH		R-CO-CH2-Br		R-COCH$_2$N(C$_2$H$_5$)$_2$		R-COCH2-O-PH-CH3	
Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
C1	-0.1293	C1	-0.1259	C1	-0.1277	C1	-0.1293	C1	-0.1282
C2	-0.1032	C2	-0.1074	C2	-0.1030	C2	-0.1032	C2	-0.1055
C3	-0.1215	C3	-0.1195	C3	-0.1207	C3	-0.1215	C3	-0.1158
C4	-0.3318	C4	-0.3379	C4	-0.3328	C4	-0.3318	C4	-0.3446
C5	0.1136	C5	0.1205	C5	0.1159	C5	0.1136	C5	0.1149
C6	-0.1035	C6	-0.1049	C6	-0.1002	C6	-0.1035	C6	-0.1017
S7	1.3201	S7	1.3067	S7	1.3415	S7	1.3201	S7	1.3832
N8	-0.7717	N8	-0.7951	N8	-0.7887	N8	-0.7717	N8	-0.7706
C9	0.5227	C9	0.5371	C9	0.5432	C9	0.5227	C9	0.5161
C10	0.5583	C10	0.4838	C10	0.5973	C10	0.5583	C10	0.5424
C11	-0.1659	O11	-0.531	C11	-0.5379	C11	-0.1659	C11	-0.0979
O12	-0.5048	O12	-0.5010	O12	-0.4933	O12	-0.5048	O12	-0.5088
O13	-0.5054	O13	-0.3748	O13	-0.4938	O13	-0.5054	O13	-0.5294
O14	-0.4130	O14	-0.3722	O14	-0.3998	O14	-0.4130	O 14	-0.3557
O15	-0.3995	C15	-0.1359	O15	-0.3661	O15	-0.3995	O 15	-0.3610
N16	-0.4483	C16	-0.1136	Br16	0.0546	N16	-0.4483	O16	-0.5904
C17	-0.41157	C17	0.0658	H17	0.1639	C17	-0.4115	C17	0.2891
C18	-0.0852	C18	-0.1553	H18	0.1660	C18	-0.0852	C18	-0.1147
C19	-0.4007	C19	-0.1308	H19	0.1987	C19	-0.4007	C19	-0.1678
C20	-0.1034	C20	-0.1102	H20	0.1917	C20	-0.1034	C20	0.1260
H21	0.1601	C21	-0.1329	H21	0.2548	H21	0.1601	C21	-0.1776
H22	0.1623	C 22	-0.1237	H22	0.2365	H22	0.1623	C22	-0.1214
		H 23	0.1607			H23	0.1957	C23	-0.4815
		H24	0.1619			H24	0.1876	H24	0.1606
		H25	0.1943			H25	0.1894	H25	0.1618
		H26	0.1911			H26	0.1868	H26	0.1944
		H27	0.1590			H27	0.1349	H27	0.1902
		H28	0.1867			H28	0.1404	H28	0.1902
		H 29	0.1575			H29	0.1425	H29	0.2042
		H30	0.1366			H30	0.1308	H30	0.1741
		H31	0.1355			H31	0.1560	H31	0.1246
		H32	0.1361			H32	0.1222	H32	0.1228
						H33	0.1405	H33	0.1321
						H34	0.1627	H34	0.1522
						H35	0.1298	H35	0.1522
						H36	0.1419	H36	0.1415

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