وزارة التعليم العالي والبحث العملي

جامعة القادسية

كلية العلوم / علوم الكيمياء

عنوان البحث

COMPUTATIONAL CHEMISTRY STUDY FOR THE ORIENTATION EFFECTS IN SUBSTITUTED ANILINE COMPOUNDS

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1-1 Computational chemistry

Computational chemistry is a branch of chemistry that uses computer simulation to assist in solving chemical problems. It uses methods of theoretical chemistry, incorporated into efficient computer programs, to calculate the structures and properties of molecules and solids. It is necessary because, apart from relatively recent results concerning the hydrogen molecular ion ,the quantum many-body problem cannot be solved analytically, much less in closed form. While computational

results normally complement the information obtained by chemical experiments, it can in some cases predict hitherto unobserved chemical phenomena. It is widely used in the design of new drugs and materials.[1]

Examples of such properties are structure (i.e., the expected positions of the constituent atoms), absolute (interaction) energies, electronic charge density distributions, dipoles and higher multipole moments, vibrational frequencies, reactivity, or other spectroscopic quantities, and cross sections for collision with other particles.[2]

The methods used cover both static and dynamic situations. In all cases, the computer time and other resources (such as memory and disk space) increase rapidly with the size of the system being studied. That system can be one molecule, a group of molecules, or a solid. Computational chemistry methods range from very approximate to highly accurate; the latter are usually feasible for small systems only. *Ab initio* methods are based entirely on quantum mechanics and basic physical constants. Other methods are called empirical or semi-empirical because they use additional empirical parameters.[3]

Both *ab initio* and semi-empirical approaches involve approximations. These range from simplified forms of the first-principles equations that are easier or faster to solve, to approximations limiting the size of the system (for example, periodic boundary conditions), to fundamental approximations to the underlying equations that are required to achieve any solution to them at all[4]. For example, most *ab initio* calculations make the Born–Oppenheimer approximation, which greatly simplifies the underlying Schrödinger equation by assuming that the nuclei remain in place during the calculation. In principle, *ab initio* methods eventually

converge to the exact solution of the underlying equations as the number of approximations is reduced. In practice, however, it is impossible to eliminate all approximations, and residual error inevitably remains. The goal of computational chemistry is to minimize this residual error while keeping the calculations tractable.[5]

In some cases, the details of electronic structure are less important than the long-time phase space behavior of molecules. This is the case in conformational studies of proteins and protein-ligand binding thermodynamics[6]. Classical approximations to the potential energy surface are used, as they are computationally less intensive than electronic calculations, to enable longer simulations of molecular dynamics. Furthermore, cheminformatics uses even more empirical (and computationally cheaper) methods like machine learning based on physicochemical properties. One typical problem in cheminformatics is to predict the binding affinity of drug molecules to a given target[7].

1-2 Semi empirical methods:

Semiempirical may be defined as involving assumptions ,approximation , or generalization designed to simplify calculation or to yield a result in accord with observation . thus the semiempirical method of quantum chemistry start out from the ab initio formalism and then introduce rather drastic assumptions to speed up the calculations. [8]

Semiempirical quantum chemistry attempts to address two limitations, namely slow speed and low accuracy, of the Hartree-Fock calculation by omitting or parameterizing certain integrals based on

experimental data, such as ionization energies of atoms, or dipole moments of molecules. As a result, semiempirical methods are very fast, applicable to large molecules, and may give accurate results when applied to molecules that are similar to the molecules used for parameterization. On the downside, accuracy of semiempirical methods is erratic on many systems. [9]

Parametric Method 3, PM3 uses a Hamiltonian that is very similar to the AM1 Hamiltonian but the parameterization strategy is different. While AM1 was parameterized largely based on a small number of atomic data, PM3 is parameterized to reproduce a large number of molecular properties[10]. In some sense, chemistry gave way to statistics with the PM3 model. Different parameterization, and slightly different treatment of nuclear repulsion allow PM3 to treat hydrogen bonds rather well but it amplifies non-physical hydrogen-hydrogen attractions in other cases[11]. The accuracy of thermochemical predictions with PM3 is slightly better than that of AM1. The PM3 model has been widely used for rapid estimation of molecular properties and has been recently extended to include many elements, including some transition metals. [12]

1-3 Gaussian Software :

Gaussian is an electronic structure modeling software application ,it is arguably the most-used computational quantum-chemistry program. It does electronic-structure calculations and standard quantum chemical calculations[13].

Gaussian is a general purpose ab initio electronic structure package that is capable of computing energies, geometries, vibrational

frequencies, transition states, reaction paths, excited states and a variety of properties based on various uncorrelated and correlated wave functions. Gaussian is used by chemists, chemical engineers, biochemists, physicists and others for research in established and emerging areas of chemical interest. [14]

There are two versions of Gaussian:

1. Gaussian 03
2. Gaussian 09

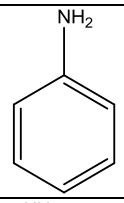
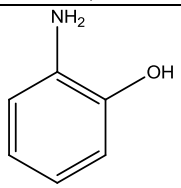
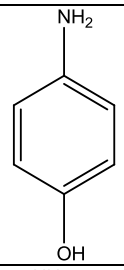
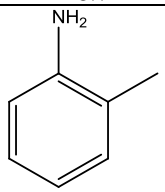
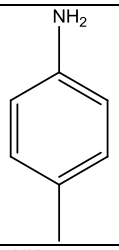
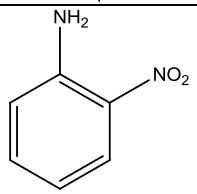
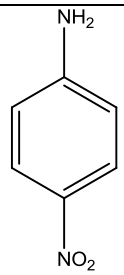
Starting from the basic laws of quantum mechanics, Gaussian predicts the energies, molecular structures, and vibrational frequencies of molecular systems, along with numerous molecular properties derived from these basic computation types[15]. It can be used to study molecules and reactions under a wide range of conditions, including both stable species and compounds which are difficult or impossible to observe experimentally such as short-lived intermediates and transition structures. [16]

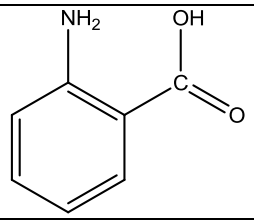
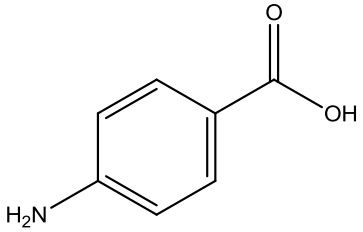
2-1 Computational Methodology :

Complete geometrical optimizations of the investigated molecules 1-9 table (2-1) are performed using Semiempirical method at PM3 level This approach is shown to yield favorable geometries for a wide variety of systems.

The geometry structure was optimized using Gaussian software . The following quantum chemical parameters were calculated from the obtained optimized structure: The highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, Bonds length and bonds angle

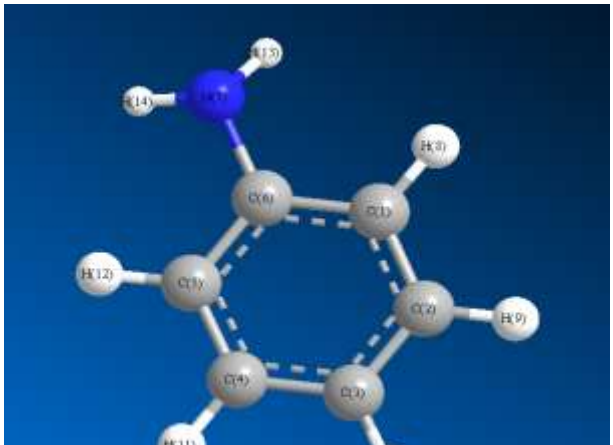
Table (2-1) : Aniline compounds included in the study

Comp.no.	IUPAC name	Structure
1	Aniline	
2	2-amino phenol	
3	4-amino phenol	
4	o-toluidine	
5	o-toluidine	
6	2-nitroaniline	
7	4-nitroaniline	

8	2-amino benzoic acid	
9	4-amino benzoic acid	

3-1 Optimized geometries of compounds 1-9

Optimized geometries of compounds 1-11 have been studied in semiempirical PM3 level ,the result shown in figure(3-1) , table (3-10)



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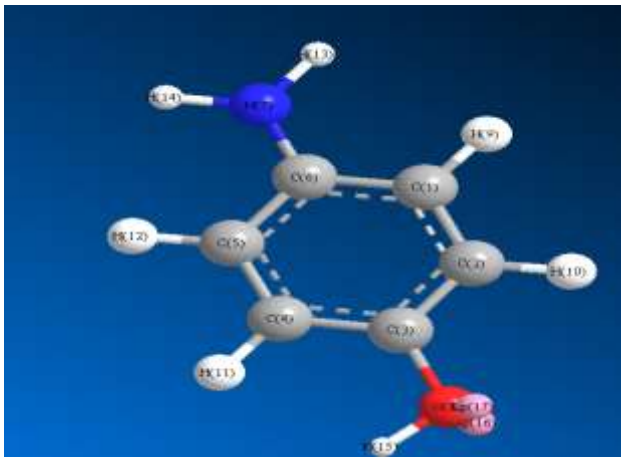
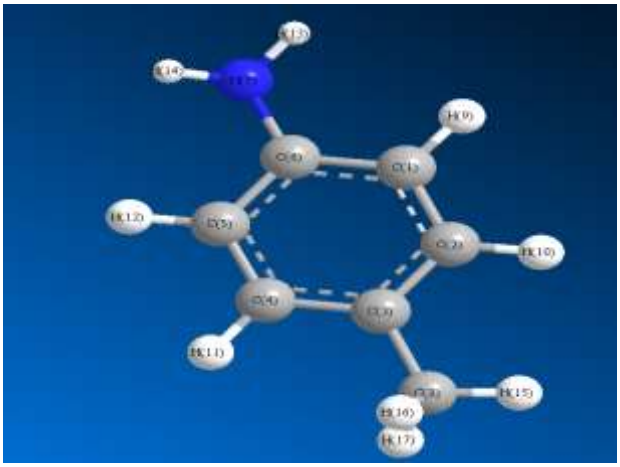
1

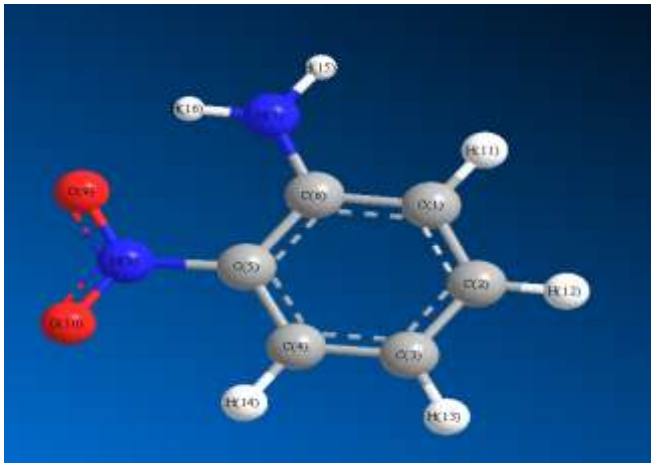


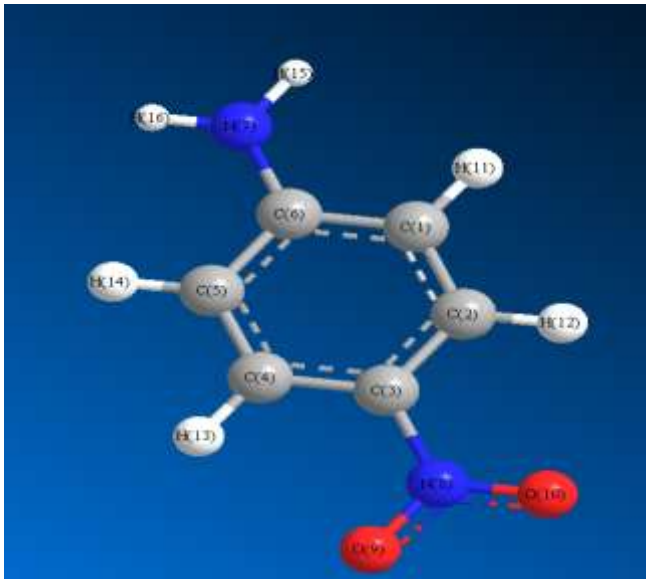
2

3



4





7 8

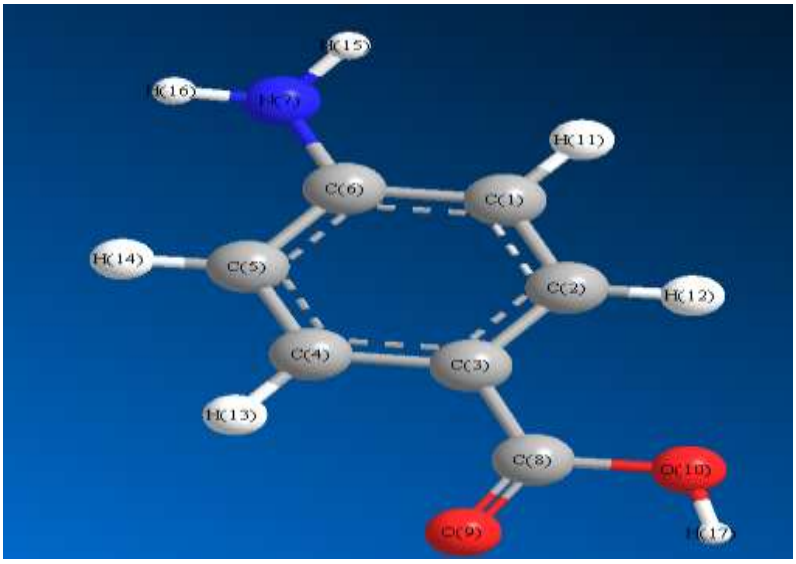


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Figure-3-1 optimized geometry for compounds 1-9 at Semiempirical PM3 level

3-2 Determination of bonds length and bonds angles :

Bonds length and bonds angled have been determined in semiempirical PM3 level , optimal and actual values of B.L and B.A of each compound listed in tables (3-1) to (3-9**)**

Table (3-1): bond angle and bond angle for compound 1

No.	Atoms	Actual (° / Å)	Optimal (° / Å)
1.	N(7)-H(14)	0.9958	1.05
2.	N(7)-H(13)	0.9958	1.05

3.	C(5)-H(12)	1.0963	1.1
4.	C(4)-H(11)	1.095	1.1
5.	C(3)-H(10)	1.0944	1.1
6.	C(2)-H(9)	1.095	1.1
7.	C(1)-H(8)	1.0963	1.1
8.	C(1)-C(6)	1.4021	1.42
9.	C(5)-C(6)	1.4021	1.42
10.	C(4)-C(5)	1.3887	1.42
11.	C(3)-C(4)	1.391	1.42
12.	C(2)-C(3)	1.391	1.42
13.	C(1)-C(2)	1.3886	1.42
14.	C(6)-N(7)	1.43	1.462
15.	H(14)-N(7)-H(13)	111.0601	118.8
16.	H(14)-N(7)-C(6)	111.5795	
17.	H(13)-N(7)-C(6)	111.58	
18.	C(1)-C(6)-C(5)	119.7683	120
19.	C(1)-C(6)-N(7)	120.0327	120
20.	C(5)-C(6)-N(7)	120.0331	120
21.	H(12)-C(5)-C(6)	120.6561	120
22.	H(12)-C(5)-C(4)	119.6033	120
23.	C(6)-C(5)-C(4)	119.7402	
24.	H(11)-C(4)-C(5)	119.6714	120
25.	H(11)-C(4)-C(3)	119.8801	120
26.	C(5)-C(4)-C(3)	120.4485	
27.	H(10)-C(3)-C(4)	120.0767	120
28.	H(10)-C(3)-C(2)	120.0701	120
29.	C(4)-C(3)-C(2)	119.8532	
30.	H(9)-C(2)-C(3)	119.8736	120
31.	H(9)-C(2)-C(1)	119.6779	120
32.	C(3)-C(2)-C(1)	120.4485	
33.	H(8)-C(1)-C(6)	120.6501	120
34.	H(8)-C(1)-C(2)	119.6091	120
35.	C(6)-C(1)-C(2)	119.7405	

Table (3-2): bond angle and bond angle for compound 2

No.	Atoms	Actual (° / Å)	Optimal (° / Å)
1.	O(8)-H(15)	0.9494	0.972
2.	N(7)-H(14)	0.9977	1.05
3.	N(7)-H(13)	0.9968	1.05
4.	C(4)-H(12)	1.0961	1.1
5.	C(3)-H(11)	1.0948	1.1
6.	C(2)-H(10)	1.0947	1.1
7.	C(1)-H(9)	1.0969	1.1
8.	C(1)-C(6)	1.3992	1.42

9.	C(5)-C(6)	1.4114	1.42
10.	C(4)-C(5)	1.4006	1.42
11.	C(3)-C(4)	1.3884	1.42
12.	C(2)-C(3)	1.3914	1.42
13.	C(1)-C(2)	1.3887	1.42
14.	C(5)-O(8)	1.3708	1.355
15.	C(6)-N(7)	1.4407	1.462
16.	H(15)-O(8)-C(5)	107.8166	108
17.	H(14)-N(7)-H(13)	110.0117	118.8
18.	H(14)-N(7)-C(6)	109.7254	
19.	H(13)-N(7)-C(6)	110.5977	
20.	C(1)-C(6)-C(5)	118.8537	120
21.	C(1)-C(6)-N(7)	121.2574	120
22.	C(5)-C(6)-N(7)	119.7478	120
23.	C(6)-C(5)-C(4)	120.4084	120
24.	C(6)-C(5)-O(8)	123.6446	124.3
25.	C(4)-C(5)-O(8)	115.8765	124.3
26.	H(12)-C(4)-C(5)	120.0096	120
27.	H(12)-C(4)-C(3)	120.419	120
28.	C(5)-C(4)-C(3)	119.5712	
29.	H(11)-C(3)-C(4)	119.7015	120
30.	H(11)-C(3)-C(2)	119.9376	120
31.	C(4)-C(3)-C(2)	120.36	
32.	H(10)-C(2)-C(3)	119.9055	120
33.	H(10)-C(2)-C(1)	119.6914	120
34.	C(3)-C(2)-C(1)	120.4028	
35.	H(9)-C(1)-C(6)	120.3249	120
36.	H(9)-C(1)-C(2)	119.3	120
37.	C(6)-C(1)-C(2)	120.3751	

Table (3-3): bond angle and bond angle for compound 3

No.	Atoms	Actual (° / Å)	Optimal (° / Å)
1.	O(8)-H(15)	0.9489	0.972
2.	N(7)-H(14)	0.9962	1.05
3.	N(7)-H(13)	0.9961	1.05
4.	C(5)-H(12)	1.0966	1.1
5.	C(4)-H(11)	1.0961	1.1
6.	C(2)-H(10)	1.0959	1.1
7.	C(1)-H(9)	1.0967	1.1
8.	C(1)-C(6)	1.4032	1.42
9.	C(5)-C(6)	1.4006	1.42
10.	C(4)-C(5)	1.3883	1.42

11.	C(3)-C(4)	1.3999	1.42
12.	C(2)-C(3)	1.4018	1.42
13.	C(1)-C(2)	1.386	1.42
14.	C(3)-O(8)	1.3706	1.355
15.	C(6)-N(7)	1.4332	1.462
16.	H(15)-O(8)-C(3)	107.685	108
17.	H(14)-N(7)-H(13)	110.8047	118.8
18.	H(14)-N(7)-C(6)	111.2714	
19.	H(13)-N(7)-C(6)	111.2753	
20.	C(1)-C(6)-C(5)	119.8984	120
21.	C(1)-C(6)-N(7)	119.9442	120
22.	C(5)-C(6)-N(7)	119.9736	120
23.	H(12)-C(5)-C(6)	120.6201	120
24.	H(12)-C(5)-C(4)	119.1964	120
25.	C(6)-C(5)-C(4)	120.1834	
26.	H(11)-C(4)-C(5)	119.6872	120
27.	H(11)-C(4)-C(3)	120.8435	120
28.	C(5)-C(4)-C(3)	119.4693	
29.	C(4)-C(3)-C(2)	120.7949	120
30.	C(4)-C(3)-O(8)	123.0962	124.3
31.	C(2)-C(3)-O(8)	116.1081	124.3
32.	H(10)-C(2)-C(3)	120.2629	120
33.	H(10)-C(2)-C(1)	120.3764	120
34.	C(3)-C(2)-C(1)	119.3607	
35.	H(9)-C(1)-C(6)	120.4846	120
36.	H(9)-C(1)-C(2)	119.2221	120
37.	C(6)-C(1)-C(2)	120.293	

Table (3-4): bond angle and bond angle for compound 4

No.	Atoms	Actual (° / Å)	Optimal (° / Å)
1.	C(8)-H(17)	1.0989	1.113
2.	C(8)-H(16)	1.0997	1.113
3.	C(8)-H(15)	1.0988	1.113
4.	N(7)-H(14)	0.9966	1.05
5.	N(7)-H(13)	0.9962	1.05
6.	C(4)-H(12)	1.0965	1.1
7.	C(3)-H(11)	1.0944	1.1
8.	C(2)-H(10)	1.0948	1.1
9.	C(1)-H(9)	1.0968	1.1
10.	C(1)-C(6)	1.4032	1.42

11.	C(5)-C(6)	1.4081	1.42
12.	C(4)-C(5)	1.3955	1.42
13.	C(3)-C(4)	1.3888	1.42
14.	C(2)-C(3)	1.3907	1.42
15.	C(1)-C(2)	1.3871	1.42
16.	C(5)-C(8)	1.4871	1.497
17.	C(6)-N(7)	1.4309	1.462
18.	H(17)-C(8)-H(16)	107.7325	109
19.	H(17)-C(8)-H(15)	107.1407	109
20.	H(17)-C(8)-C(5)	111.4305	110
21.	H(16)-C(8)-H(15)	107.0185	109
22.	H(16)-C(8)-C(5)	111.4406	110
23.	H(15)-C(8)-C(5)	111.829	110
24.	H(14)-N(7)-H(13)	110.8562	118.8
25.	H(14)-N(7)-C(6)	111.7178	
26.	H(13)-N(7)-C(6)	111.4098	
27.	C(1)-C(6)-C(5)	119.7469	120
28.	C(1)-C(6)-N(7)	118.927	120
29.	C(5)-C(6)-N(7)	121.1622	120
30.	C(6)-C(5)-C(4)	118.9391	120
31.	C(6)-C(5)-C(8)	121.9161	121.4
32.	C(4)-C(5)-C(8)	119.1448	121.4
33.	H(12)-C(4)-C(5)	119.471	120
34.	H(12)-C(4)-C(3)	119.514	120
35.	C(5)-C(4)-C(3)	121.0149	
36.	H(11)-C(3)-C(4)	120.0129	120
37.	H(11)-C(3)-C(2)	120.1024	120
38.	C(4)-C(3)-C(2)	119.8847	
39.	H(10)-C(2)-C(3)	120.0056	120
40.	H(10)-C(2)-C(1)	119.8317	120
41.	C(3)-C(2)-C(1)	120.1627	
42.	H(9)-C(1)-C(6)	120.4532	120
43.	H(9)-C(1)-C(2)	119.2951	120
44.	C(6)-C(1)-C(2)	120.2513	

Table (3-5): bond angle and bond angle for compound 5

No.	Atoms	Actual (° / Å)	Optimal (° / Å)
1.	C(8)-H(17)	1.0984	1.113
2.	C(8)-H(16)	1.0983	1.113
3.	C(8)-H(15)	1.098	1.113
4.	N(7)-H(14)	0.9959	1.05
5.	N(7)-H(13)	0.9959	1.05
6.	C(5)-H(12)	1.0964	1.1
7.	C(4)-H(11)	1.0957	1.1
8.	C(2)-H(10)	1.0961	1.1
9.	C(1)-H(9)	1.0964	1.1
10.	C(1)-C(6)	1.4011	1.42

11.	C(5)-C(6)	1.4024	1.42
12.	C(4)-C(5)	1.3868	1.42
13.	C(3)-C(4)	1.3965	1.42
14.	C(2)-C(3)	1.3948	1.42
15.	C(1)-C(2)	1.3884	1.42
16.	C(3)-C(8)	1.4853	1.497
17.	C(6)-N(7)	1.4304	1.462
18.	H(17)-C(8)-H(16)	107.4857	109
19.	H(17)-C(8)-H(15)	107.5508	109
20.	H(17)-C(8)-C(3)	110.853	110
21.	H(16)-C(8)-H(15)	107.5612	109
22.	H(16)-C(8)-C(3)	110.9019	110
23.	H(15)-C(8)-C(3)	112.2794	110
24.	H(14)-N(7)-H(13)	110.9985	118.8
25.	H(14)-N(7)-C(6)	111.5046	
26.	H(13)-N(7)-C(6)	111.5114	
27.	C(1)-C(6)-C(5)	119.6519	120
28.	C(1)-C(6)-N(7)	120.1175	120
29.	C(5)-C(6)-N(7)	120.0625	120
30.	H(12)-C(5)-C(6)	120.6354	120
31.	H(12)-C(5)-C(4)	119.5158	120
32.	C(6)-C(5)-C(4)	119.8485	
33.	H(11)-C(4)-C(5)	119.8509	120
34.	H(11)-C(4)-C(3)	119.4957	120
35.	C(5)-C(4)-C(3)	120.6533	
36.	C(4)-C(3)-C(2)	119.3487	120
37.	C(4)-C(3)-C(8)	119.7929	121.4
38.	C(2)-C(3)-C(8)	120.8584	121.4
39.	H(10)-C(2)-C(3)	119.8369	120
40.	H(10)-C(2)-C(1)	119.578	120
41.	C(3)-C(2)-C(1)	120.585	
42.	H(9)-C(1)-C(6)	120.6436	120
43.	H(9)-C(1)-C(2)	119.4443	120
44.	C(6)-C(1)-C(2)	119.9119	

Table (3-6): bond angle and bond angle for compound 6

No.	Atoms	Actual (° / Å)	Optimal (° / Å)
1.	N(7)-H(16)	1.001	1.05
2.	N(7)-H(15)	0.9874	1.05
3.	C(4)-H(14)	1.0993	1.1
4.	C(3)-H(13)	1.0948	1.1
5.	C(2)-H(12)	1.0957	1.1
6.	C(1)-H(11)	1.0971	1.1
7.	C(1)-C(6)	1.4209	1.42
8.	C(5)-C(6)	1.4197	1.42
9.	C(4)-C(5)	1.4121	1.42
10.	C(3)-C(4)	1.3758	1.42

11.	C(2)-C(3)	1.4037	1.42
12.	C(1)-C(2)	1.3737	1.42
13.	C(5)-N(8)	1.4725	1.444
14.	C(6)-N(7)	1.3781	1.462
15.	N(8)-O(10)	1.2137	1.3625
16.	N(8)-O(9)	1.229	1.3625
17.	C(5)-N(8)-O(10)	121.0499	120
18.	C(5)-N(8)-O(9)	119.1208	120
19.	O(10)-N(8)-O(9)	119.8292	120
20.	H(16)-N(7)-H(15)	121.1393	118.8
21.	H(16)-N(7)-C(6)	119.2773	
22.	H(15)-N(7)-C(6)	119.5833	
23.	C(1)-C(6)-C(5)	119.1151	120
24.	C(1)-C(6)-N(7)	119.2158	120
25.	C(5)-C(6)-N(7)	121.6691	120
26.	C(6)-C(5)-C(4)	118.8424	120
27.	C(6)-C(5)-N(8)	122.0095	120
28.	C(4)-C(5)-N(8)	119.1482	120
29.	H(14)-C(4)-C(5)	119.7593	120
30.	H(14)-C(4)-C(3)	119.2655	120
31.	C(5)-C(4)-C(3)	120.9752	
32.	H(13)-C(3)-C(4)	120.2383	120
33.	H(13)-C(3)-C(2)	119.6186	120
34.	C(4)-C(3)-C(2)	120.143	
35.	H(12)-C(2)-C(3)	119.4132	120
36.	H(12)-C(2)-C(1)	120.0662	120
37.	C(3)-C(2)-C(1)	120.5207	
38.	H(11)-C(1)-C(6)	119.7983	120
39.	H(11)-C(1)-C(2)	119.7981	120
40.	C(6)-C(1)-C(2)	120.4036	

Table (3-7): bond angle and bond angle for compound 7

No.	Atoms	Actual (° / Å)	Optimal (° / Å)
1.	N(7)-H(16)	0.9879	1.05
2.	N(7)-H(15)	0.9879	1.05
3.	C(5)-H(14)	1.0968	1.1
4.	C(4)-H(13)	1.0992	1.1
5.	C(2)-H(12)	1.0992	1.1
6.	C(1)-H(11)	1.0968	1.1
7.	C(1)-C(6)	1.4103	1.42
8.	C(5)-C(6)	1.4103	1.42
9.	C(4)-C(5)	1.3812	1.42
10.	C(3)-C(4)	1.404	1.42

11.	C(2)-C(3)	1.404	1.42
12.	C(1)-C(2)	1.3812	1.42
13.	C(3)-N(8)	1.4844	1.444
14.	C(6)-N(7)	1.387	1.462
15.	N(8)-O(10)	1.2174	1.3625
16.	N(8)-O(9)	1.2174	1.3625
17.	C(3)-N(8)-O(10)	119.7391	120
18.	C(3)-N(8)-O(9)	119.7398	120
19.	O(10)-N(8)-O(9)	120.5211	120
20.	H(16)-N(7)-H(15)	119.6609	118.8
21.	H(16)-N(7)-C(6)	120.1695	
22.	H(15)-N(7)-C(6)	120.1696	
23.	C(1)-C(6)-C(5)	119.5354	120
24.	C(1)-C(6)-N(7)	120.2324	120
25.	C(5)-C(6)-N(7)	120.2323	120
26.	H(14)-C(5)-C(6)	120.5611	120
27.	H(14)-C(5)-C(4)	119.4553	120
28.	C(6)-C(5)-C(4)	119.9837	
29.	H(13)-C(4)-C(5)	119.1362	120
30.	H(13)-C(4)-C(3)	120.3347	120
31.	C(5)-C(4)-C(3)	120.5291	
32.	C(4)-C(3)-C(2)	119.4391	120
33.	C(4)-C(3)-N(8)	120.2807	120
34.	C(2)-C(3)-N(8)	120.2802	120
35.	H(12)-C(2)-C(3)	120.3344	120
36.	H(12)-C(2)-C(1)	119.1364	120
37.	C(3)-C(2)-C(1)	120.5292	
38.	H(11)-C(1)-C(6)	120.5616	120
39.	H(11)-C(1)-C(2)	119.4547	120
40.	C(6)-C(1)-C(2)	119.9836	

Table (3-8): bond angle and bond angle for compound 8

No.	Atoms	Actual (° / Å)	Optimal (° / Å)
1.	O(10)-H(17)	0.9529	0.972
2.	N(7)-H(16)	1.0026	1.05
3.	N(7)-H(15)	0.9867	1.05
4.	C(4)-H(14)	1.0964	1.1
5.	C(3)-H(13)	1.0943	1.1
6.	C(2)-H(12)	1.0954	1.1
7.	C(1)-H(11)	1.0964	1.1
8.	C(1)-C(6)	1.4158	1.42
9.	C(5)-C(6)	1.4178	1.42
10.	C(4)-C(5)	1.4023	1.42

11.	C(3)-C(4)	1.382	1.42
12.	C(2)-C(3)	1.3994	1.42
13.	C(1)-C(2)	1.3782	1.42
14.	C(8)-O(10)	1.3516	1.338
15.	C(8)-O(9)	1.2312	1.208
16.	C(5)-C(8)	1.4673	1.517
17.	C(6)-N(7)	1.3837	1.462
18.	H(17)-O(10)-C(8)	108.6807	106.1
19.	O(10)-C(8)-O(9)	114.0342	122
20.	O(10)-C(8)-C(5)	118.3918	124.3
21.	O(9)-C(8)-C(5)	127.574	123
22.	H(16)-N(7)-H(15)	121.6282	118.8
23.	H(16)-N(7)-C(6)	118.4734	
24.	H(15)-N(7)-C(6)	119.8975	
25.	C(1)-C(6)-C(5)	119.3235	120
26.	C(1)-C(6)-N(7)	120.1848	120
27.	C(5)-C(6)-N(7)	120.4917	120
28.	C(6)-C(5)-C(4)	119.2061	120
29.	C(6)-C(5)-C(8)	119.4838	117.6
30.	C(4)-C(5)-C(8)	121.3101	117.6
31.	H(14)-C(4)-C(5)	119.7956	120
32.	H(14)-C(4)-C(3)	119.5048	120
33.	C(5)-C(4)-C(3)	120.6995	
34.	H(13)-C(3)-C(4)	120.1592	120
35.	H(13)-C(3)-C(2)	119.7411	120
36.	C(4)-C(3)-C(2)	120.0996	
37.	H(12)-C(2)-C(3)	119.4783	120
38.	H(12)-C(2)-C(1)	119.8582	120
39.	C(3)-C(2)-C(1)	120.6635	
40.	H(11)-C(1)-C(6)	120.065	120
41.	H(11)-C(1)-C(2)	119.9272	120
42.	C(6)-C(1)-C(2)	120.0078	

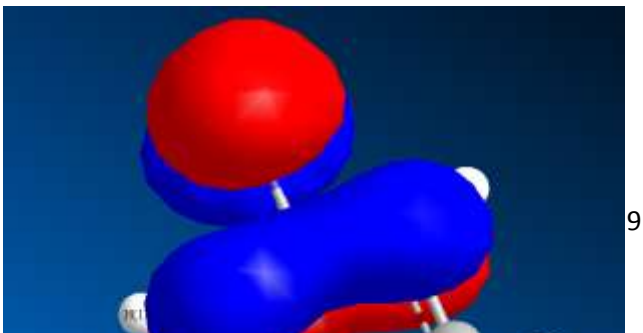
Table (3-9): bond angle and bond angle for compound 9

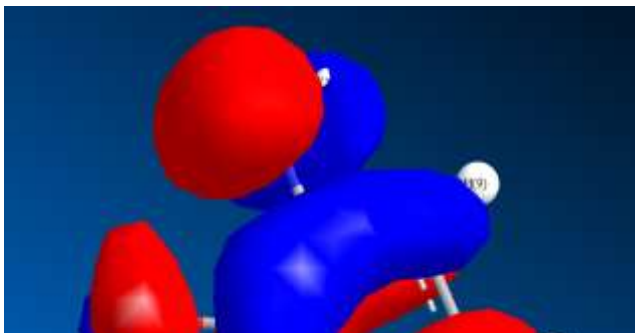
No.	Atoms	Actual (° / Å)	Optimal (° / Å)
1.	O(10)-H(17)	0.9524	0.972
2.	N(7)-H(16)	0.9951	1.05
3.	N(7)-H(15)	0.9951	1.05
4.	C(5)-H(14)	1.0968	1.1
5.	C(4)-H(13)	1.0976	1.1
6.	C(2)-H(12)	1.0966	1.1
7.	C(1)-H(11)	1.0968	1.1
8.	C(1)-C(6)	1.4037	1.42
9.	C(5)-C(6)	1.4036	1.42
10.	C(4)-C(5)	1.3861	1.42

11.	C(3)-C(4)	1.3993	1.42
12.	C(2)-C(3)	1.3983	1.42
13.	C(1)-C(2)	1.3865	1.42
14.	C(8)-O(10)	1.3566	1.338
15.	C(8)-O(9)	1.2213	1.208
16.	C(3)-C(8)	1.477	1.517
17.	C(6)-N(7)	1.4226	1.462
18.	H(17)-O(10)-C(8)	108.9103	106.1
19.	O(10)-C(8)-O(9)	114.3809	122
20.	O(10)-C(8)-C(3)	116.997	124.3
21.	O(9)-C(8)-C(3)	128.6221	123
22.	H(16)-N(7)-H(15)	111.739	118.8
23.	H(16)-N(7)-C(6)	112.3189	
24.	H(15)-N(7)-C(6)	112.3199	
25.	C(1)-C(6)-C(5)	119.6417	120
26.	C(1)-C(6)-N(7)	120.0913	120
27.	C(5)-C(6)-N(7)	120.1017	120
28.	H(14)-C(5)-C(6)	120.6545	120
29.	H(14)-C(5)-C(4)	119.413	120
30.	C(6)-C(5)-C(4)	119.9321	
31.	H(13)-C(4)-C(5)	119.7903	120
32.	H(13)-C(4)-C(3)	119.7646	120
33.	C(5)-C(4)-C(3)	120.4451	
34.	C(4)-C(3)-C(2)	119.6032	120
35.	C(4)-C(3)-C(8)	118.6766	117.6
36.	C(2)-C(3)-C(8)	121.72	117.6
37.	H(12)-C(2)-C(3)	120.4683	120
38.	H(12)-C(2)-C(1)	119.2119	120
39.	C(3)-C(2)-C(1)	120.3197	
40.	H(11)-C(1)-C(6)	120.5783	120
41.	H(11)-C(1)-C(2)	119.3649	120
42.	C(6)-C(1)-C(2)	120.0563	

3-3 Determination of HOMO-LUMO energy gap :

The energy of the highest occupied molecular orbital HOMO and the lowest unoccupied molecular orbital LUMO of each compound have been calculated at semiempirical PM3 level , as a result HOMO-LUMO energy cap for each compound has been calculated , the result shown in figure (3-2) and table (3-10)





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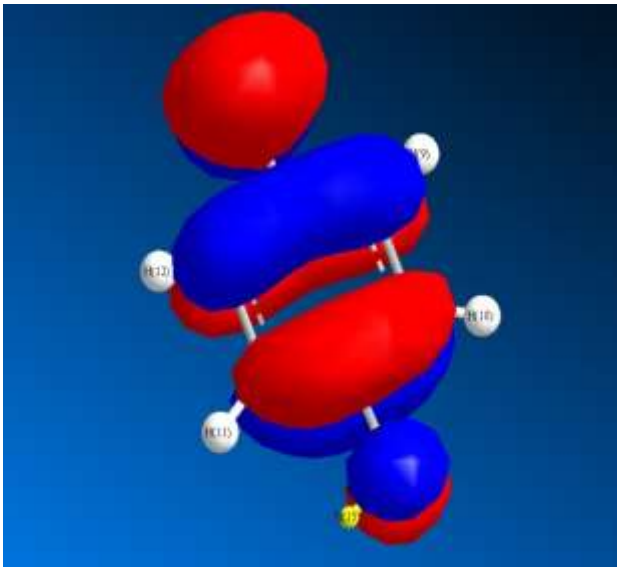

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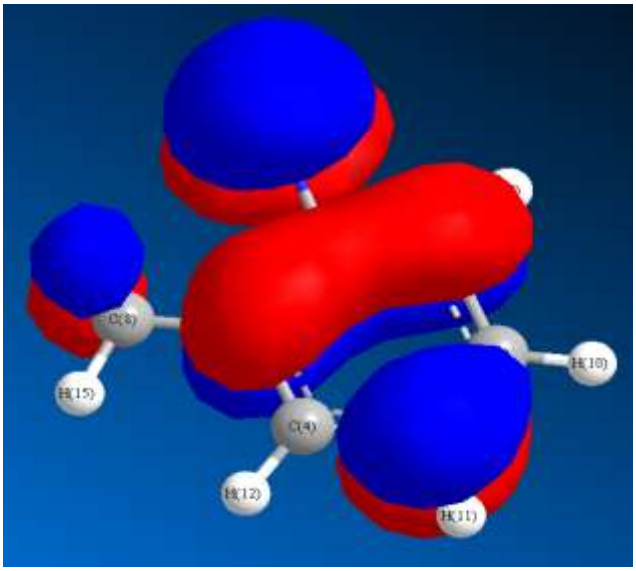

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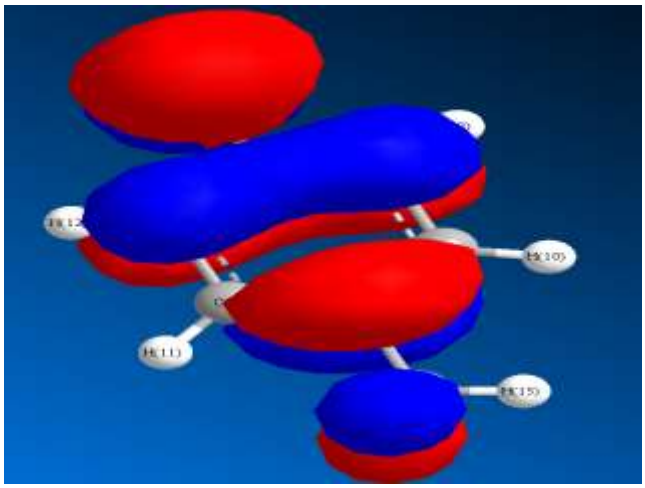

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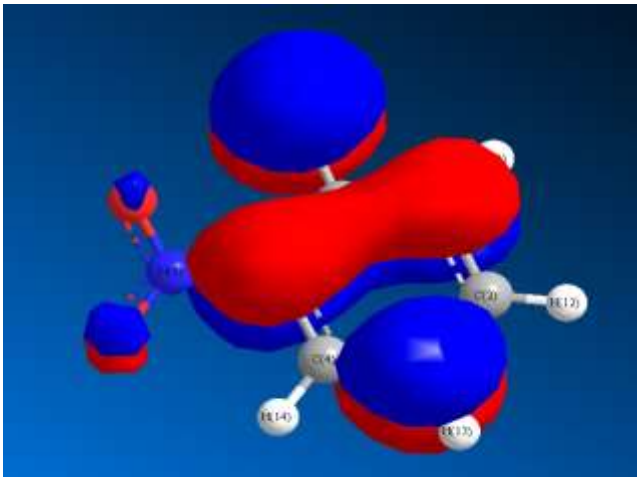

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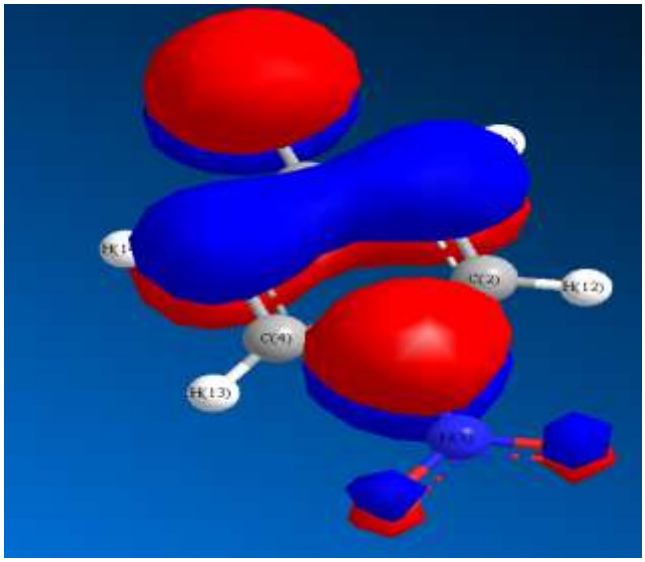

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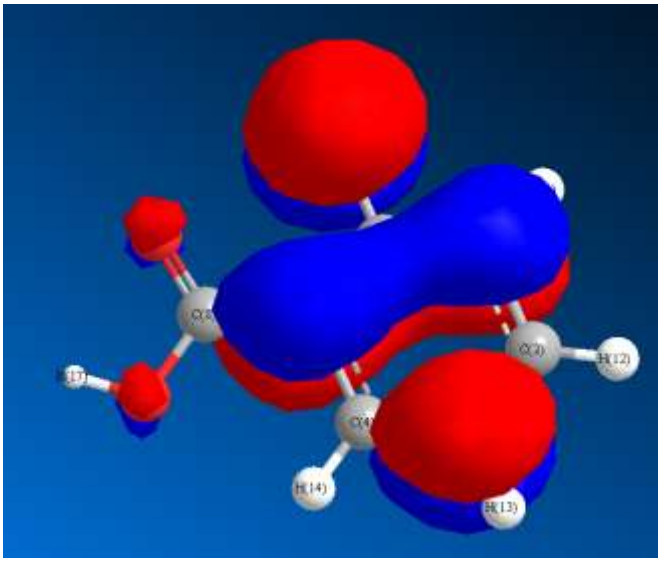

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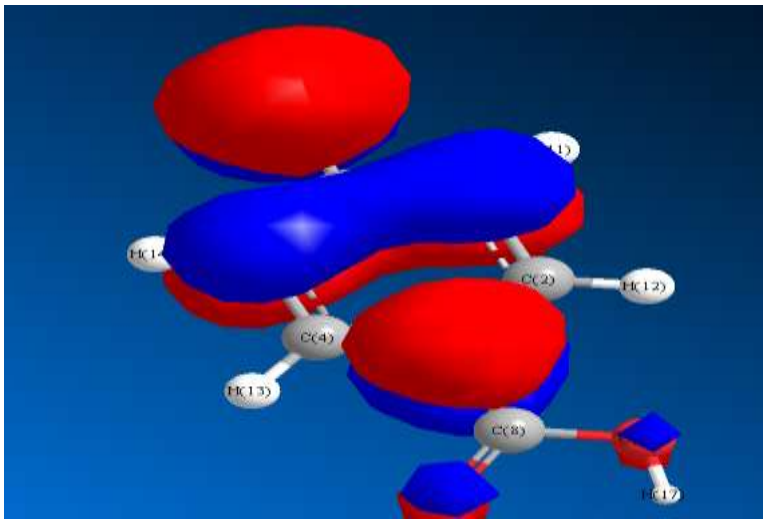

9

Figure-3-2 HOMO-LUMO molecular orbitals for compounds 1-9 at Semiempirical PM3 level

Table(3-10): Energy of HOMO,LUMO and HOMO-LUMO gap for compounds 1-9

Comp.	HOMO/eV	LUMO/eV	ΔHOMO-LUMO
1	-11.693	-0.965	10.73
2	-10.898	-0.205	10.693
3	-10.356	-0.966	9.39
4	-11.462	-0.601	10.861
5	-11.289	-0.945	10.344
6	-11.243	-3.186	8.057

7	-11.220	-2.210	9.01
8	-11.310	-3.585	7.725
9	-11.738	-2.923	8.815

Comp .3 increase activity of compound by decreasing the HOMO-LUMO energy gap , where the substituted of hydroxyl group positioned on Para increase the energy of HOMO

Substitute of the withdrawing group (NO2) and (COOH) increase the activity of compounds in both Ortho and Para positioned as it is decreased the HOMO-LUMO gap as a result of decreasing the energy of LUMO

The bond angle C(1)-C(6)-C(5) also affected , hence by substitute OH group positioned on Ortho the value of B.A decrease from 119.768 to 118.853 ,while it is increase to 119.898 when the substitution positioned on Para

When aniline substitute by withdrawing the value B.A decrease for different types of substitution , this was may be due to decreasing of electron density on the aromatic ring

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