وزارة التعليم العالي والبحث العلمي

جامعة القادسية

كلية العلوم

قسم الكيمياء

بحث مقدم من قبل الطالبان

(مصطفى رزاق طحيول –مصطفى كريم جازع) الى مجلس كلية العلوم /

قسم الكيمياء / وهوة جزء من متطلبات نيل شهادة البكالوريوس في علوم الحياة

م / عنوان البحث

Determination of stability for Naphthalene substituted compounds by computational chemistry methods

بأشراف

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١٤٣٩هـ
٢٠١٨م

الإهداء

أهدي هذا البحث الى روح ابي التي ترفرف في جنان الرحمن ...

الى ابي الثاني المرحوم الدكتور عباس الذي ذكراه دائماً تتردد

بلخير على ذاكرتي رجل اتمنتى القاء معه...

الى امي التي لا اقدر على وصف حبي وامتناني لها الغالية على

قلبي...

الى اخواني ...

الى اساتذتي في كلية العلوم – قسم الكيمياء...

الشُكر والتقدير

الشكر لله وحده الذي كان لي خير معين.

اتقدم بجزيل الشكر الى عمادة كلية العلوم / جامعة القادسية, ولا سيما قسم الكيمياء, ثم اتقدم بلشكر والتقدير لاستاذتي الدكتورة اوراس عدنان التي مهدت لنا طريق العلم والمعرفة واضاءت بعلمها وتوجيهاتها المباركة عقولنا فلكي منا كل التقدير و الوفاء.

بِسْمِ اللَّـهِ الرَّحْمَـٰنِ الرَّحِيمِ

﴿ إِنَّمَا يَخْشَى اللَّهَ مِنْ عِبَادِهِ الْعُلَمَاءُ إِنَّ اللَّهَ عَزِيزٌ غَفُورٌ ﴾

صدق الله العظيم.

1- <u>Introduction</u>

During the last few decades, computer simulations have become more relevant as a tool for acquisition of knowledge and for process decisions. The simulations make feasible the study of complex theoretical models in different areas of science such as physics and chemistry [1]

In addition, the continuous development of computer and processing technologies is disseminating the use of computer simulations in all fields. Starting in the 1960´s, the fundaments of Classical Physics and Quantum Chemistry were slowly described and implemented in computer models. This field developed rapidly during the last two decades of the 20th century. The continuous progress led to the creation of a new field of study for the scientists that investigate matter and its properties and interactions: the Computational Chemistry. The optimization of operational conditions of a process usually needs the values of equilibrium constants of all reactions present. These data allow the calculation of mole fractions of all species present at equilibrium, conditions which lead to the maximum theoretical conversions. Sometimes there is a lack of experimental energies of formation ($\Delta H0$ f and $\Delta G0$ f). Although there has been continuous progress in the publication of experimental data, there are still a very large number of substances for which no thermodynamic data are available [2]. One of the causes for this lack of data is the complexity of experimental setups required to obtain thermodynamic data. In this context, considering the large improvement of computer hardware technologies and Computational Chemistry in the last decade and the lack of experimental data, the use of computational chemistry methods could be a valuable tool to obtain thermodynamic data. Several researches have been published in the literature applying computational chemistry to predict thermodynamic parameters of interesting reactions. Ramos et al. [3] used quantum chemical methods to evaluate thermodynamic and kinetic parameters for a set of reactions involved in the oxidation pathway of phenol by reactive oxygen species. Hydrogen has been attracting great interest as a clean energy source. Generally, hydrogen can be produced by processes such as steam reforming, partial oxidation and autothermal reforming of hydrocarbons. Hydrogen can also be obtained from the reforming of liquefied petroleum gas (LPG), which is is a commercial gas that is easily transported and stored on-site[4]
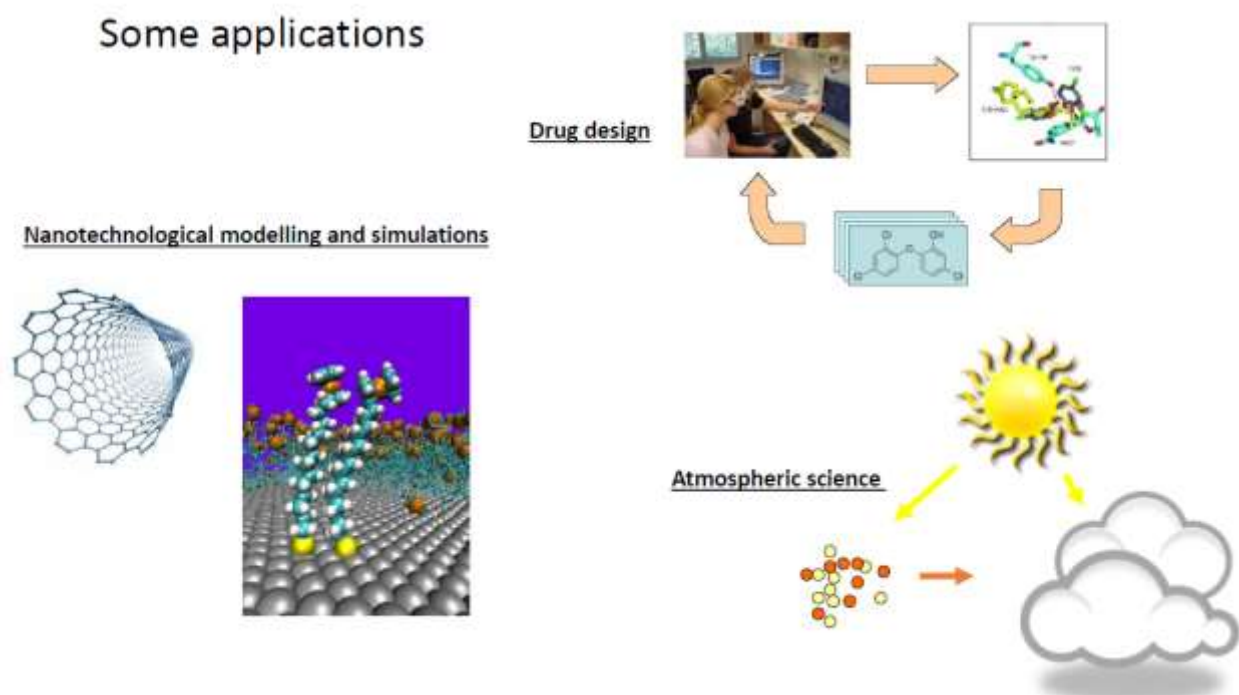
1-1   Computational Chemistry :

Computational Chemistry is the modeling of chemical phenomenon using computers rather than chemicals. The models used vary in their sophistication: Cheminformatics Molecular mechanics Semi-empirical methods Ab initio quantum chemistry All these methods, except the last, rely on empirical information (parameters, energy levels etc.). In this course we will focus on ab initio quantum chemistry.[5]

There are two different aspects to computational chemistry:

1.Computational studies can be carried out to find a starting point for a laboratory synthesis, or to assist in understanding experimental data, such as the position and source of spectroscopic peaks.

2.Computational studies can be used to predict the possibility of so far entirely unknown molecules or to explore reaction mechanisms that are not readily studied by experimental means.

Thus, computational chemistry can assist the experimental chemist or it can challenge the experimental chemist to find entirely new chemical objects.[6]

Figure (1-1): Some applications of computational chemistry

1-2   Semiempirical methods

In principle, any observable property of an atomic or molecular system can be obtained from the Schrodinger equation. Over the past decades the semiempirical molecular orbital methods have been used widely in computational studies[7] Semiempirical approaches neglect many smaller integrals to speed up the calculations. In order to compensate for the errors caused by these approximations, empirical parameters are introduced into the remaining integrals and calibrated against reliable experimental or theoretical reference data[8]. This strategy can only be successful if the semiempirical model retains the essential physics to describe the properties of interest[9]. Provided that this is the case, the parameterization can account for all other effects in an average sense, and it is then a matter of validation to establish the numerical accuracy of a given approach[10]. In current practice, semiempirical methods serve as efficient computational tools which can yield fast quantitative estimates for a number of properties[11]. This may be particularly useful for correlating large sets of experimental and theoretical data, for establishing trends in classes of related molecules, and for scanning a computational problem before proceeding with higher level treatments[12]. There remains the need to improve semiempirical methods with regard to their accuracy and range of applicability, without, compromising their computational efficiency[13]. In addition, there is a need to develop new algorithms in order to exploit modern computer architectures and extend semiempirical calculations to ever larger molecules. Over the years, a large number of methods with different acronyms have been developed, including MNDO [14], AM1 [15], PM3 [16]. Semiempirical methods differ in the details of the approximations (e.g. the core–core repulsion functions) and in particular in the values of the parameters. The semiempirical methods can be optimized for different purposes. The MNDO, AM1 and PM3 methods were designed to reproduce heats of formation and structures of a large number of organic molecules. Other semiempirical methods are specifically optimized for spectroscopic properties (e.g. INDO/S or CNDO/S).

1-2-1 MNDO (modified neglect of differential overlap)

It is based on the NDDO (neglect of diatomic differential overlap) approximation and in turn NDDO is an improved version of INDO (intermediate neglect of differential overlap) method. INDO itself is an improvement over the CNDO (complete neglect of differential overlap) approximation. There are several such semiempirical LCAO MO methods, developed for specific purposes.[17]

1-2-2 AM1 (Austin model 1)

AM1 is a semiempirical method based on the neglect of differential diatomic overlap integral approximation. Specifically, it is a generalization of the modified neglect of diatomic differential overlap approximation. AM1 was developed by Michael Dewar and coworkers reported in 1985 [18]. AM1 is an attempt to improve the MNDOmodel by reducing the repulsion of atoms at close separation distances. The atomic core–atomic core terms in the MNDO equations were modified through the addition of off-center attractive and repulsive Gaussian functions. The complexity of the parameterization problem increased in AM1 as the number of parameters per atom increased from seven in MNDO to 13–16 per atom in AM1

1.2.3 - PM3 (parameterized model number 3)

PM3 is another semiempirical method based on the neglect of differential diatomic overlap integral approximation. The PM3method uses the same formalism and equations as the AM1 method. The only differences are: (a) PM3 uses two Gaussian functions for the core repulsion function, instead of the variable number used by AM1 (which uses between one and four Gaussians per element); (b) the numerical values of the parameters are different. The other differences lie in the philosophy and the methodology used during the parameterization: whereas AM1 takes some of the parameter values from spectroscopic measurements, PM3 treats them as optimised values. The method was developed by Stewart and first reported in 1989 [19].

1-4 Gaussian Program.

Pople et.al. put Gaussian software package where used atomic functions contain Gaussian–Type orbital which appeared for the first time in Gaussian software package [20], starting from Gaussian software package 70 [21] and ended of Gaussian programs set 2003 [22], Gaussian program is based to solve Roothaan-Hull equation and be able to calculate the most elements of the periodic table and the accuracy of calculations in this program relies on the number of wave function or basis set used ,whenever the number was larger resulting values were more accurate.

The program includes several mathematical methods to calculate the total energy of the atoms or molecules of different sizes and configuration with access to its equilibrium shape and calculate the molecular characteristics and physical properties, and the most important of these mathematical methods are molecular mechanics (MM) [23], semi-empirical calculations, Hartree-Fock (HF) calculations, Density functional theory (DFT) which included correlation energy calculation and hybrid method between Hartree–Fock method (HF) and density functional theory (DFT).[24]

2-1 Computational Methodology :

Complete geometrical optimizations of the investigated molecules 1-11 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) : Naphthalene compounds included in the study

Comp.no	IUPAC name
1	Naphthalene
2	1-Methyl naphthalene
3	1-Hydroxy naphthalene
4	1-Methoxy naphthalene
5	Naphthalene-1- amine
6	N-Methyl naphthalene -1- amine
7	1-Nitro Naphthalene
8	1- Naphthoic acid
9	1- (Naphthalene-1-yl) ethanone
10	1- Naphthaldehyde
11	Naphthalene- 1- Sulfonic acid

3-1 Optimized geometries of compounds 1-11

Optimized geometries of compounds 1-11 have been studied in semiempirical PM3 level ,the result shown in figure(3-1) , table (3-12)
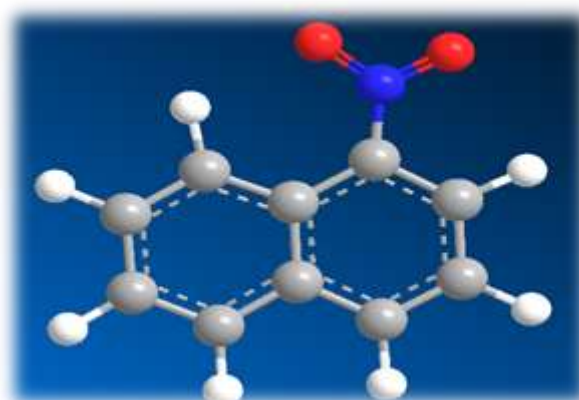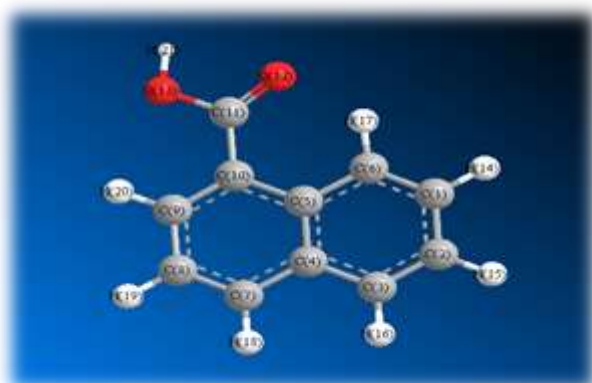

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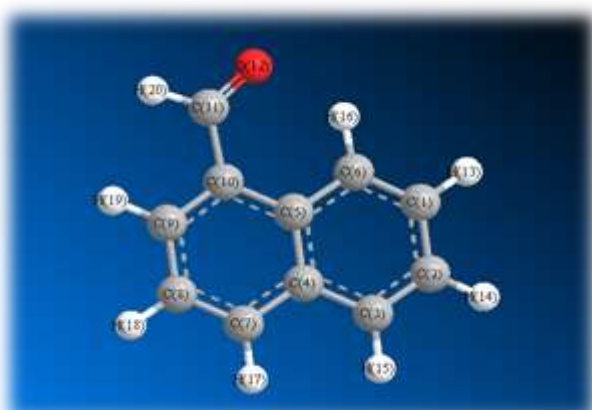

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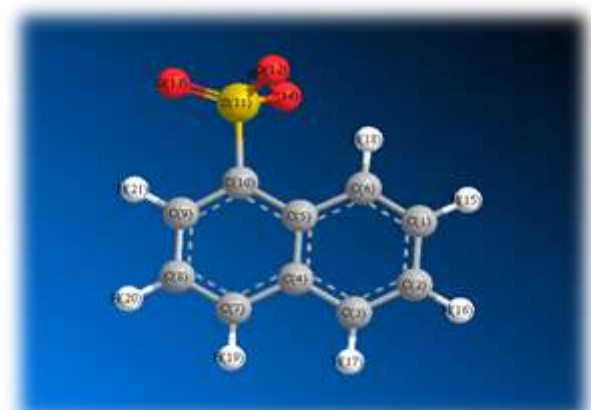

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Figure-3-1 optimized geometry for compounds 1-11 at Semiempirical PM3 level

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 (3-11)

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

	BOND LENGTH AND BOND ANGLE		
NO.	BONDS	Actual (° / Å)	Optimal (° / Å)
1	C(10)-H(18)	1.0958	1.1
2	C(9)-H(17)	1.0947	1.1
3	C(8)-H(16)	1.0947	1.1
4	C(7)-H(15)	1.0958	1.1
5	C(6)-H(14)	1.0958	1.1
6	C(3)-H(13)	1.0958	1.1
7	C(2)-H(12)	1.0947	1.1
8	C(1)-H(11)	1.0947	1.1
9	C(8)-C(7)	1.3684	1.42
10	C(4)-C(7)	1.4212	1.42
11	C(5)-C(4)	1.4101	1.42
12	C(3)-C(4)	1.4212	1.42
13	C(2)-C(3)	1.3684	1.42
14	C(1)-C(2)	1.4145	1.42
15	C(6)-C(1)	1.3684	1.42
16	C(5)-C(6)	1.4212	1.42
17	C(10)-C(5)	1.4212	1.42
18	C(9)-C(10)	1.3684	1.42
19	C(8)-C(9)	1.4145	1.42
20	H(18)-C(10)-C(5)	118.8548	120
21	H(18)-C(10)-C(9)	120.89	120
22	C(5)-C(10)-C(9)	120.2552	
23	H(17)-C(9)-C(10)	120.5111	120
24	H(17)-C(9)-C(8)	119.0461	120
25	C(10)-C(9)-C(8)	120.4428	
26	H(16)-C(8)-C(7)	120.511	120
27	H(16)-C(8)-C(9)	119.046	120
28	C(7)-C(8)-C(9)	120.443	
29	H(15)-C(7)-C(8)	120.8901	120
30	H(15)-C(7)-C(4)	118.8548	120
31	C(8)-C(7)-C(4)	120.2551	
32	H(14)-C(6)-C(1)	120.89	120
33	H(14)-C(6)-C(5)	118.8549	120
34	C(1)-C(6)-C(5)	120.2551	
35	C(4)-C(5)-C(6)	119.302	120
36	C(4)-C(5)-C(10)	119.3019	120
37	C(6)-C(5)-C(10)	121.3961	120
38	C(7)-C(4)-C(5)	119.302	120
39	C(7)-C(4)-C(3)	121.3961	120
40	C(5)-C(4)-C(3)	119.3019	120
41	H(13)-C(3)-C(4)	118.8549	120
42	H(13)-C(3)-C(2)	120.89	120
43	C(4)-C(3)-C(2)	120.2552	
44	H(12)-C(2)-C(3)	120.5109	120
45	H(12)-C(2)-C(1)	119.0461	120
46	C(3)-C(2)-C(1)	120.443	
47	H(11)-C(1)-C(2)	119.0462	120
48	H(11)-C(1)-C(6)	120.5109	120
49	C(2)-C(1)-C(6)	120.4428	

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

NO.	BONDS	Actual (° / Å)	Optimal (° / Å)
	BOND LENGTH AND BOND ANGLE		
1	C(11)-H(21)	1.0989	1.113
2	C(11)-H(20)	1.0989	1.113
3	C(11)-H(19)	1.0986	1.113
4	C(9)-H(18)	1.0964	1.1
5	C(8)-H(17)	1.0949	1.1
6	C(7)-H(16)	1.0958	1.1
7	C(6)-H(15)	1.0964	1.1
8	C(3)-H(14)	1.096	1.1
9	C(2)-H(13)	1.0948	1.1
10	C(1)-H(12)	1.095	1.1
11	C(8)-C(7)	1.3672	1.42
12	C(4)-C(7)	1.421	1.42
13	C(5)-C(4)	1.4116	1.42
14	C(3)-C(4)	1.4214	1.42
15	C(2)-C(3)	1.368	1.42
16	C(1)-C(2)	1.4132	1.42
17	C(6)-C(1)	1.3686	1.42
18	C(5)-C(6)	1.422	1.42
19	C(10)-C(5)	1.4298	1.42
20	C(9)-C(10)	1.3745	1.42
21	C(8)-C(9)	1.4123	1.42
22	C(10)-C(11)	1.487	1.497
23	H(21)-C(11)-H(20)	107.7025	109
24	H(21)-C(11)-H(19)	107.3188	109
25	H(21)-C(11)-C(10)	111.1033	110
26	H(20)-C(11)-H(19)	107.3334	109
27	H(20)-C(11)-C(10)	111.0872	110
28	H(19)-C(11)-C(10)	112.0774	110
29	H(18)-C(9)-C(10)	120.2842	120
30	H(18)-C(9)-C(8)	118.6619	120
31	C(10)-C(9)-C(8)	121.0539	
32	H(17)-C(8)-C(7)	120.6251	120
33	H(17)-C(8)-C(9)	119.0149	120
34	C(7)-C(8)-C(9)	120.3599	
35	H(13)-C(2)-C(3)	120.661	120
36	H(13)-C(2)-C(1)	119.2141	120
37	C(3)-C(2)-C(1)	120.1249	
38	H(12)-C(1)-C(2)	119.0695	120
39	H(12)-C(1)-C(6)	120.4344	120
40	C(2)-C(1)-C(6)	120.4961	
41	C(5)-C(10)-C(9)	119.6073	120
42	C(5)-C(10)-C(11)	120.6908	121.4
43	C(9)-C(10)-C(11)	119.7019	121.4
44	H(15)-C(6)-C(1)	120.0189	120
45	H(15)-C(6)-C(5)	119.2198	120
46	C(1)-C(6)-C(5)	120.7613	
47	H(16)-C(7)-C(8)	120.92	120
48	H(16)-C(7)-C(4)	118.9669	120
49	C(8)-C(7)-C(4)	120.1131	
50	H(14)-C(3)-C(4)	118.8068	120
51	H(14)-C(3)-C(2)	120.7714	120
52	C(4)-C(3)-C(2)	120.4218	
53	C(4)-C(5)-C(6)	118.5359	120
54	C(4)-C(5)-C(10)	119.024	120
55	C(6)-C(5)-C(10)	122.4401	120
56	C(7)-C(4)-C(5)	119.8418	120
57	C(7)-C(4)-C(3)	120.4983	120
58	C(5)-C(4)-C(3)	119.6599	120

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

NO.	BONDS	Actual (° / Å)	Optimal (° / Å)
	BOND LENGTH AND BOND ANGLE		
1	O(11)-H(19)	0.9533	0.972
2	C(9)-H(18)	1.0957	1.1
3	C(8)-H(17)	1.0952	1.1
4	C(7)-H(16)	1.0956	1.1
5	C(6)-H(15)	1.0996	1.1
6	C(3)-H(14)	1.096	1.1
7	C(2)-H(13)	1.095	1.1
8	C(1)-H(12)	1.0949	1.1
9	C(8)-C(7)	1.3697	1.42
10	C(4)-C(7)	1.4199	1.42
11	C(5)-C(4)	1.4098	1.42
12	C(3)-C(4)	1.4225	1.42
13	C(2)-C(3)	1.368	1.42
14	C(1)-C(2)	1.4146	1.42
15	C(6)-C(1)	1.3676	1.42
16	C(5)-C(6)	1.4207	1.42
17	C(10)-C(5)	1.4331	1.42
18	C(9)-C(10)	1.3808	1.42
19	C(8)-C(9)	1.4102	1.42
20	C(10)-O(11)	1.3681	1.355
21	H(19)-O(11)-C(10)	107.5036	108
22	C(5)-C(10)-C(9)	120.9976	120
23	C(5)-C(10)-O(11)	122.5056	124.3
24	C(9)-C(10)-O(11)	116.4968	124.3
25	H(18)-C(9)-C(10)	120.7993	120
26	H(18)-C(9)-C(8)	119.6788	120
27	C(10)-C(9)-C(8)	119.522	
28	H(17)-C(8)-C(7)	120.3478	120
29	H(17)-C(8)-C(9)	118.6765	120
30	C(7)-C(8)-C(9)	120.9757	
31	H(16)-C(7)-C(8)	120.7895	120
32	H(16)-C(7)-C(4)	118.8332	120
33	C(8)-C(7)-C(4)	120.3773	
34	H(15)-C(6)-C(1)	120.7996	120
35	H(15)-C(6)-C(5)	118.6745	120
36	C(1)-C(6)-C(5)	120.5259	
37	C(4)-C(5)-C(6)	119.277	120
38	C(4)-C(5)-C(10)	118.3177	120
39	C(6)-C(5)-C(10)	122.4053	120
40	C(7)-C(4)-C(5)	119.8097	120
41	C(7)-C(4)-C(3)	121.1134	120
42	C(5)-C(4)-C(3)	119.0768	120
43	H(14)-C(3)-C(4)	118.7204	120
44	H(14)-C(3)-C(2)	120.8133	120
45	C(4)-C(3)-C(2)	120.4663	
46	H(13)-C(2)-C(3)	120.5651	120
47	H(13)-C(2)-C(1)	119.0283	120
48	C(3)-C(2)-C(1)	120.4066	
49	H(12)-C(1)-C(2)	119.1697	120
50	H(12)-C(1)-C(6)	120.5828	120
51	C(2)-C(1)-C(6)	120.2475	

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

NO.	BONDS	Actual (° / Å)	Optimal (° / Å)
	BOND LENGTH AND BOND ANGLE		
1	C(12)-H(22)	1.0959	1.111
2	C(12)-H(21)	1.096	1.111
3	C(12)-H(20)	1.0927	1.111
4	C(9)-H(19)	1.0959	1.1
5	C(8)-H(18)	1.095	1.1
6	C(7)-H(17)	1.0959	1.1
7	C(6)-H(16)	1.0964	1.1
8	C(3)-H(15)	1.0959	1.1
9	C(2)-H(14)	1.0949	1.1
10	C(1)-H(13)	1.095	1.1
11	C(8)-C(7)	1.3683	1.42
12	C(4)-C(7)	1.4212	1.42
13	C(5)-C(4)	1.4114	1.42
14	C(3)-C(4)	1.4215	1.42
15	C(2)-C(3)	1.3682	1.42
16	C(1)-C(2)	1.4138	1.42
17	C(6)-C(1)	1.3688	1.42
18	C(5)-C(6)	1.4209	1.42
19	C(10)-C(5)	1.431	1.42
20	C(9)-C(10)	1.3773	1.42
21	C(8)-C(9)	1.4123	1.42
22	O(11)-C(12)	1.4109	1.396
23	C(10)-O(11)	1.3946	1.355
24	H(22)-C(12)-H(21)	109.573	109
25	H(22)-C(12)-H(20)	110.2643	109
26	H(22)-C(12)-O(11)	112.0322	106.7
27	H(21)-C(12)-H(20)	110.2275	109
28	H(21)-C(12)-O(11)	111.7109	106.7
29	H(20)-C(12)-O(11)	102.8764	106.7
30	C(12)-O(11)-C(10)	113.2868	110.8
31	H(19)-C(9)-C(10)	120.7288	120
32	H(19)-C(9)-C(8)	119.5003	120
33	C(10)-C(9)-C(8)	119.7702	
34	H(18)-C(8)-C(7)	120.5454	120
35	H(18)-C(8)-C(9)	118.8633	120
36	C(7)-C(8)-C(9)	120.5913	
37	C(5)-C(10)-C(9)	121.2012	120
38	C(5)-C(10)-O(11)	119.5095	124.3
39	C(9)-C(10)-O(11)	119.1048	124.3
40	H(17)-C(7)-C(8)	120.7152	120
41	H(17)-C(7)-C(4)	118.7801	120
42	C(8)-C(7)-C(4)	120.5047	
43	C(4)-C(5)-C(6)	119.088	120
44	C(4)-C(5)-C(10)	118.0242	120
45	C(6)-C(5)-C(10)	122.8876	120
46	H(16)-C(6)-C(1)	120.5282	120
47	H(16)-C(6)-C(5)	119.071	120
48	C(1)-C(6)-C(5)	120.4004	
49	C(7)-C(4)-C(5)	119.9084	120
50	C(7)-C(4)-C(3)	120.7501	120
51	C(5)-C(4)-C(3)	119.3415	120
52	H(15)-C(3)-C(4)	118.8162	120
53	H(15)-C(3)-C(2)	120.8102	120
54	C(4)-C(3)-C(2)	120.3736	
55	H(14)-C(2)-C(3)	120.5792	120
56	H(14)-C(2)-C(1)	119.1232	120
57	C(3)-C(2)-C(1)	120.2976	
58	H(13)-C(1)-C(2)	119.0624	120
59	H(13)-C(1)-C(6)	120.4387	120
60	C(2)-C(1)-C(6)	120.4989	

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

NO.	BONDS	Actual (° / Å)	Optimal (° / Å)
	BOND LENGTH AND BOND ANGLE		
1	N(11)-H(20)	0.9871	1.05
2	N(11)-H(19)	0.9917	1.05
3	C(9)-H(18)	1.096	1.1
4	C(8)-H(17)	1.095	1.1
5	C(7)-H(16)	1.0951	1.1
6	C(6)-H(15)	1.0993	1.1
7	C(3)-H(14)	1.0959	1.1
8	C(2)-H(13)	1.0948	1.1
9	C(1)-H(12)	1.0946	1.1
10	C(8)-C(7)	1.3699	1.42
11	C(4)-C(7)	1.4194	1.42
12	C(5)-C(4)	1.4103	1.42
13	C(3)-C(4)	1.4222	1.42
14	C(2)-C(3)	1.3681	1.42
15	C(1)-C(2)	1.4133	1.42
16	C(6)-C(1)	1.3686	1.42
17	C(5)-C(6)	1.4204	1.42
18	C(10)-C(5)	1.4366	1.42
19	C(9)-C(10)	1.3869	1.42
20	C(8)-C(9)	1.4068	1.42
21	C(10)-N(11)	1.3983	1.462
22	H(20)-N(11)-H(19)	120.514	118.8
23	H(20)-N(11)-C(10)	120.4161	
24	H(19)-N(11)-C(10)	119.0697	
25	C(5)-C(10)-C(9)	120.1005	120
26	C(5)-C(10)-N(11)	119.7912	120
27	C(9)-C(10)-N(11)	120.1082	120
28	H(18)-C(9)-C(10)	121.0388	120
29	H(18)-C(9)-C(8)	118.8327	120
30	C(10)-C(9)-C(8)	120.1285	
31	H(17)-C(8)-C(7)	120.2625	120
32	H(17)-C(8)-C(9)	118.7575	120
33	C(7)-C(8)-C(9)	120.98	
34	H(16)-C(7)-C(8)	120.8528	120
35	H(16)-C(7)-C(4)	118.9702	120
36	C(8)-C(7)-C(4)	120.1771	
37	H(15)-C(6)-C(1)	120.255	120
38	H(15)-C(6)-C(5)	119.0868	120
39	C(1)-C(6)-C(5)	120.6582	
40	C(4)-C(5)-C(6)	119.0311	120
41	C(4)-C(5)-C(10)	118.6045	120
42	C(6)-C(5)-C(10)	122.3643	120
43	C(7)-C(4)-C(5)	120.0094	120
44	C(7)-C(4)-C(3)	120.7817	120
45	C(5)-C(4)-C(3)	119.2089	120
46	H(14)-C(3)-C(4)	118.6941	120
47	H(14)-C(3)-C(2)	120.7836	120
48	C(4)-C(3)-C(2)	120.5223	
49	H(13)-C(2)-C(3)	120.5951	120
50	H(13)-C(2)-C(1)	119.1156	120
51	C(3)-C(2)-C(1)	120.2893	
52	H(12)-C(1)-C(2)	119.1793	120
53	H(12)-C(1)-C(6)	120.5304	120
54	C(2)-C(1)-C(6)	120.2903	

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

NO.	BONDS	Actual (° / Å)	Optimal (° / Å)
	BOND LENGTH AND BOND ANGLE		
1	C(12)-H(23)	1.0997	1.113
2	C(12)-H(22)	1.1021	1.113
3	C(12)-H(21)	1.0975	1.113
4	N(11)-H(20)	0.9985	1.05
5	C(9)-H(19)	1.0975	1.1
6	C(8)-H(18)	1.095	1.1
7	C(7)-H(17)	1.0958	1.1
8	C(6)-H(16)	1.1	1.1
9	C(3)-H(15)	1.096	1.1
10	C(2)-H(14)	1.0948	1.1
11	C(1)-H(13)	1.0949	1.1
12	C(8)-C(7)	1.3671	1.42
13	C(4)-C(7)	1.4204	1.42
14	C(5)-C(4)	1.4128	1.42
15	C(3)-C(4)	1.4219	1.42
16	C(2)-C(3)	1.3676	1.42
17	C(1)-C(2)	1.4128	1.42
18	C(6)-C(1)	1.3685	1.42
19	C(5)-C(6)	1.4223	1.42
20	C(10)-C(5)	1.4341	1.42
21	C(9)-C(10)	1.381	1.42
22	C(8)-C(9)	1.4101	1.42
23	N(11)-C(12)	1.4759	1.47
24	C(10)-N(11)	1.4485	1.462
25	H(23)-C(12)-H(22)	108.2175	109
26	H(23)-C(12)-H(21)	108.3726	109
27	H(23)-C(12)-N(11)	114.1169	
28	H(22)-C(12)-H(21)	108.0456	109
29	H(22)-C(12)-N(11)	109.0323	
30	H(21)-C(12)-N(11)	108.8935	
31	H(20)-N(11)-C(12)	109.6749	
32	H(20)-N(11)-C(10)	109.5929	118
33	C(12)-N(11)-C(10)	115.8981	
34	C(5)-C(10)-C(9)	119.8296	120
35	C(5)-C(10)-N(11)	120.7869	120
36	C(9)-C(10)-N(11)	119.2107	120
37	H(19)-C(9)-C(10)	121.1109	120
38	H(19)-C(9)-C(8)	117.9806	120
39	C(10)-C(9)-C(8)	120.907	
40	H(18)-C(8)-C(7)	120.6189	120
41	H(18)-C(8)-C(9)	118.9633	120
42	C(7)-C(8)-C(9)	120.4177	
43	H(17)-C(7)-C(8)	120.8585	120
44	H(17)-C(7)-C(4)	118.991	120
45	C(8)-C(7)-C(4)	120.1501	
46	H(16)-C(6)-C(1)	119.7753	120
47	H(16)-C(6)-C(5)	119.2552	120
48	C(1)-C(6)-C(5)	120.9676	
49	C(4)-C(5)-C(6)	118.2442	120
50	C(4)-C(5)-C(10)	118.4532	120
51	C(6)-C(5)-C(10)	123.2991	120
52	C(7)-C(4)-C(5)	120.2412	120
53	C(7)-C(4)-C(3)	120.0058	120
54	C(5)-C(4)-C(3)	119.7513	120
55	H(15)-C(3)-C(4)	118.7486	120
56	H(15)-C(3)-C(2)	120.7337	120
57	C(4)-C(3)-C(2)	120.5175	
58	H(14)-C(2)-C(3)	120.7257	120
59	H(14)-C(2)-C(1)	119.2755	120
60	C(3)-C(2)-C(1)	119.9988	
61	H(13)-C(1)-C(2)	119.0864	120
62	H(13)-C(1)-C(6)	120.3947	120
63	C(2)-C(1)-C(6)	120.5189	

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

NO.	BONDS	Actual (° / Å)	Optimal (° / Å)
	BOND LENGTH AND BOND ANGLE		
1	C(9)-H(20)	1.1093	1.1
2	C(8)-H(19)	1.0955	1.1
3	C(7)-H(18)	1.0951	1.1
4	C(6)-H(17)	1.0962	1.1
5	C(4)-H(16)	1.0969	1.1
6	C(3)-H(15)	1.0957	1.1
7	C(2)-H(14)	1.1004	1.1
8	C(8)-C(9)	1.3679	1.42
9	C(10)-C(9)	1.4226	1.42
10	C(5)-C(10)	1.4128	1.42
11	C(1)-C(10)	1.433	1.42
12	C(2)-C(1)	1.3826	1.42
13	C(3)-C(2)	1.4083	1.42
14	C(4)-C(3)	1.3693	1.42
15	C(5)-C(4)	1.4186	1.42
16	C(6)-C(5)	1.4223	1.42
17	C(7)-C(6)	1.3675	1.42
18	C(8)-C(7)	1.4139	1.42
19	C(1)-N(11)	1.4964	1.444
20	N(11)-O(13)	1.2189	1.3625
21	N(11)-O(12)	1.216	1.3625
22	C(1)-N(11)-O(13)	120.7298	120
23	C(1)-N(11)-O(12)	119.2332	120
24	O(13)-N(11)-O(12)	120.0371	120
25	H(19)-C(8)-C(9)	120.1602	120
26	H(19)-C(8)-C(7)	119.2057	120
27	C(9)-C(8)-C(7)	120.6342	
28	H(18)-C(7)-C(6)	120.6639	120
29	H(18)-C(7)-C(8)	119.2956	120
30	C(6)-C(7)-C(8)	120.0405	
31	H(15)-C(3)-C(2)	118.9565	120
32	H(15)-C(3)-C(4)	120.6418	120
33	C(2)-C(3)-C(4)	120.4016	
34	H(14)-C(2)-C(1)	121.1888	120
35	H(14)-C(2)-C(3)	117.8629	120
36	C(1)-C(2)-C(3)	120.9483	
37	H(17)-C(6)-C(5)	118.7684	120
38	H(17)-C(6)-C(7)	120.8011	120
39	C(5)-C(6)-C(7)	120.4305	
40	H(16)-C(4)-C(3)	120.7439	120
41	H(16)-C(4)-C(5)	119.0658	120
42	C(3)-C(4)-C(5)	120.1903	
43	H(20)-C(9)-C(8)	121.6903	120
44	H(20)-C(9)-C(10)	117.5764	120
45	C(8)-C(9)-C(10)	120.7331	
46	C(10)-C(1)-C(2)	119.6718	120
47	C(10)-C(1)-N(11)	121.7668	120
48	C(2)-C(1)-N(11)	118.5614	120
49	C(9)-C(10)-C(5)	118.4596	120
50	C(9)-C(10)-C(1)	122.875	120
51	C(5)-C(10)-C(1)	118.6654	120
52	C(10)-C(5)-C(4)	120.1225	120
53	C(10)-C(5)-C(6)	119.702	120

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

NO.			
	BOND LENGTH AND BOND ANGLE		
NO.	BONDS	Actual (° / Å)	Optimal (° / Å)
1	O(13)-H(21)	0.9527	0.972
2	C(9)-H(20)	1.097	1.1
3	C(8)-H(19)	1.0953	1.1
4	C(7)-H(18)	1.0963	1.1
5	C(6)-H(17)	1.1111	1.1
6	C(3)-H(16)	1.0959	1.1
7	C(2)-H(15)	1.095	1.1
8	C(1)-H(14)	1.095	1.1
9	C(8)-C(7)	1.3685	1.42
10	C(4)-C(7)	1.4197	1.42
11	C(5)-C(4)	1.411	1.42
12	C(3)-C(4)	1.4218	1.42
13	C(2)-C(3)	1.368	1.42
14	C(1)-C(2)	1.4145	1.42
15	C(6)-C(1)	1.3673	1.42
16	C(5)-C(6)	1.4222	1.42
17	C(10)-C(5)	1.4308	1.42
18	C(9)-C(10)	1.378	1.42
19	C(8)-C(9)	1.4118	1.42
20	C(11)-O(13)	1.3548	1.338
21	C(11)-O(12)	1.2239	1.208
22	C(10)-C(11)	1.482	1.517
23	H(21)-O(13)-C(11)	108.905	106.1
24	O(13)-C(11)-O(12)	113.8096	122
25	O(13)-C(11)-C(10)	117.1036	124.3
26	O(12)-C(11)-C(10)	129.0868	123
27	C(5)-C(10)-C(9)	119.766	120
28	C(5)-C(10)-C(11)	119.5233	117.6
29	C(9)-C(10)-C(11)	120.7107	117.6
30	H(20)-C(9)-C(10)	121.1553	120
31	H(20)-C(9)-C(8)	118.156	120
32	C(10)-C(9)-C(8)	120.6886	
33	H(19)-C(8)-C(7)	120.569	120
34	H(19)-C(8)-C(9)	118.8936	120
35	C(7)-C(8)-C(9)	120.5373	
36	H(18)-C(7)-C(8)	120.8227	120
37	H(18)-C(7)-C(4)	118.9768	120
38	C(8)-C(7)-C(4)	120.2006	
39	H(17)-C(6)-C(1)	122.691	120
40	H(17)-C(6)-C(5)	116.7874	120
41	C(1)-C(6)-C(5)	120.5215	
42	C(4)-C(5)-C(6)	118.9135	120
43	C(4)-C(5)-C(10)	119.0396	120
44	C(6)-C(5)-C(10)	122.0469	120
45	C(7)-C(4)-C(5)	119.7679	120
46	C(7)-C(4)-C(3)	120.7788	120
47	C(5)-C(4)-C(3)	119.4533	120
48	H(16)-C(3)-C(4)	118.7837	120
49	H(16)-C(3)-C(2)	120.8556	120
50	C(4)-C(3)-C(2)	120.3607	
51	H(15)-C(2)-C(3)	120.5724	120
52	H(15)-C(2)-C(1)	119.1691	120
53	C(3)-C(2)-C(1)	120.2585	
54	H(14)-C(1)-C(2)	119.2075	120
55	H(14)-C(1)-C(6)	120.3	120
56	C(2)-C(1)-C(6)	120.4925	

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

NO.	BONDS	Actual (° / Å)	Optimal (° / Å)
	BOND LENGTH AND BOND ANGLE		
1	C(13)-H(23)	1.0981	1.113
2	C(13)-H(22)	1.0973	1.113
3	C(13)-H(21)	1.1022	1.113
4	C(9)-H(20)	1.1014	1.1
5	C(8)-H(19)	1.095	1.1
6	C(7)-H(18)	1.0962	1.1
7	C(6)-H(17)	1.107	1.1
8	C(3)-H(16)	1.0959	1.1
9	C(2)-H(15)	1.0949	1.1
10	C(1)-H(14)	1.095	1.1
11	C(8)-C(7)	1.3689	1.42
12	C(4)-C(7)	1.4196	1.42
13	C(5)-C(4)	1.4116	1.42
14	C(3)-C(4)	1.4221	1.42
15	C(2)-C(3)	1.3678	1.42
16	C(1)-C(2)	1.4147	1.42
17	C(6)-C(1)	1.3673	1.42
18	C(5)-C(6)	1.4225	1.42
19	C(10)-C(5)	1.4287	1.42
20	C(9)-C(10)	1.3765	1.42
21	C(8)-C(9)	1.4102	1.42
22	C(11)-C(13)	1.5068	1.509
23	C(11)-O(12)	1.2199	1.208
24	C(10)-C(11)	1.4947	1.517
25	H(23)-C(13)-H(22)	107.7063	109
26	H(23)-C(13)-H(21)	107.4813	109
27	H(23)-C(13)-C(11)	109.8238	109.47
28	H(22)-C(13)-H(21)	108.0961	109
29	H(22)-C(13)-C(11)	112.5963	109.47
30	H(21)-C(13)-C(11)	110.9498	109.47
31	C(13)-C(11)-O(12)	121.0013	122.5
32	C(13)-C(11)-C(10)	116.6867	115
33	O(12)-C(11)-C(10)	122.303	123
34	C(5)-C(10)-C(9)	119.4159	120
35	C(5)-C(10)-C(11)	121.1703	117.6
36	C(9)-C(10)-C(11)	119.4136	117.6
37	H(20)-C(9)-C(10)	119.4805	120
38	H(20)-C(9)-C(8)	119.3157	120
39	C(10)-C(9)-C(8)	121.202	
40	H(19)-C(8)-C(7)	120.6846	120
41	H(19)-C(8)-C(9)	119.0659	120
42	C(7)-C(8)-C(9)	120.2488	
43	H(18)-C(7)-C(8)	120.8217	120
44	H(18)-C(7)-C(4)	119.011	120
45	C(8)-C(7)-C(4)	120.1665	
46	H(17)-C(6)-C(1)	122.4214	120
47	H(17)-C(6)-C(5)	116.9403	120
48	C(1)-C(6)-C(5)	120.6138	
49	C(4)-C(5)-C(6)	118.8257	120
50	C(4)-C(5)-C(10)	119.1423	120
51	C(6)-C(5)-C(10)	122.0315	120
52	C(7)-C(4)-C(5)	119.7904	120
53	C(7)-C(4)-C(3)	120.756	120
54	C(5)-C(4)-C(3)	119.4515	120
55	H(16)-C(3)-C(4)	118.7881	120
56	H(16)-C(3)-C(2)	120.8292	120
57	C(4)-C(3)-C(2)	120.3826	
58	H(15)-C(2)-C(3)	120.5793	120
59	H(15)-C(2)-C(1)	119.1521	120
60	C(3)-C(2)-C(1)	120.2678	
61	H(14)-C(1)-C(2)	119.1913	120
62	H(14)-C(1)-C(6)	120.3665	120
63	C(2)-C(1)-C(6)	120.4417	

Table (3-10): bond length and bond angle for compound 10

NO.	BONDS	Actual (° / Å)	Optimal (° / Å)
	BOND LENGTH AND BOND ANGLE		
1	C(11)-H(20)	1.1042	1.113
2	C(9)-H(19)	1.0973	1.1
3	C(8)-H(18)	1.0951	1.1
4	C(7)-H(17)	1.0963	1.1
5	C(6)-H(16)	1.1088	1.1
6	C(3)-H(15)	1.0959	1.1
7	C(2)-H(14)	1.0949	1.1
8	C(1)-H(13)	1.095	1.1
9	C(8)-C(7)	1.3696	1.42
10	C(4)-C(7)	1.4193	1.42
11	C(5)-C(4)	1.4114	1.42
12	C(3)-C(4)	1.4222	1.42
13	C(2)-C(3)	1.3679	1.42
14	C(1)-C(2)	1.415	1.42
15	C(6)-C(1)	1.3672	1.42
16	C(5)-C(6)	1.4224	1.42
17	C(10)-C(5)	1.4272	1.42
18	C(9)-C(10)	1.3775	1.42
19	C(8)-C(9)	1.4105	1.42
20	C(11)-O(12)	1.2126	1.208
21	C(10)-C(11)	1.4851	1.517
22	H(20)-C(11)-O(12)	119.3465	120.3
23	H(20)-C(11)-C(10)	116.0734	112
24	O(12)-C(11)-C(10)	124.5801	
25	C(5)-C(10)-C(9)	119.6117	120
26	C(5)-C(10)-C(11)	122.5341	117.6
27	C(9)-C(10)-C(11)	117.8542	117.6
28	H(19)-C(9)-C(10)	120.345	120
29	H(19)-C(9)-C(8)	118.699	120
30	C(10)-C(9)-C(8)	120.9559	
31	H(18)-C(8)-C(7)	120.5778	120
32	H(18)-C(8)-C(9)	119.1019	120
33	C(7)-C(8)-C(9)	120.3203	
34	H(17)-C(7)-C(8)	120.7753	120
35	H(17)-C(7)-C(4)	118.9924	120
36	C(8)-C(7)-C(4)	120.2322	
37	H(16)-C(6)-C(1)	122.8843	120
38	H(16)-C(6)-C(5)	116.6162	120
39	C(1)-C(6)-C(5)	120.4994	
40	C(4)-C(5)-C(6)	118.9824	120
41	C(4)-C(5)-C(10)	119.1856	120
42	C(6)-C(5)-C(10)	121.832	120
43	C(7)-C(4)-C(5)	119.6942	120
44	C(7)-C(4)-C(3)	120.9127	120
45	C(5)-C(4)-C(3)	119.3931	120
46	H(15)-C(3)-C(4)	118.7993	120
47	H(15)-C(3)-C(2)	120.8554	120
48	C(4)-C(3)-C(2)	120.3453	
49	H(14)-C(2)-C(3)	120.5529	120
50	H(14)-C(2)-C(1)	119.1253	120
51	C(3)-C(2)-C(1)	120.3217	
52	H(13)-C(1)-C(2)	119.1878	120
53	H(13)-C(1)-C(6)	120.3542	120
54	C(2)-C(1)-C(6)	120.458	

Table (3-11): bond length and bond angle for compound 11

NO.	BONDS	Actual (° / Å)	Optimal (° / Å)
	BOND LENGTH AND BOND ANGLE		
1	O(14)-H(22)	0.9474	0.942
2	C(9)-H(21)	1.1007	1.1
3	C(8)-H(20)	1.0955	1.1
4	C(7)-H(19)	1.0967	1.1
5	C(6)-H(18)	1.0979	1.1
6	C(3)-H(17)	1.0962	1.1
7	C(2)-H(16)	1.0949	1.1
8	C(1)-H(15)	1.0956	1.1
9	C(8)-C(7)	1.368	1.42
10	C(4)-C(7)	1.4187	1.42
11	C(5)-C(4)	1.4138	1.42
12	C(3)-C(4)	1.4223	1.42
13	C(2)-C(3)	1.3669	1.42
14	C(1)-C(2)	1.4134	1.42
15	C(6)-C(1)	1.3684	1.42
16	C(5)-C(6)	1.4249	1.42
17	C(10)-C(5)	1.4314	1.42
18	C(9)-C(10)	1.3792	1.42
19	C(8)-C(9)	1.4091	1.42
20	S(11)-O(14)	1.6859	
21	S(11)-O(13)	1.444	1.45
22	S(11)-O(12)	1.4324	1.45
23	C(10)-S(11)	1.7828	
24	H(22)-O(14)-S(11)	115.9675	
25	O(14)-S(11)-O(13)	103.9988	
26	O(14)-S(11)-O(12)	106.4369	
27	O(14)-S(11)-C(10)	101.0127	
28	O(13)-S(11)-O(12)	119.4809	116.6
29	O(13)-S(11)-C(10)	111.1007	
30	O(12)-S(11)-C(10)	112.5695	
31	C(5)-C(10)-C(9)	118.474	120
32	C(5)-C(10)-S(11)	123.885	
33	C(9)-C(10)-S(11)	117.6365	
34	H(21)-C(9)-C(10)	120.2541	120
35	H(21)-C(9)-C(8)	117.6605	120
36	C(10)-C(9)-C(8)	122.0854	
37	H(20)-C(8)-C(7)	120.8059	120
38	H(20)-C(8)-C(9)	119.1501	120
39	C(7)-C(8)-C(9)	120.044	
40	H(19)-C(7)-C(8)	120.8899	120
41	H(19)-C(7)-C(4)	119.1565	120
42	C(8)-C(7)-C(4)	119.9535	
43	H(18)-C(6)-C(1)	119.1188	120
44	H(18)-C(6)-C(5)	119.9333	120
45	C(1)-C(6)-C(5)	120.9477	
46	C(4)-C(5)-C(6)	117.9139	120
47	C(4)-C(5)-C(10)	119.3473	120
48	C(6)-C(5)-C(10)	122.7384	120
49	C(7)-C(4)-C(5)	120.0937	120
50	C(7)-C(4)-C(3)	119.825	120
51	C(5)-C(4)-C(3)	120.0812	120
52	H(17)-C(3)-C(4)	118.7786	120
53	H(17)-C(3)-C(2)	120.7871	120
54	C(4)-C(3)-C(2)	120.4343	
55	H(16)-C(2)-C(3)	120.7848	120
56	H(16)-C(2)-C(1)	119.3384	120
57	C(3)-C(2)-C(1)	119.8768	
58	H(15)-C(1)-C(2)	119.0397	120
59	H(15)-C(1)-C(6)	120.2149	120
60	C(2)-C(1)-C(6)	120.7454	

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 (3-12)

1

2

3

4

5
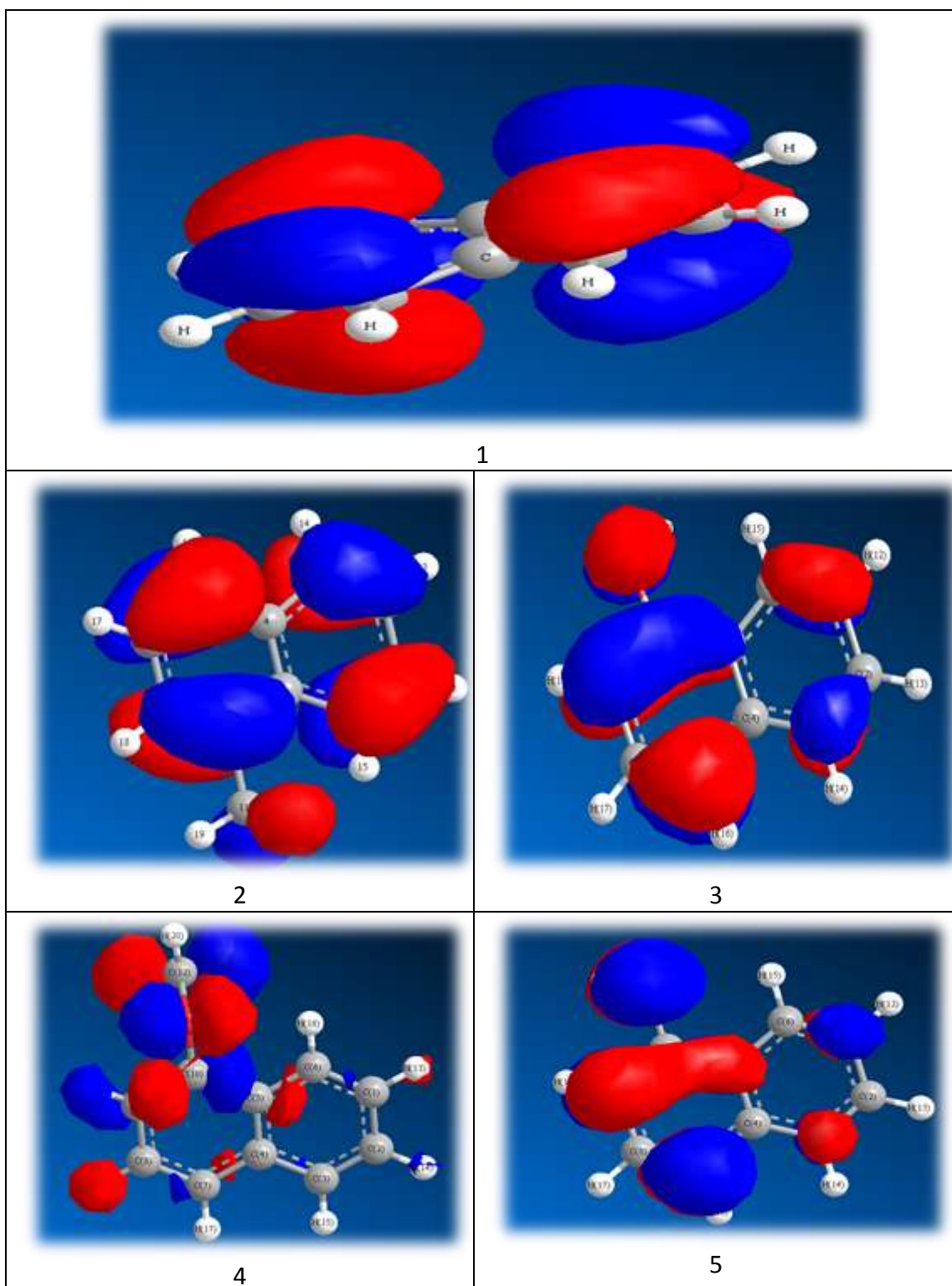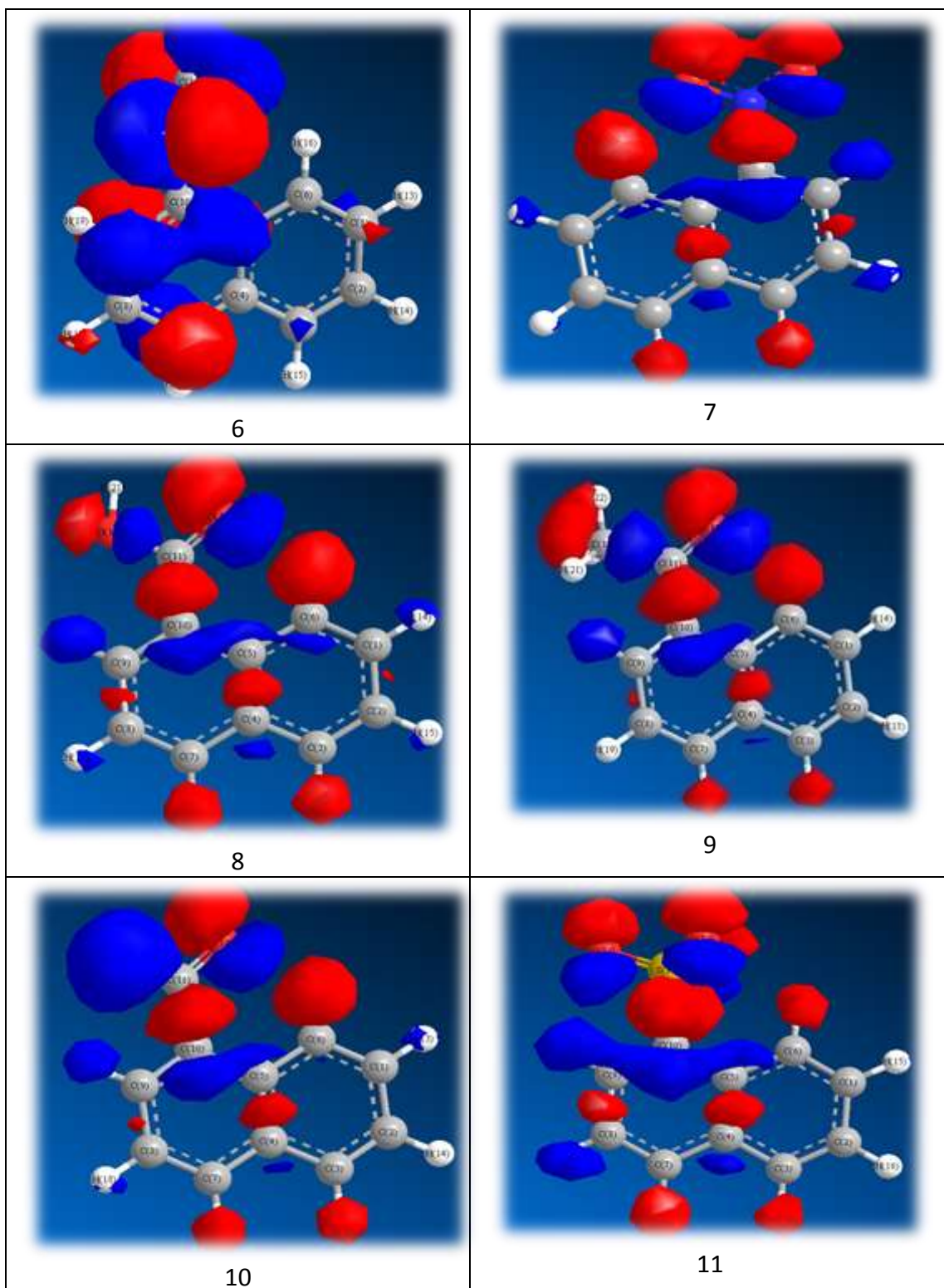
Figure-3-2 HOMO-LUMO molecular orbitals for compounds 1-11 at Semiempirical PM3 level

Table(3-12): Energy of HOMO,LUMO,HOMO-LUMO gap for compounds 1-11

Comp.	HOMO/eV	LUMO/eV	ΔHOMO-LUMO
1	-14.018	-4.002	10.016
2	-13.626	-3.798	9.828
3	-12.087	-3.365	8.722
4	-12.121	-3.534	8.587
5	-10.832	-2.825	8.007
6	-10.491	-3.283	7.209
7	-11.819	-5.031	6.788
8	-12.215	-5.257	6.958
9	-11.401	-5.322	6.079
10	-11.627	-5.957	5.67
11	-11.948	-4,063	7.885

From all above result it is clearly notice that the withdrawing groups decrease the stability(so increasing the activity) of compounds ,hence it is reduced the HOMO-LUMO energy gap   where it is decreasing the energy of LUMO

For compounds 7,8,9,10,11 it is observed that the HOMO & LUMO IS Located nearby the withdrawing group figure (3-2) while the donating group shown less effect on the location of molecular orbitals .

By follow the change in the bond angle of C5-C10-C9 , it was clearly noted that the bond angle is reduced when naphthalene substitute by withdrawing group , it is me be due to reduced the electron density on the carbon atoms so decrease the repulsion forces

On the other hand the donating group increase the value of bond angle as a result of increasing electron density

Abstract

The use of theoretical approaches to determined the stability of   compounds has accomplished more and more along the later years.

In the this research , a set of naphthalene compounds was studied .bonds length , bonds angle , HOMO energy, LUMO energy and HOMO-LUMO energy gap have been determined using GAUSSAIN software in semiempirical PM3 level

The result shown that the withdrawing group increasing the activity of compound by decreasing the HOMO-LUMO energy gap , on the other hand the donating group decrease the activity of compound by increasing the HOMO-LUMO energy gap

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