Iranian Journal of Organic Chemistry Vol. 10, No. 2 (2018) 2357-2372

Synthesis, characterization and Density Functional Theory study of some new Benzotriazole derivatives

Noor HatifOda, Ezzat H. Zimam* and MuhsenAboud Al-Ibadi

Department of Chemistry,Faculty of Science, University of Kufa, An-Najaf, Iraq.

Received: February2018; Revised: March2018; April 2018

Abstract: In this research some 1,3-oxazepine and 1,3-diazepine derivatives were prepared through a two-step process:- first step benzotriazole was converted to [1-(1H-benzo[d][1,2,3]triazol-1-yl)-2-chloroethanone] **[A]** by the reaction betweenbenzotriazole with chloroacetyl chloride in the presence of triethylamine in DMF, Then the conversion of**[A]** to 1-(1H-benzo[d][1,2,3]triazol-1-yl)-2-hydrazinylethanone] **[B]** by reaction with hydrazine in absoluteethanol. Schiff bases **[C_1-C_5]** were synthesized by the condensation of different aromatic aldehydes such as [*p*-dimethylaminobenzaldehyde , 4-chlorobenzaldehyde ,4-nitrobenzaldehyde,4-hydroxybenzaldehyde,4-hydroxy-3-methoxy benzaldehyde]with **[B]**in the presence of glacial acetic acid as catalyst in absolute ethanol, Then the resulting imines derivatives **[C_1-C_5]** were reacted with maleic anhydride and phathalic anhydride in dry benzene to give new 1,3-oxazepine-4,7-dione ring derivatives **[D_1-D_5]** and **[D_6-D_{10}]**respectively. The last prepared compounds were reacted with Benzidineto give 1, 3-diazepine-4, 7-dione derivatives **[F_1-F_{10}]**.All prepared compounds were characterized by melting points and FT-IR spectroscopy, some of them were characterized by ^{1}H-NMR andC.H.N analysis.The molecular geometry, bond lengths, bond angles and energies of the new compound have been investigated by Density Functional Theory (DFT) using B3LYP functional with 6-31G (d, P) basis sets. The frontier molecular orbital (FMO) analysis were considered by theoretical calculations using B3LYP/6-311G (d, P) level.

Keywords: Benztriazole, DFT, 1, 3-Diazepine, 1, 3-Oxazepine, Schiff bases.

Introduction

Benzotriazole and its derivatives are important nitrogen containing heterocyclic compounds with biologically interesting properties and some pharmaceutical applications [1].Benzotriazole derivatives has developed rapidly and has now become an important synthetic tool for many chemical processes, including multistep preparations of drugs, biologically active compounds, and synthetic analogs of natural products.

The multifaceted nature ofbenzotriazole intermediates is embedded in their versatile electronic character: in many cases the benzotriazole hetero-ring can act as an electron-donating or electron-withdrawing moiety, depending on the type of substituent that is attached to nitrogen as shown below [2]. Schiff bases are the important compound owing to their wide range of biological activities and industrial application [3]. Oxazepine-diones is a seven-membered ring containing nitrogen, oxygen and two carbonyl group [4]. Oxazepine and their derivatives have some important biological pharmacological activities [5], psychoactive drugs [6] such as enzyme inhibitors [7], analgesic [8] and antidepressant [9].

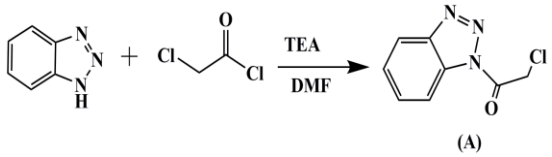
Density Functional Theory (DFT) derives properties of a molecule as a functional of electron density ρ(r). The electron density is defined as the probability of locating an electron(s) in a specific place and tends to zero as the distance between the electron and nucleus tends to infinity. Use of the electron density as the fundamental entity rather than wave function can

*Corresponding author. Tel.: +(96) 47801432660; E-mail: ezat_ahlam@yahoo.com

provide significant advantages [10]. In this research some 1, 3-oxazepine and 1, 3-diazepine derivatives Were prepared via Schiff bases and Density functional theory (DFT) have been investigated.

Results and discussion

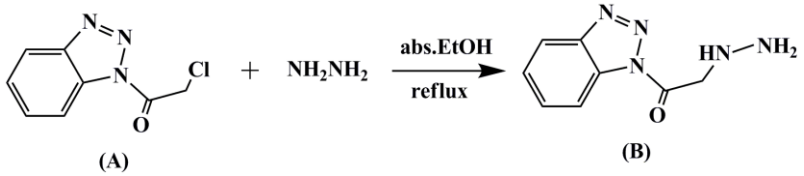
First compound 1-(1*H*-benzo[d][1,2,3]triazol-1-yl)-2-chloroethanone [A] was prepared by reaction benzotriazole with Chloroacetyl chloride in the presence of triethylamine in DMF.



(A)

Scheme 1: Synthesis of compound (A)

The synthesized compound [A] was characterized by sodium fusion which gave the positive test ; that is good evidence for formation this compound .The FT-IR spectrum showed the band at (1722 cm^{-1}) of carbonyl groupsand absorption band at (2991 cm^{-1}) was attributed to the (-CH_2) group. The band at (781 cm^{-1}) was due to the stretching band of (C-Cl) group. The absorption band at (3084 cm^{-1}) was due to the stretching band of (C-H) aromatic ring. The appearance of the band at (1670 cm^{-1}) was due to the (C=C) aromatic group. The absorption band at (1629cm^{-1}) was due to the stretching band of (N=N) of benzotriazolegroup. Compound [A] was converted to the 1-(1H-benzo[d][1,2,3]triazol-1-yl)-2-hydrazinylethanone[B] by reaction with hydrazine in abs. ethanol.

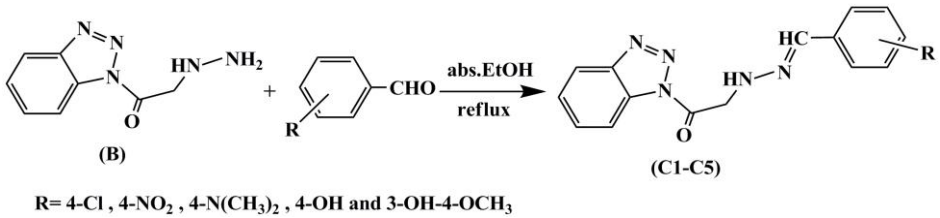


(A) (B)

Scheme 2: Synthesis of compound (B)

The compound [A] undergoes substitution nucleophilic-bimolecular mechanism (S_N2) with hydrazine to give 1-(1H-benzo[d][1,2,3]triazol-1-yl)-2-hydrazinylethanone[B] [11]. The synthesized compound [B] was characterized by FT-IR spectrum showed absorption band at (1622 cm^{-1}) was due to the stretching band of (C=O) group of two absorption bands at (3338) cm^{-1} and (3250) cm^{-1} of the asymmetric and symmetric stretching vibration of the two (-NH_2)groups. Schiff bases [C_1-C_5] were synthesized by the condensation of differentaromatic aldehydes such as:- [*p*-dimethylaminobenzaldehyde,4-chloro benzaldehyde, 4-nitro benzaldehyde, 4-hydroxy benzaldehyde and 4-hydroxy-3-methoxy benzaldehyde with1-(1H-benzo[d][1,2,3]triazol-1-yl)-2-hydrazinylethanone[B] in the presence of two drops of glacial acetic acid as catalyst in absolute ethanol to form:

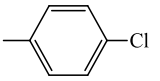
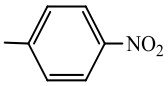
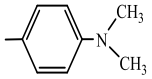
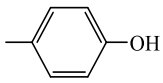
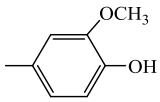
1-(1H-benzo[d][1,2,3]triazol-1-yl)-2-(2-(4-chlorobenzylidene) hydrazinyl)ethanone[C_1] , 1-(1H-benzo[d][1,2,3]triazol-1-yl)-2-(2-(4-nitrobenzylidene)hydrazinyl)ethanone[C_2] , 1-(1H-benzo[d][1,2,3] triazol-1-yl)-2-(2-(4-(dimethylamino)benzylidene)hydrazinyl)ethanone[C_3], 1-(1H-benzo[d][1,2,3]triazol-1-yl)-2-(2-(4-hydroxybenzylidene)hydrazinyl)ethanone[C_4]and 1-(1H-benzo[d][1,2,3]triazol-1-yl)-2-(2-(3-hydroxy-4-methoxybenzylidene) hydrazinyl)ethanone[C_5].



Scheme 3: Synthesis of Schiff bases [C_1-C_5]

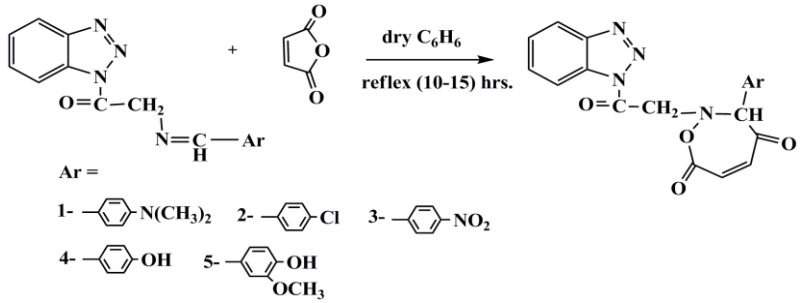
The synthesized compounds [C_1-C_5] were characterized by FT-IR which showed disappearance of two absorption bands at (3338) $cm^{-1}$and (3250) cm^{-1} of the asymmetric and symmetric stretching vibration of the two ($-NH_2$) groups and appearance band at (1597-1685) cm^{-1} of stretching vibration of two (C=N) imine group [12]. Other data of functional groups were showed in Table **1**.

Table 1: FT-IR data of Schiff bases compounds [C_1-C_5].

Comp. No.	Ar.	υ (C=C) Aromatic cm^{-1}	υ (C=N) Imine cm^{-1}	υ (C=O) cm^{-1}	δ(C-H) Bending cm^{-1}	Others cm^{-1}
C_1		1311	1685	1631	935	υ (C-Cl) 815
C_2		1415	1597	1514	941	υ (C-NO_2) 1348
C_3		1369	1647	1598	815	υ (C-N) 1166
C_4		1386	1656	1600	900	υ(C-OH) 3088
C_5		1301	1651	1595	854	υ(C-OH) 3064

Pericyclic reactions, between imine groups of schiff bases [C_1-C_5] and cyclic acid anhydride [maleic anhydride] in dry benzene, were carried out to the synthesis of 1, 3-oxazepine derivatives [D_1-D_5] [13].

Pericyclic reaction is a concerted process based on principle of conservation of molecular orbital symmetry between the reaction components during the reaction proceeding which is leading to a cyclic transition state corresponds with the arrangement of participating orbital's. Concerted reaction means that breaking and formation of bonds occur simultaneously via a single transition state and there is no intermediate in the process, Mechanism [14] of the pericyclic reaction for the synthesis 1, 3-oxazepine ring.



Scheme 4: Synthesis of Oxazepine derivatives [D_1-D_5]

The synthesized compounds [D_1-D_5] were characterized by FT-IR spectra, some of them were characterized by ^{1}H-NMR spectra. The FT-IR spectra of the compounds [D_1-D_5] showed disappearance of absorption bonds at (1597-1685)cm^{-1} was due to the (C=N) of imine group and appearance of the strong absorption band at (1704-1726) cm^{-1} was due to the stretching vibration of the (C=O) lactone group [15], the appearance of the strong absorption band at (1633-1674) cm^{-1} was due to the stretching vibration of the (C=O) lactam group [16]. The other data of functional groups were shown in the following Table **2**. ^{1}H-NMR spectrum (δ ppm), of compound [**D_1**] showed the following characteristic of chemical signals (DMSO-d_6) as a solvent:

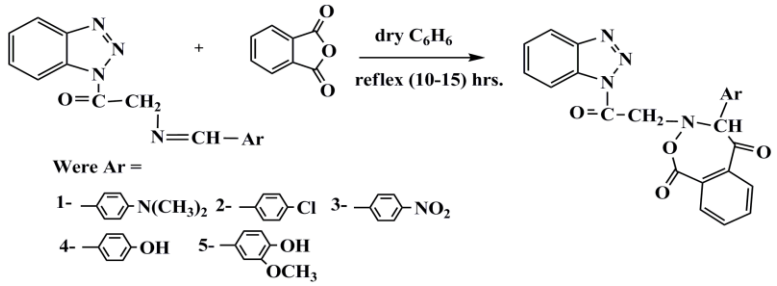
[(2H) (CO-C<u>H</u>$_2$) 3.43-3.50],[(1H)(N<u>H</u>)8.75], [(2<u>H</u>)$_{oxazepine}$ 6.27][(Ar-<u>H</u>) 6.95-7.94]

^{1}H-NMR spectrum (δ ppm), of compound [D_2] showed the following characteristic of chemical signals (DMSO-d_6) as a solvent:

[(1H)(N<u>H</u>)8.85], [(2H) (CO-C<u>H</u>$_2$) 3.43-3.45], [(2<u>H</u>)$_{oxazepine}$ 6.26][(Ar-<u>H</u>) 6.95-8.07

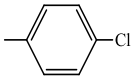
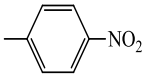
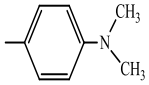
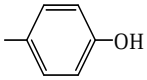
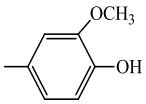
Pericyclic reactions, between imine groups of Schiff bases [C_1-C_5] and cyclic acid anhydride [phathalic anhydride] in dry benzene, were carried out to the synthesis of1, 3-oxazepine derivatives [D_6-D_{10}].

The synthesized compounds [D_6-D_{10}] were characterized by melting points and FT-IR spectra, some of them were characterized by ^{1}H-NMR spectra. The FT-IR spectra of the compounds [D_6-D_{10}] showed disappearance of absorption bonds at (1597-1685)cm^{-1} was due to the (C=N) of imine group and appearance of the strong absorption band at (1681-1714) cm^{-1} was due to the stretching vibration of the (C=O) lactone group [17],The appearance of the strong absorption band at (1585-1699) cm^{-1} was due to the stretching vibration of the (C=O) lactam group [18]. The other data of functional groups were shown in the following Table **3**.



Scheme 5: Synthesis of Oxazepine derivatives [D_6-D_{10}]

Table 2: FT-IR data of compound [D_1-D_5]

Comp. No.	Ar.	υ (C=C) Aromatic cm^{-1}	υ (C-H) oxazepine ring cm^{-1}	υ(C=O)str. Lactone Lactam cm^{-1}	υ (C-N) cm^{-1}	υ (C-O) Lactone cm^{-1}	Others cm^{-1}
D_6		1450	3082	1691 1585	1141	1213	υ (C-Cl) 831
D_7		1490	3082	1689 1585	1141	1211	υ (C-NO_2) 1404
D_8		1404	3525	1693 1591	1172	1213	υ (C-N) 1172
D_9		1446	3338	1681 1593	1165	1278	υ(C-OH) 3338
10		1438	3427	1714 1699	1138	1211	υ(C-OH) 3427

^{1}H-NMR spectrum (δ ppm), of compound [D_9] showed the following characteristic of chemical signals (DMSO-d_6) as a solvent:
[(1H)(N<u>H</u>)10.15], [(2H) (CO-C<u>H</u>$_2$) 3.50-3.62], [(2<u>H</u>)$_{oxazepine}$ 6.85-6.87],[(Ar-<u>H</u>) 7.43-7.92],[(1H) (O-<u>H</u>) 9.78].

^{1}H-NMR spectrum (δ ppm), of compound [D_{10}] showed the following characteristic of chemical signals (DMSO-d_6) as a solvent:
[(1H)(N<u>H</u>)9.78], [(2H) (CO-C<u>H</u>$_2$) 3.83], [(2<u>H</u>)$_{oxazepine}$ 6.86-6.88],(Ar-<u>H</u>) 7.23-7.92].

1, 3-Dizepine derivatives were prepared from reaction between 1, 3-oxazepine withbenzidinein dry benzene and the following compounds are prepared [F_1-F_{10}] is shown in Scheme **6**. Mechanism [19] of the synthesis 1, 3-diazepine ring. The synthesized compounds [F_1-F10] were characterized by FT-IR spectra, some of them were characterized by ^{1}H-NMR spectra. The FT-IR spectra of the compounds [F_1-F_{10}] showed disappearance of the strong absorption band at (1680-1733) cm^{-1} was due to the stretching vibration of the (C=O) lactone group [20], the appearance of the strong absorption band at (1705-1743) cm^{-1} was due to the stretching vibration of the (C=O) lactam group [21].Following Table **4**.

Table 3: FT-IR data ofcompound [D_6-D_{10}].

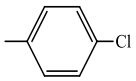
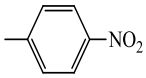
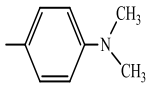
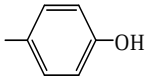
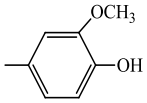
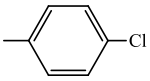
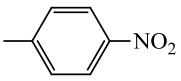
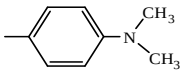
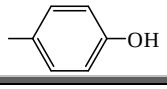
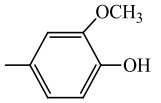
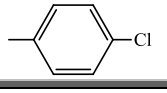
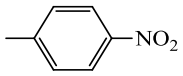
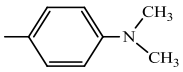
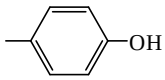
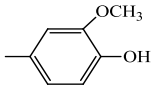
Comp. No.	Ar.	υ (C=C) Aromatic cm^{-1}	υ (C-H) oxazepine ring cm^{-1}	υ(C=O)str. Lactone Lactam cm^{-1}	υ (C-N) cm^{-1}	υ (C-O) Lactone cm^{-1}	Others cm^{-1}
D_6		1450	3082	1691 1585	1141	1213	υ (C-Cl) 831
D_7		1490	3082	1689 1585	1141	1211	υ (C-NO_2) 1404
D_8		1404	3525	1693 1591	1172	1213	υ (C-N) 1172
D_9		1446	3338	1681 1593	1165	1278	υ(C-OH) 3338
D_{10}		1438	3427	1714 1699	1138	1211	υ(C-OH) 3427

Table 4: FT-IR data of compound [F_1-F_{10}]

Comp. No.	Ar.	υ (NH) cm^{-1}	υ (C=C) Aromatic cm^{-1}	υ (C-H) diazepine ring cm^{-1}	υ(C=O)str. Lactone Lactam cm^{-1}	υ (C-N) Lactone cm^{-1}	Others cm^{-1}
F_1		3049	1361	2874	1581 1479	1166	υ (C-Cl) 813
F_2		3043	1357	2874	1589 1492	1163	υ (C-NO_2) 1163
F_3		3035	1363	2802	1600 1490	1180	υ (C-N) 1180

F_4		3049	1492	2927	1668 1593	1168	υ(C-OH) 3413
F_5		3030	1489	2508	1716 1600	1170	υ(C-OH) 3417
F_6		3051	1492	2987	1716 1598	1170	υ (C-Cl) 902
F_7		3028	1494	2920	1701 1668	1170	υ (C-NO_2) 1382
F_8		3053	1498	2922	1705 1614	1176	υ (C-N) 1176
F_9		3032	1444	2858	1600 1494	1174	υ(C-OH) 3419
F_{10}		3030	1496	2860	1597 1558	1170	υ(C-OH) 3030

^{1}H-NMR spectrum (δ ppm), Figure **2**of compound [**F_1**] showed the following characteristic of chemical signals (DMSO-d_6) as a solvent:
[(1H)(N<u>H</u>) 9.3], [(2H) (CO-C<u>H</u>$_2$) 3.38], [(2<u>H</u>)$_{oxazepine}$ 6.20], [(Ar-<u>H</u>)$_{benzidine}$ 6.69-6.78], [(Ar-<u>H</u>) 7.14-7.61]

^{1}H-NMR spectrum (δ ppm), Figure 3 of compound [F_2] showed the following characteristic of chemical signals (DMSO-d_6) as a solvent:
[(1H)(NH)10], [(2H) (CO-C<u>H</u>$_2$) 3.37], [(2<u>H</u>)$_{oxazepine}$ 6.19], [(Ar-<u>H</u>)$_{benzidine}$ 6.67-6.74], [(Ar-<u>H</u>) 7.31-7.61]

^{1}H-NMR spectrum (δ ppm), Figure**4**of compound [**F_9**] showed the following characteristic of chemical signals (DMSO-d_6) as a solvent:
[(1H)(NH)9.9],[(2H) (CO-C<u>H</u>$_2$) 3.37], [(2<u>H</u>)$_{oxazepine}$ 6.69-6.73], [(Ar-<u>H</u>)$_{benzidine}$ 7.30-7.32],[(Ar-<u>H</u>) 7.57-7.59]

^{1}H-NMR spectrum (δ ppm), of compound [**F_{10}**] showed the following characteristic of chemical signals (DMSO-d_6) as a solvent:
[(1H)(N<u>H</u>)9.6], [(2H) (CO-C<u>H</u>$_2$) 3.39], [(2<u>H</u>)$_{oxazepine}$ 6.58-6.66], [(Ar-<u>H</u>)$_{benzidine}$ 7.20-7.77],[(Ar-<u>H</u>) 7.95]

It was found from (C.H.N.) analysis and comparison with the calculated data for compound [A],[B],[C_1],[C_2],[D_1],[D_6],[F_1],[F_6] that a good agreement with experimental data. This is another evidence for formation of compound, the analysis data were listed in Table **5**.

Density Functional Theory (DFT) Study:

In recent years, density functional methods have become the most commonly used theoretical methodology in all the fields of chemistry, essentially in an organic chemistry field. The emergence of hybrid quantum mechanics/molecular mechanics (QM/MM) has permitted the enclosure of the steric effects of bulky groups. Together with these developments, a number of a new tools, such as topological analysis of electron density (Atoms in Molecules Theory), for analyzing electronic structure have been emerged. Nowadays, the theory is in a position to compute ab initio many of the experimental evidences that highlight modern organic chemistry. In the present work, we report quantum chemical investigations into a series of problems related to contemporary organic chemistry. We used Density Functional Theory (DFT) approach to undertake a theoretical investigation of the

structures and stability of the core, d, d_6, f and f_6 compounds.

Table 5: C.H.N. Analysis Data of Compounds

Comp. No.	M.F.	Calculated / found		
		C %	H %	N %
A	$C_8H_6ClN_3O$	49.12 48.97	3.09 2.89	21.48 21.32
B	$C_8H_9N_5O$	50.26 50.13	4.74 4.63	36.63 36.51
C_1	$C_{15}H_{12}ClN_5O$	57.42 57.17	3.86 3.79	22.32 22.25
C_2	$C_{15}H_{12}N_6O_3$	55.55 55.42	3.73 3.64	25.91 25.82
D_1	$C_{19}H_{14}ClN_5O_4$	55.42 55.23	3.43 3.31	17.01 16.88
D_6	$C_{23}H_{16}ClN_5O_4$	59.81 59.77	3.49 3.38	15.16 15.02
F_1	$C_{50}H_{36}C_{l2}N_{12}O_6$	61.80 61.71	3.73 3.62	17.30 17.24
F_6	$C_{58}H_{40}C_{l2}N_{12}O_6$	64.99 64.87	3.76 3.68	15.68 15.57

Computational Methodology:

All gas phase geometry optimizations were performed with Gaussian09 program packages[22] using density functional theory (DFT) method. The molecular structures for all compounds were optimized using the B_3LYP functional [23] and the 6-31G (p, d) basis set [24] which was employed for all atoms. Unrestricted geometry optimizations were carried out, and stationary points were confirmed to be genuine minima by analytical calculation of their harmonic vibration frequencies. Single point energy calculations performed with the PBE1PBE functional and a 6-311G (p, d) basis sets for all atoms. The electronic properties such as energy, Frontier Molecular Orbital (FMO) energy and the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy gap were determined using level of B3LYP/6-311G*.

Geometry optimization:

The optimized structures and structural parameters of the intermediate and the new compounds are shown in figure [3-6] and tables [3-5]. The crystal structure of these new compounds is not available, therefore, the unrestricted geometry optimizations were carried out and stationary points were confirmed by an analytic frequency computation.

The N-N bond lengths lie within 1.27-1.42Å range. The C-N bonds are very close within the range (1.39-1.45Å). Interestingly, the C10-C11 bond lengths decrease from 1.41Å to 1.22Å in the sequence $d_6=f_6>d>f$. The large differences in the C10-C11 bond lengths, particularly in compound f, can be seen as indications of significant π-character between the two carbon atoms.

Molecular Orbital Analysis:

The properties of molecular orbital's such as the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and the HOMO-LUMO energy gap give very important information and easy way to understand the characteristics of an organic molecules regarding its interaction with other species. The HOMO orbital represents an electron donor whereas the LUMO orbital represents as an electron acceptor and the energy gap between these two orbital's helps to

Determine the kinetic stability and chemical reactivity of the molecules. A molecule with small energy gap, where the electrons in HOMO are

Straight away excited to LUMO, was more polarizable and is generally associated with high chemical reactivity and low kinetic stability [25].

The HOMO, LUMO and HOMO-LUMO energy gaps for core, d, d_6, f and f_6 molecules are reported in Table **6**.

The HOMO-LUMO energy gaps for d and d6 are 4.60 eV and 4.91 eV whereas the energy gaps for f and f6 are 2.97 eV and 3.44 eV, respectively. These energy gaps are significantly decreased in the sequence d6>d>f6>f. The results show a relatively large stability of d and d6 compounds whereas;f and f6 compounds show a high chemical reactivity with a good optical property. The contours of HOMO and LUMO ford**, d_6, f** and **f_6**compounds are displayed in Figure **8**. As shown in Figure **7**, in compound **d** the HOMO is focused on phenyl and 1,3oxazepine maleic rings whereas the LUMO is located over 1,3oxazepine maleic ring. Addition Phthalic ring (compound **d_6**), the LUMO is to be found over it. For compounds F and F6 the HOMO is located over benzidine group whereas the LUMO is focused on maleic ring in compound f and, interestingly, located over ring 1 in compound F_6.

Table 6: Selected bond lengths (Å) obtained for core, d, d_6, f and f_6 compounds using B3LYP functional and 6-31G* basis set (hydrogen atoms of phenyl groups omitted).

Parameter	core	D	d_6	F	f_6
C4-C5	1.40	1.41	1.41	1.40	1.40
C4-N1	1.39	1.39	1.39	1.39	1.39
C5-N3	1.39	1.39	1.39	1.39	1.39
N1-N2	1.40	1.40	1.40	1.40	1.40
N2-N3	1.27	1.27	1.27	1.27	1.27
N1-C7	1.42	1.42	1.42	1.43	1.43
C7-C8	1.53	1.53	1.53	1.53	1.53
C8-N4	1.45	1.45	1.45	1.45	1.45
C11-C12	1.34	1.34	1.41	1.22	1.41
N4-N5	-	-	-	1.40	1.42

Table 7: HOMO, LUMO and HOMO-LUMO energy gaps for the compounds core, d, d_6, f and f_6, given in eV.

Comp.	HOMO	LOMO	HOMO-LOMO
Core	-0.273	-0.107	4.53
D	-0.268	-0.099	4.60
d_6	-0.263	-0.082	4.91
F	-0.205	-0.096	2.97
f_6	-0.206	-0.079	3.44

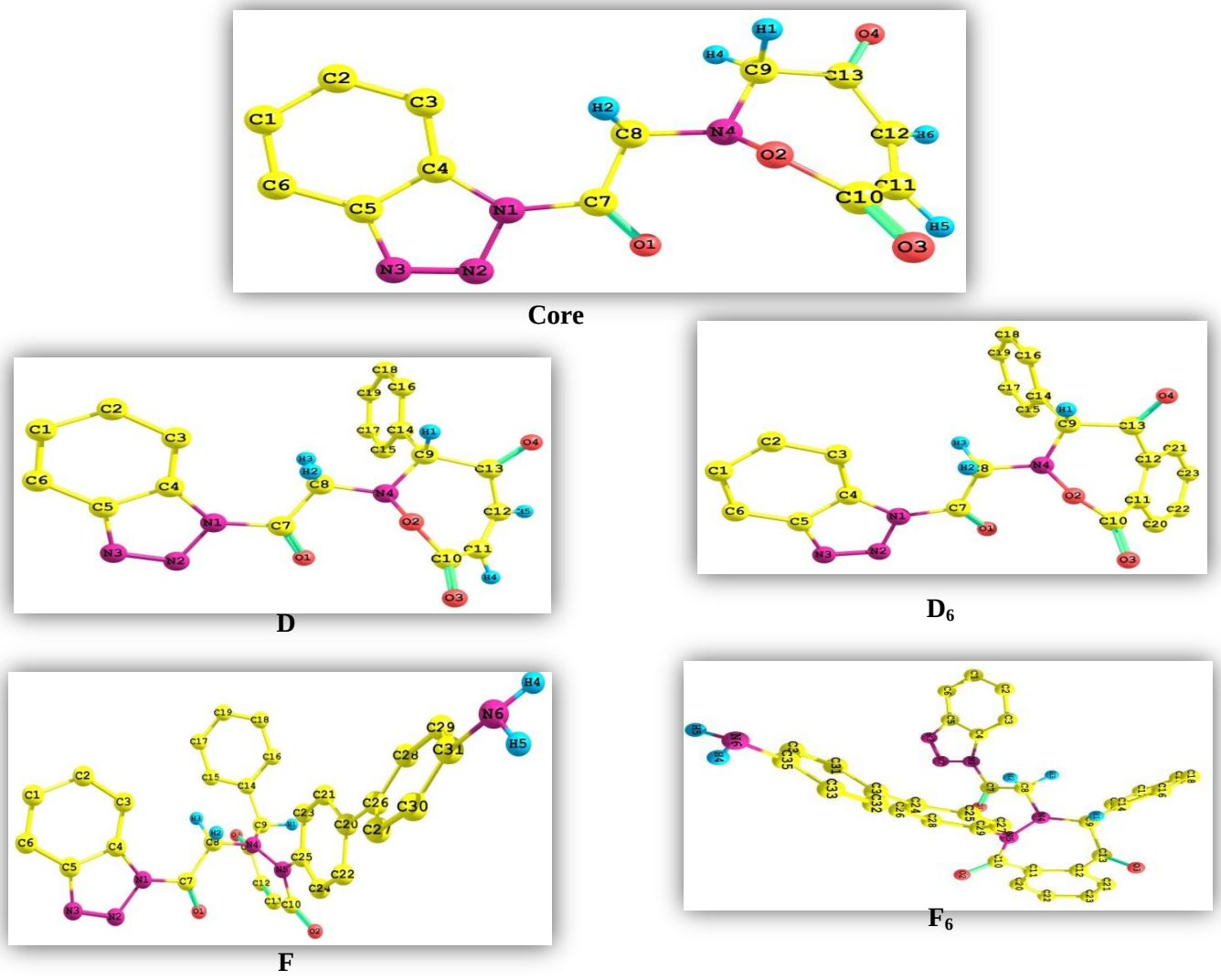
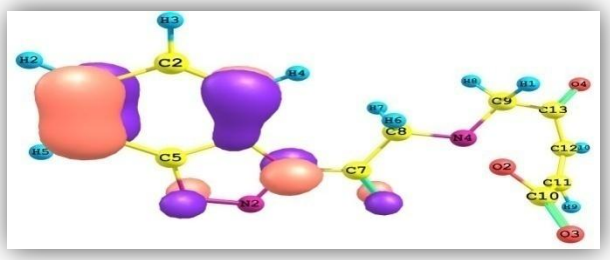
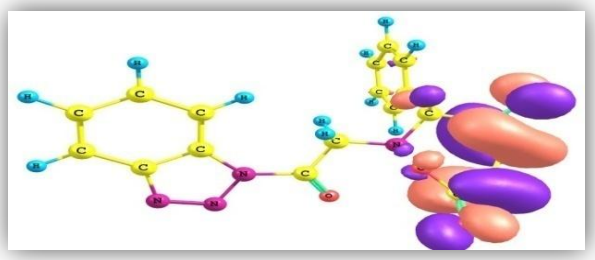


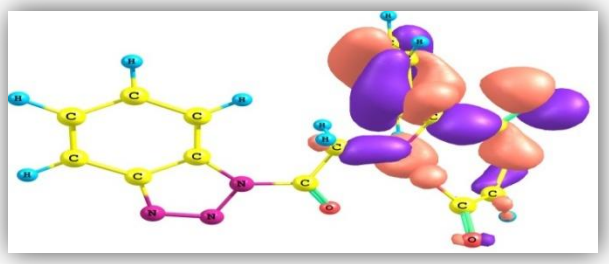
Figure 7: Optimized structures of core, d, d_6, f and $f_6$compounds using B3LYP functional and 6-31G* basis set (hydrogen atoms of phenyl groups omitted).



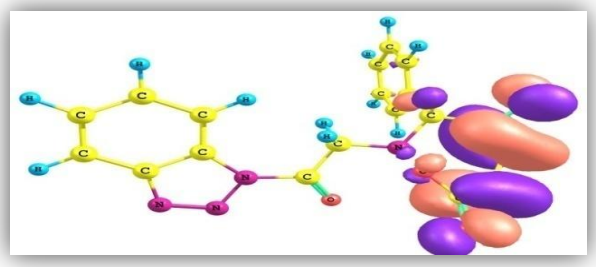
Core HOMO



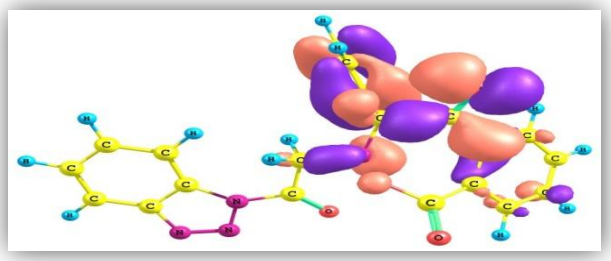
Core LOMO



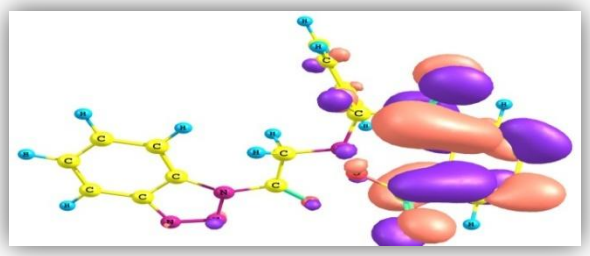
D HOMO



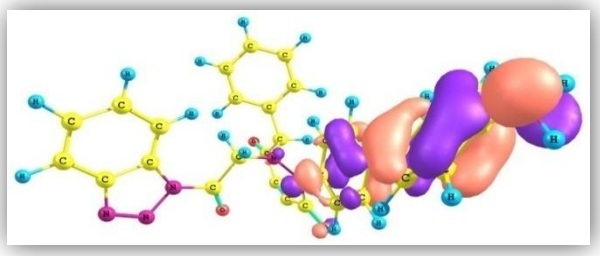
D LOMO



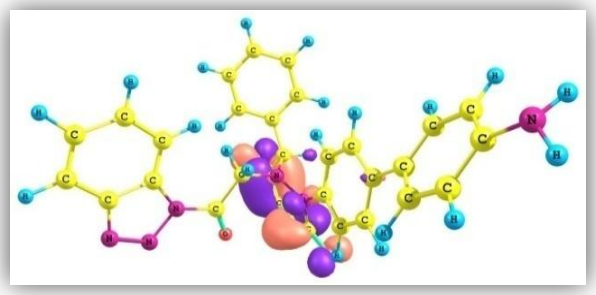
D_6HOMO



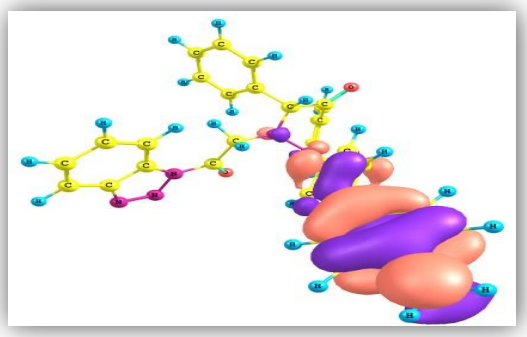
D_6 LOMO



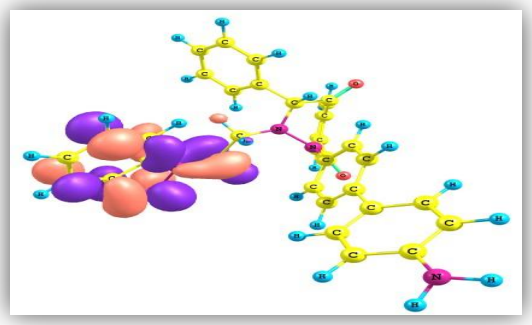
HOMO



F LOMO



HOMO



F_6 LOMO

Figure 8: Frontier molecular orbital's (HOMO and LUMO) of d, d_6, f and $f_6$compounds.

Conclusions

New 1, 3-oxazepine and 1, 3-diazepine derivatives based on benzotriazole have been successfully synthesized. All synthesized compounds were stable by resonance and having high melting points relatively; this is evidence in relation to stability. Diazepine derivatives are more stable than the other derivatives due to its connection with benzotriazole molecule, which increase stability due to high molecular weight and high resonance.The geometry optimization was obtained using Density Functional Theory calculations at the B3LYP level with the 6-31G (d,p) basis set. The HOMO-LUMO energy gaps, calculated at B3LYP/6-311G (d,p), reveals the high activity of f and f6 compound.

Experimental section

All chemicals used were supplied from Merck, BDH and Fluke Chemicals Company. Melting points were recorded using Electro thermal melting point apparatus, UK.
F.T.I.R spectra were recorded using Fourier transform infrared SHIMADZU FT.IR-8400S infrared spectrophotometer by KBr disc, University of Kufa. The elemental analysis were recorded using E.A.G.E.R.-100, Carlo Erba, Italy, measurements were made at the, Biochemistry Lab, Kashan University, Iran. Thin layer chromatography (TLC) was performed on aluminum plates and coated with layer of silica gel, compounds were detected by iodine vapor.^{1}H-NMR were recorded on Fourier transformation Varian spectrometer, operating at (400 MHz) with (DMSO-d_6), measurement were made at the department of chemistry, Kashan University, Iran.

Synthesis of 1-(1H-benzo[d] [1, 2, 3] triazol-yl)-2-chloroethanone [A][26]:

A mixture of benzotriazole (0.01 mol, 1.19g) and triethylamine (1 ml) in DMF, chloroacetyl chloride (0.01 mol, 0.79 ml) was added drop-wise. The reaction mixture was stirred for (3hrs.) at the end of the reaction; finally, the content were filtered, dried and recrystallized with ethanol. Yield dark yellow crystal (86 %),m.p. (56 - 59 ^{0}C) and R_f(0.66) (benzene: methanol, 4:1).

Synthesis of1-(1H-benzo[d][1,2,3]triazol-1-yl)-2-hydrazinylethanone[B]:

A mixture of [A] (0.01mol, 1.95 g) and hydrazine hydrate (0.01)mol in 25 ml of abs. ethanol was refluxed for (3 hrs.) The solid product was collected washed with chloroform and filtered off and recrystallized with chloroform. Yield yellow crystal (84 %),m.p. (80 ^{0}C) and R_f (0.67) (benzene: methanol, 4:1).

General procedure for Synthesis of Schiff bases derivatives [C_1-C_5][27]:

A mixture compound [B] (0.001mol, 0.191g) was added to a solution of appropriate aromatic aldehyde (0.001mol) in 15 ml of absolute ethanol and two drops of glacial acetic acid were, also, added to the above mixture. The mixture was refluxed for (1-3) hrs. The precipitates were formed collected by filtration, dried and recrystallized from ethanol. The TLC showed that the reaction was completed by using (benzene: methanol, 4:1).

General procedure for Synthesis of 1,3-oxazepine-4,7-dione[D_1-D_{10}][28]:

A mixture of Schiff bases [C] (0.01mol) and acid anhydride namely maleic anhydride or phthalic anhydride (0.02mol,1.96g) in dry benzene (250 ml), The reaction mixture was stirred for (10-15 hrs.) at(55 ^{0}C),and at the end of the reaction. The precipitates were collected by filtration and the resulting colored crystalline solid was recrystallized from dry 1,4-dioxan. The TLC showed that the reaction was completed by using (benzene: methanol, 4:1).

General procedure for Synthesis of 1, 3-diazepine-4, 7-dione [F_1-F_{10}][29]:

Mixture (0.02mol) of oxazepine compounds and (0.01mol) of benzidine in dry benzene was placed round bottom flask. The reaction mixture was refluxed in water bath at 78 ^{0}C for(3-5hrs) then allowed to cool to room temperature and separated crystalline was filtered and recrystallized from ethanol. The TLC showed that the reaction was completed by using (benzene: methanol, 4:1).

Table 8: Some physical properties of compounds [C_1-C_5].

Comp. No.	Molecular Formula	M.P ^{0}C	Yield %	R_f	Color
C_1	$C_{15}H_{12}C_lN_5O$	99-100	85	0.65	Pale yellow
C_2	$C_{15}H_{12}N_6O_3$	82-83	88	0.56	yellow
C_3	$C_{17}H_{18}N_6O$	81-82	83	0.58	Brown
C_4	$C_{15}H_{13}N_5O_2$	129-130	87	0.66	Dark Yellow
C_5	$C_{16}H_{15}N_5O_3$	147-148	85	0.75	orange

Table 9: Shows the structure, molecular formula, melting point, yield ,R_f and color of synthesis compounds [D_1-D_{10}].

Comp. No.	**Molecular Formula**	**M.P ^{0}C**	**Yield %**	**R_f**	**Color**
D_1	$C_{19}H_{13}C_lN_5O$	140-141	77	0.66	yellow
D_2	$C_{19}H_{13}N_6O_6$	134-135	78	0.72	yellow
D_3	$C_{21}H_{19}N_6O_4$	120-121	70	0.58	Brown
D_4	$C_{19}H_{14}N_5O_5$	125-126	76	0.68	Yellow
D_5	$C_{20}H_{16}N_5O_6$	120-121	72	0.76	Dark yellow
D_6	$C_{23}H_{15}C_lN_5O_4$	158-159	82	0.57	Yellow
D_7	$C_{23}H_{15}N_6O_6$	164-165	80	0.69	Pale yellow
D_8	$C_{25}H_{21}N_6O_4$	160-161	73	0.75	Red
D_9	$C_{23}H_{16}N_5O_5$	189-190	81	0.56	Yellow
D_{10}	$C_{24}H_{18}N_5O_6$	148-149	82	0.76	Orange

Table 10: shows the structure, molecular formula, melting point, yield, R_f and color of synthesis compounds [F_1-F_{10}]

Comp. No.	Molecular Formula	M.P ^0C	Yield %	R_f	Color
F_1	$C_{50}H_{36}C_{l2}N_{12}O_6$	222-223	75.2	0.62	Green
F_2	$C_{50}H_{36}N_{14}O_{10}$	200-201	73.2	0.64	Black
F_3	$C_{54}H_{48}N_{14}O_6$	195-196	70.5	0.55	Dark brown
F_4	$C_{50}H_{38}N_{12}O_8$	205-206	79.4	0.65	Dark green
F_5	$C_{52}H_{42}N_{12}O_{10}$	195-196	77.9	0.75	Blak
F_6	$C_{58}H_{40}C_{l2}N_{12}O_6$	185-186	73.9	0.61	Greenish yellow
F_7	$C_{58}H_{40}N_{14}O_{10}$	192-193	74.5	0.76	Greenish yellow
F_8	$C_{62}H_{52}N_{14}O_6$	210-211	71.3	0.68	brown
F_9	$C_{58}H_{42}N_{12}O_8$	202-203	78.6	0.58	dark brown
F_{10}	$C_{60}H_{46}N_{12}O_{10}$	220-221	80.2	0.76	Pale green

References and notes

[1] Jimit S. P.; Charoo S. G. and Dhrubo J., *Int. J. Drug Dev. & Res.*, **2012**, *4*, 322.
[2] Katrizky, A.; Lan, X.; Yang, J.; Denisko, O. V. *Chem. Rev*. **1998** , *98*, 409.
[3] Ruaa, W.; Zimam, E. H. *Kerbala J. Pharmaceutical Sci*. **2014**, *7*, 195.
[4] Mohammad A.; Osman H.; Yeap G. *Malaysia Australian J. Basic Appl. Sci*. **2011**, *5*, 192.
[5] Mikim J.; Lee, K. Y.; kim, J. N.; *Bull. Kor. Chem*.; **2002**, *23*, 1055.
[6] Magar, B. K.,; Bhosale, V. N.; Kirdant, A. S.; Chondhekar, T. K. *J. Chem. Bio. Phy. Sci.;* **2012**, 2, 127.
[7] Gauthier, D.; Rivero, R. A. *J. Org. Chem.* **1999**, *64*, 3060.
[8] Bilgic S.; Ozlem M.; Gunduz, M.; Karakoc, N. Arkivoc **2009**, 185.
[9] Jiu, J.; Mizuba, S.; Hribar, J. *Am. Soc. Microbio*. **1977**, *33*, 26.
[10] Szabo, A.; Ostlund, N. S., Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory, *MacMillan Publishing Co*., **1989** New York.
[11] Bruckner, R. "Advanced Organic Chemistry, Reaction Mechan. *Elsevier*"**2003**, p. 49,

[12] Ganesh, M.; Pankaj, N.; Avinash, A.; Sachin, D.; Sharad, S. *Int. J. Innov. Res. Sci. Eng.& Tech.*,**2014**, *3*, 1.
[13] Zainab Amer, S.; AL-Shukry, M. Sc. Thesis, College of Science, *University of Kufa*, **2010**.
[14] Hussain, K. F. Ph.D. Thesis, Faculty of Education Ibn-Al-Haitham, *University of Baghdad* **2005**.
[15] Haiwal, R.T. *J. Kerbala University*, **2008**, 6, 4.
[16] Mukhlus, A. A.; Al-Rawi, M. S.; Tomma, J. H.; Al-Dujaili, A. H.; Ibn Al-Haitham *J. Pure & Appl. Sci.* **2012**, 2, 25.
[17] Ali, F. & Faze A. *AL-Qadisiya J. Science*, **2013**, 18. 2.
[18] Ahmed, N. A.; Obaid, H. A. *Int. J. Appl. Nat. Sci.* **2013** , 2, 3.
[19] Eissa,H. *Org. Chem. Curr. Res*. **2013**, 2.
[20] Emad, Y.; Ayad, H.; Nadia, S.; Jumat, S.; Bashar; M. *SpringerPlus*, **2013**.
[21] Anastasia, A. F.; Ludmila, A. T.; Anatoly, D. Shutalev, *Organic &Biomolecular Chemistry*.**2012**
[22] Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Scalmani G., Barone V., Mennucci B., Petersson G. A., Nakatsuji H., Caricato M., X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L.Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida,T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E.Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N.Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C.Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E.Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E.Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L.Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J.Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J.Cioslowski, and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, **2009** ,*Inc.*,*Wallingford CT*,.
[23] Becke A. D., *J. Chem. Phys.*, **1997**, 107, 8554.
[24] Hehre W. J., Ditchfield R. and Pople J. A., *J. Chem. Phys*., **1972**, 56, 2257.
[25] Ainscough, E. W.; Brodie, A. M.; Dobbs, A. J.; Ranford, J.D,. *Inorg. Chim .Acta*, **1998**, 267, 27.
[26] Hayder, M.; Ezzat K. H. Zimam, *Int. J. Pharma. Sci.* **2014,** 4, 677.
[27] Ezzat, H. Zimam, *Acta. Chim. Pharm. Indica*, **2014**, 4, 180.
[28] AfafH. AFahmy, H. H. and Ali S.H., *Molecules*, **2002**, 5, 1429.
[29] Yass, I. A. Kerbala *J. Sciences*, **2010**,1.