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DFT and HF Studies: Geometry, Hydrogen Bonding, Vibrational Frequencies and Electronic Properties of Enaminones and Their Complexes with Transition Metals

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ABSTRACT

Enaminones are those structures made up three various functional groups including carbonyl, alkene and amine groups which arelocated along with each other in a conjugate fashion. These compounds are of much attention due to special characteristics and numerous applications. In the paper, six various enaminone structures were theoretically optimized and after concluding, were compared with equivalent experimental results. These enaminone structures have been studied for substituent effect on hydrogen bond, method and basic set effects on the geometrical parameters, vibrational frequencies, stability, complex forming, NBO computation and etc. Drawing molecular structures and computer calculations were performed with Gauss view (5.0) and Gaussian (09) software respectively. The utilized methods in the paper were the HF and DFT and of DFT methods of basic functions BLYP, B3LYP, B3P86, B3PW91, SVWN, BVWN and BPV86. Also Basis sets of 6-311G, 6-311G*, 6-311G**, 6-311+G*, 6-311+G**, 6-311++G* 6-311++G**, LANL2DZ and SDD have been utilized which have been applied as proportional to molecular structure and desirable purpose. Generally the results of computer calculations and comparing them with experimental equivalents indicate that theoretical procedures could well be helpful and effective in enaminone studies and offer reasonable and well results.

Keywords: DFT; HF; Enaminone; Complex; Hydrogen bonding.

INTRODUCTION

The term Enaminone is used to indicate any chemical compound containing the conjugated system N-C=C-C=O in its structure [1]. These compounds have shown synthetic utility in therapeutic and biological agents such as ciprofloxacin, taxol, ducarmycin, quinoline, anti-convulsant, anti-malarial, anti-flammatory, anti-fungal, anti-bacterial and anti-tumor [2-10]. In the figure 1 basic structure of enaminones has been illustrated where from R^1 to R^5 functional groups and different substituents could be placed in that. Enaminones contain a wide range of chemical compounds because of possibility of placing different substituents on their conjugated system.

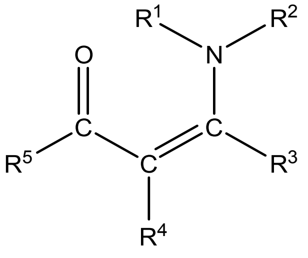

Fig. 1. The general structure of enaminones.

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The conjugated carbonyl group with enaminone generates one stable system for enaminones which cause to make easy synthesizing these compounds at atmospheric conditions and ambient temperature [11, 12]. With regarding to figure 1, if R^1=H holds, then condition for forming hydrogen bond among H and O atoms will be provided. This hydrogen bond which is intramolecular, lead to become stable the enaminone system and subsequently its properties. Moreover, hydrogen bond forming in enaminones lead to generate one six-member ring in the center of enaminone which provide the condition for tautomerism (Figure 2).

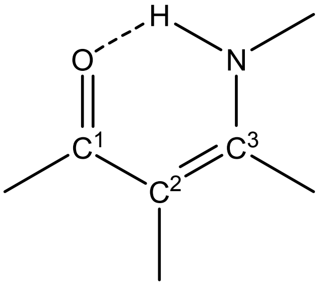


Fig. 2. 6-member ring of enaminones.

Enolimine and Ketamine are two structures of enaminone tautomer which may be formed depending on medium condition and molecular stability (figure 3) [13]. The substituent effect on hydrogen bond strength of enaminones is served as one of the major issues in their stability which has been paid attention to it from both theoretical and experimental aspects in the recent years [14]. Placing substituents with various electron effects in R^2 to R^5 positions contribute on hydrogen bond strength and subsequently enaminone molecule stability that it cause to form the preferred tautomer. In the recent years, enaminones also has received much attention for complex forming to intermediate metals because of improving properties and efficiency of enaminones following complexion [15, 16].

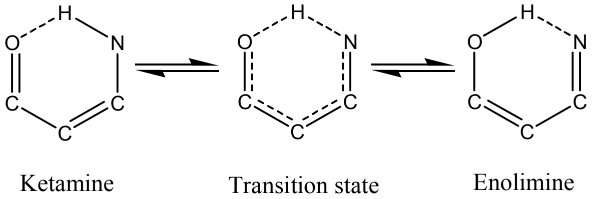


Fig. 3. Enaminone tautomers and their transition state.

The carbonyl group eases the preparation, isolation and storage of the complex, by providing required stability to the system [17]. For instance, Tariq Mahmud et al have synthesized the enaminone complexes using Fe and Zn and then have studied its antibacterial properties [18]. In the paper, various structures of enaminones has been studied from two viewpoints: 1- the substituent effect on the hydrogen bond and its stability and 2- complex forming of enaminones which have a ligand role and be able to form complex to transition metals. This paper which is as theoretical computations and then comparing the results with experimental values, will be given rise to further recognize the enaminones and better investigate their properties.

THEORETICAL METHOD

Computational approach

Density functional (DF) and Hartree-Fock (HF) calculations were performed with Gaussian program. With respect to different enaminone structures in this study, of the various methods in computational chemistry, two methods of HF and DFT and of DFT, seven hybrid functions of BLYP, B3LYP, B3P86, B3PW91, SVWN, BVWN and BPV86 are employed that will be used according to need. Moreover, In Table 1, the used basis sets (BS) and their codes have been listed that will be selected based on the structure elements for each of the enaminones. After complex formation or putting substituent's in R-position, the structures were plotted through Gauss View (version 5.0) software. Then all enaminone structures in selected route sections were calculated and optimized through Gaussian (version 09) program. All information related to geometric parameters and vibrational frequencies were drawn out from Output files.

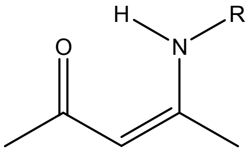
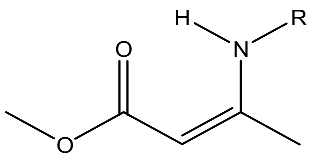
Table 1. Basis sets and their codes

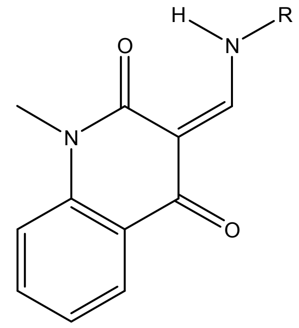
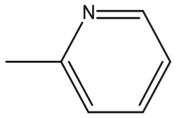
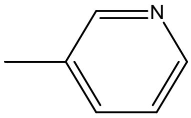
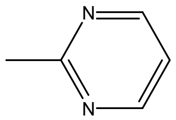
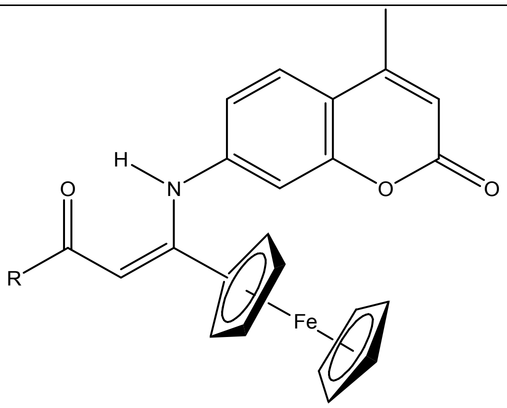
Code	Basis set
BS1	6-311G
BS2	6-311G*
BS3	6-311G**
BS4	6-311+G*
BS5	6-311+G**
BS6	6-311++G*
BS7	6-311++G**
BS8	LANL2DZ
BS9	SDD

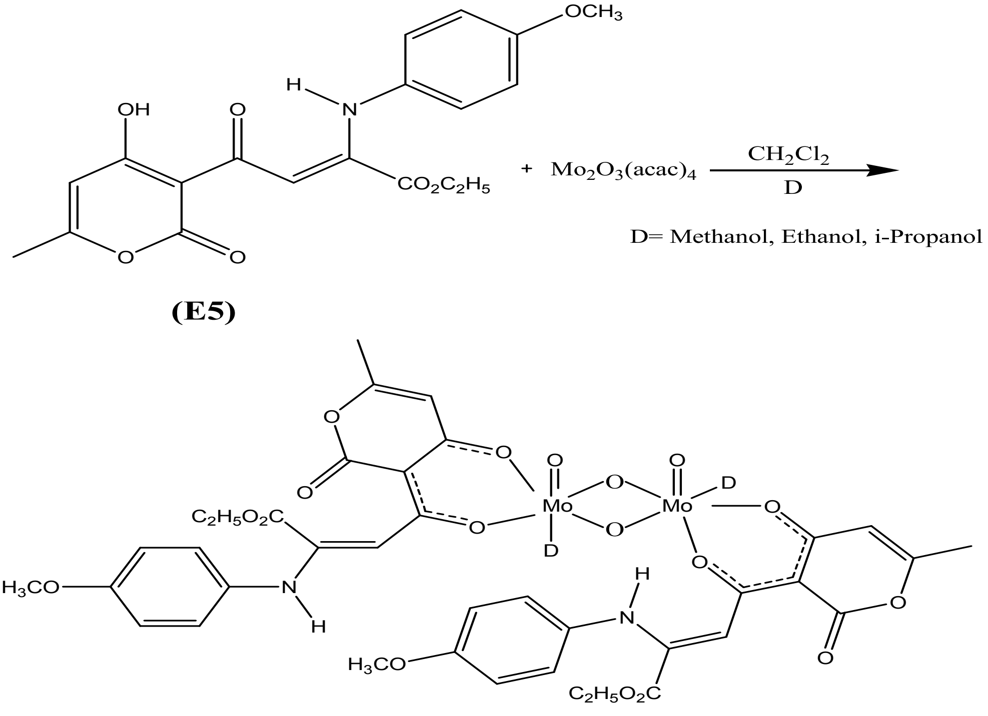
Enaminone structures and complexes

In the paper six structures of enaminone (E1 to E6) were studied which first four of them (E1 to E4) were investigated for the substituent effect on the hydrogen bond and two other structures (E5 and E6) were studied for complex-forming aspect. In Table 2 the structural formulas E1 to E4 and those substituents which are substituted for R group, also have been showed. In each one of E1 to E4 structures firstly individual substituents were substituted in R position and then were optimized in all methods and related basis sets. In figure 4, the structural formula of E5 enaminone and the chemical reaction with molybdenum metal has been showed which leads to form complex [19]. Also in figure 5 enaminone structure E6 and its complex with copper metal is observable [16].

Table 2. Molecular structure of enaminones and their substituents (R)

Enaminone label	Structural formula	R (Substitution)
E1		-ph
		-p-phCH_3
		-p-phOCH_3
		-p-phCl
E2		-o-phCl
		-m-phCl
		-p-phCl
		-o-phOH
		-m-phOH
		-p-phOH
		-o-phCH_3
		-m-phCH_3
		-p-phCH_3
		-o-phOCH_3
		-m-phOCH_3
		-p-phOCH_3

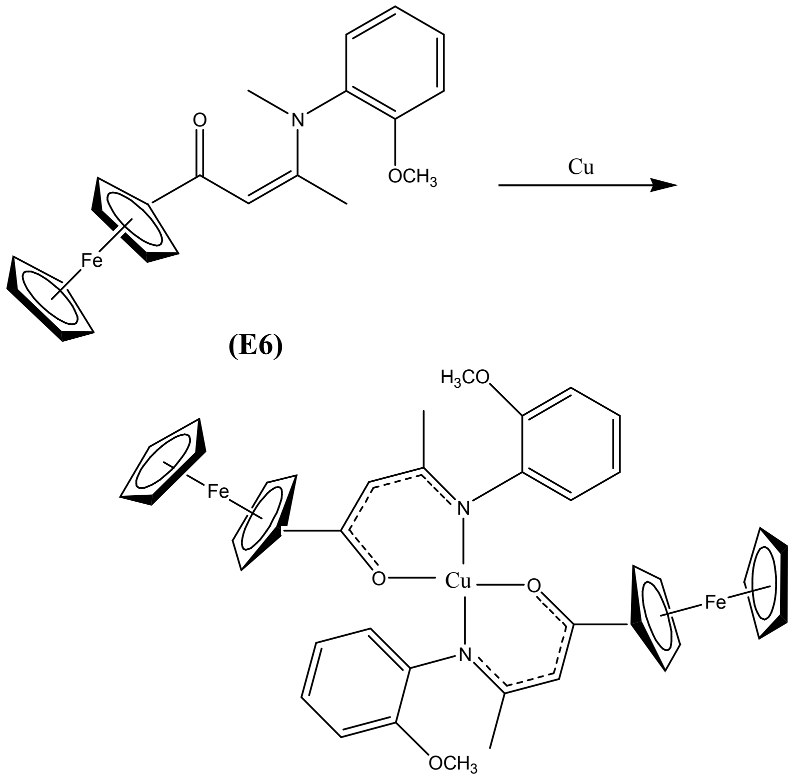
E3		  
E4		-m-phCH$_3$ -p-phCH$_3$ -p-phBr 3,5-dimethylphenyl



D= Methanol, Ethanol, i-Propanol

(Complex 1)

Fig. 4. E5 enaminone structure and its complex with molybdenum metal.



(E6)

(Complex 2)

Fig. 5. E6 enaminone structure and its complex with molybdenum metal.

RESULTS AND DISCUSSION

E1 enaminone

Considering Table 2, four various substituents were placed in R position related to E1 structure and then were optimized. It is necessary to note that four structures of substituents replacing in the E1 molecule were experimentally synthesized and have been studied [20]. In Tables 3 through 5 the results of bond lengths in six-member central ring (fig. 2) corresponded to E1 structure has been reported that in every these tables, method, basis sets, substituents and measured parameters have been given. With regarding to mention results in these tables it could be said that:

- About bond length N-H, DFT methods in compared to HF method has computed more values. Also the results reported in two B3LYP and B3P86 are in relative agreement to each other.
- The computed bond length for N-C by HF and DFT methods does not substantially varied with each other and the results of B3LYP and B3P86 methods have reported the same values.
- About C=C bond length , the results of DFT methods yield higher values than HF results and conversely in the case of C-C bond length, HF results yield higher values than the results of DFT methods.
- The results calculated for C=O bond length does not substantially varies with each other.
- In all three methods of HF, B3LYP and B3P86, -ph and –p-phCl substituents reduce the length of H...O hydrogen bond and cause to increase the its

strength while –p-phOCH$_3$ and –p-phCH$_3$ increase this bond length and reduce the strength of it.

- In one special method, substituent changes do not have any substantial effect on the N-H, N-C, C=C, C-C and C=O bonds length.

Table 3. Geometric results (Å) of E1 structure in HF method

R	Basis set	H-N	N-C	C=C	C-C	C=O	O…H
-ph	BS1	0.99	1.35	1.36	1.43	1.24	1.92
	BS2	0.99	1.35	1.36	1.45	1.21	1.96
	BS3	0.99	1.35	1.36	1.45	1.20	1.95
	BS5	0.99	1.34	1.36	1.45	1.20	1.95
	BS7	0.99	1.35	1.36	1.45	1.20	1.95
-p-phOCH$_3$	BS1	0.99	1.36	1.36	1.43	1.24	1.92
	BS2	0.99	1.35	1.36	1.45	1.21	1.96
	BS3	0.99	1.34	1.36	1.45	1.20	1.95
	BS5	0.99	1.34	1.36	1.45	1.20	1.96
	BS7	0.99	1.35	1.36	1.45	1.21	1.96
-p-phCH$_3$	BS1	0.99	1.36	1.37	1.44	1.24	1.93
	BS2	0.99	1.35	1.36	1.45	1.20	1.97
	BS3	0.99	1.34	1.36	1.45	1.20	1.95
	BS5	0.99	1.35	1.36	1.45	1.21	1.96
	BS7	0.99	1.34	1.36	1.45	1.21	1.96
-p-phCl	BS1	0.99	1.36	1.36	1.44	1.24	1.92
	BS2	0.99	1.35	1.35	1.45	1.20	1.96
	BS3	0.99	1.35	1.36	1.46	1.21	1.95
	BS5	0.99	1.35	1.36	1.45	1.20	1.95
	BS7	0.99	1.35	1.36	1.45	1.21	1.95

Table 4. Geometric results (Å) of E1 structure in B3LYP method

R	Basis set	H-N	N-C	C=C	C-C	C=O	O…H
-ph	BS1	1.03	1.36	1.39	1.43	1.28	1.76
	BS2	1.02	1.35	1.38	1.44	1.24	1.81
	BS3	1.02	1.35	1.38	1.44	1.24	1.81
	BS5	1.03	1.35	1.38	1.44	1.25	1.77
	BS7	1.02	1.35	1.38	1.43	1.24	1.81
-p-phOCH$_3$	BS1	1.03	1.36	1.39	1.43	1.28	1.76
	BS2	1.02	1.35	1.38	1.44	1.24	1.80
	BS3	1.02	1.35	1.38	1.44	1.24	1.81
	BS5	1.03	1.35	1.38	1.44	1.24	1.81
	BS7	1.03	1.35	1.38	1.44	1.24	1.82
-p-phCH$_3$	BS1	1.03	1.36	1.38	1.43	1.28	1.76
	BS2	1.02	1.36	1.37	1.44	1.24	1.81
	BS3	1.02	1.35	1.38	1.44	1.24	1.81
	BS5	1.03	1.35	1.38	1.43	1.24	1.82
	BS7	1.03	1.35	1.38	1.44	1.24	1.82
-p-phCl	BS1	1.03	1.36	1.38	1.43	1.28	1.78
	BS2	1.02	1.36	1.37	1.44	1.24	1.80
	BS3	1.02	1.36	1.38	1.44	1.24	1.79
	BS5	1.02	1.36	1.38	1.44	1.24	1.81
	BS7	1.03	1.35	1.37	1.44	1.24	1.80

In order to study the method effect on the IR frequencies, in Tables 6 through 8 which everyone relates to one method, vibrational modes corresponded to C=O and N-H stretching have been showed. Reason of selecting these two stretching vibrations was due to higher strength of them in IR range than other vibrations. In respect to the results, it is found that generally those frequencies values calculated in HF method in compared to DFT are higher. Also about stretching vibration N-H, the results show that basis sets of BS2 and BS7 yielded highest values respectively for DFT and HF methods which indicates the effect of basis sets on the IR frequencies.

Table 5. Geometric results (Å) of E1 structure in B3P86 method

R	Basis set	H-N	N-C	C=C	C-C	C=O	O…H
-ph	BS1	1.03	1.36	1.39	1.42	1.27	1.70
	BS2	1.02	1.35	1.37	1.43	1.24	1.79
	BS3	1.03	1.35	1.38	1.43	1.24	1.74
	BS5	1.03	1.34	1.38	1.43	1.24	1.71
	BS7	1.03	1.34	1.38	1.43	1.24	1.73
-p-phOCH$_3$	BS1	1.03	1.35	1.38	1.42	1.28	1.71
	BS2	1.02	1.34	1.38	1.43	1.24	1.79
	BS3	1.02	1.35	1.38	1.43	1.24	1.75
	BS5	1.03	1.35	1.38	1.43	1.24	1.75
	BS7	1.03	1.34	1.37	1.43	1.24	1.75
-p-phCH$_3$	BS1	1.03	1.35	1.38	1.43	1.28	1.74
	BS2	1.02	1.35	1.37	1.43	1.23	1.79
	BS3	1.03	1.35	1.38	1.43	1.24	1.75
	BS5	1.03	1.34	1.37	1.43	1.24	1.75
	BS7	1.03	1.35	1.38	1.43	1.24	1.75
-p-phCl	BS1	1.03	1.36	1.38	1.42	1.27	1.73
	BS2	1.02	1.35	1.37	1.44	1.24	1.78
	BS3	1.03	1.35	1.37	1.43	1.24	1.74
	BS5	1.03	1.34	1.38	1.43	1.24	1.74
	BS7	1.03	1.34	1.37	1.43	1.24	1.74

Table 6. Vibrational frequencies (cm^{-1}) of E1 structure in HF method

Stretch mode (Substitution)	BS1	BS2	BS3	BS5	BS7
N-H (-ph)	3730.68	3806.92	3761.23	3758.36	3758.40
N-H (-p-phOCH$_3$)	3732.82	3805.90	3764.06	3761.60	3761.69
N-H (-p-phCH$_3$)	3734.42	3809.71	3764.03	3761.63	3761.80
N-H (-p-phCl)	3723.19	3802.57	3757.52	3755.36	3755.54
C=O (-ph)	1771.57	1895.62	1891.93	1874.98	1874.89
C=O (-p-phOCH$_3$)	1799.41	1895.01	1891.50	1874.46	1874.38
C=O (-p-phCH$_3$)	1799.71	1894.89	1891.36	1874.18	1874.12
C=O (-p-phCl)	1803.69	1898.19	1894.32	1877.46	1877.39

Table 7. Vibrational frequencies (cm^{-1}) of E1 structure in B3LYP method

Stretch mode (Substitution)	**BS1**	**BS2**	**BS3**	**BS5**	**BS7**
N-H (-ph)	3201.70	3330.06	3293.42	3244.13	3300.48
N-H (-p-phOCH$_3$)	3209.70	3318.37	3299.53	3305.71	3305.89
N-H (-p-phCH$_3$)	3204.85	3332.09	3299.98	3307.14	3307.09
N-H (-p-phCl)	3238.83	3319.88	3279.13	3287.92	3288.28
C=O (-ph)	1669.29	1677.83	1675.52	1643.81	1662.84
C=O (-p-phOCH$_3$)	1689.40	1663.83	1675.58	1662.84	1662.73
C=O (-p-phCH$_3$)	1669.52	1675.97	1675.23	1662.79	1662.69
C=O (-p-phCl)	1667.77	1679.89	1676.24	1663.49	1663.41

Table 8. Vibrational frequencies (cm^{-1}) of E1 structure in B3P86 method

Stretch mode (Substitution)	**BS1**	**BS2**	**BS3**	**BS5**	**BS7**
N-H (-ph)	3129.84	3304.85	3224.74	3160.96	3191.73
N-H (-p-phOCH$_3$)	3141.71	3308.79	3234.34	3239.37	3239.68
N-H (-p-phCH$_3$)	3211.43	3311.14	3234.67	3240.48	3240.78
N-H (-p-phCl)	3179.14	3290.88	3206.13	3214.98	3215.39
C=O (-ph)	1605.38	1697.29	1690.35	1660.57	1670.64
C=O (-p-phOCH$_3$)	1602.98	1697.22	1690.84	1679.88	1679.78
C=O (-p-phCH$_3$)	1613.89	1696.95	1690.42	1679.72	1679.70
C=O (-p-phCl)	1615.05	1697.80	1690.85	1680.01	1679.95

HOMO and LUMO are acronyms for Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital, respectively. The energy difference between the HOMO and LUMO is termed the HOMO-LUMO Gap (Gap$_{\text{HO-LU}}$). Gap$_{\text{HO-LU}}$ can be a criterion for estimation of molecules stability. The more is (Gap$_{\text{HO-LU}}$), the more stable is the structure because if the molecule has been excited, the more rigid electron can transition from HOMO into LUMO and as result thestructure becomes more stable. In Table 9, energy level values of HOMO and LUMO related to enaminone structure E1 have been listed. In this table, methods and basis sets for each substituent has been indicated. With looking closely at the results of Table 9, it could be concluded that in DFT methods, order of energy level increasing HOMO in compared to substituents is as following:

(-p-phCl) < (-ph) < (-p-phCH$_3$) < (-p-phOCH$_3$)

Since for energy level LUMO this order is as following:

(-ph) < (-p-phCH$_3$) < (-p-phOCH$_3$) < (-p-phCl)

Therefore it could be concluded that enaminone structure containing substituent -p-phCl with highest level of LUMO and lowest level HOMO has most Gap $_{\text{HO-LU}}$ and more stability than other substituents. Also the results reveal that in HF calculations, the order of energies increasing for level HOMO is as:

(-p-phCl) < (-p-phCH$_3$) < (-ph) < (-p-phOCH$_3$)

and for level LUMO is as:

(-p-phCH$_3$) < (-ph) < (-p-phOCH$_3$) < (-p-phCl) which indicate being effective of substituent effect on the Gap $_{\text{HO-LU}}$ besides relative supporting the DFT method.

Table 9. HOMO and LUMO values of E1 structure

R	Basis set	HF		B3LYP		B3P86	
		HOMO	**LUMO**	**HOMO**	**LUMO**	**HOMO**	**LUMO**
-ph	**BS1**	-0.31169	0.11968	-0.21183	-0.05121	-0.23432	-0.07311
-p-phOCH_3		-0.31225	0.11718	-0.20478	-0.04523	-0.22655	-0.06705
-p-phCH_3		-0.30978	0.12071	-0.20822	-0.04825	-0.23574	-0.05395
-p-phCl		-0.32070	0.10368	-0.22290	-0.04210	-0.24537	-0.06311
-ph	**BS2**	-0.30808	0.11965	-0.20875	-0.04500	-0.23567	-0.04996
-p-phOCH_3		-0.30970	0.11890	-0.20151	-0.03989	-0.23559	-0.04996
-p-phCH_3		-0.30797	0.12120	-0.20526	-0.04242	-0.23450	-0.04888
-p-phCl		-0.31430	0.10642	-0.21441	-0.05308	-0.24311	-0.05756
-ph	**BS3**	-0.30977	0.12178	-0.21324	-0.02848	-0.23602	-0.05010
-p-phOCH_3		-0.30968	0.11786	-0.21313	-0.02853	-0.23589	-0.05008
-p-phCH_3		-0.30796	0.12065	-0.21142	-0.02683	-0.23412	-0.04832
-p-phCl		-0.31685	0.10679	-0.21944	-0.03757	-0.24204	-0.05885
-ph	**BS5**	-0.31269	0.05778	-0.21556	-0.05419	-0.23680	-0.07512
-p-phOCH_3		-0.31244	0.05865	-0.21891	-0.03573	-0.24039	-0.05574
-p-phCH_3		-0.31063	0.05875	-0.21692	-0.03381	-0.23838	-0.05379
-p-phCl		-0.31907	0.05502	-0.22443	-0.04341	-0.24584	-0.06305
-ph	**BS7**	-0.31267	0.03486	-0.21892	-0.03569	-0.24165	-0.05918
-p-phOCH_3		-0.31243	0.03509	-0.21892	-0.03581	-0.24039	-0.05578
-p-phCH_3		-0.31062	0.03464	-0.21692	-0.03390	-0.23837	-0.05383
-p-phCl		-0.31906	0.03363	-0.22444	-0.04340	-0.24584	-0.06303

In quantum chemistry, a natural bond orbital or NBO is a calculated bonding orbital with maximum electron density. The NBOs are one of a sequence of natural localized orbital sets that include "natural atomic orbitals" (NAO), "natural hybrid orbitals" (NHO), "natural bonding orbitals" (NBO) and "natural (semi-)localized molecular orbitals" (NLMO). In the paper, the charge of any of atoms involved at hydrogen bond and quantity of energy interaction of their orbitals for enaminone structure E1 have been calculated using theoretical calculations NBO. It is clear that in six-members ring center of enaminone, more the positive charge on hydrogen and negative charge on oxygen, subsequently stronger the hydrogen bond among these two atoms and as result more stable of enaminone structure. In Table 10 through 12 the results of these calculations has been showed which each table corresponds to one method. Through closely looking at the results it could be concluded that substituents -p-phOCH_3 and -p-phCH_3 reduce the negative charge on the nitrogen atom and positive charge on hydrogen atom but enhance the negative charge on the oxygen atom. Also substituent -p-phCl in compared to substituent –ph enhance the negative charge on the nitrogen and positive charge on the hydrogen but lead to lessen the negative charge on the oxygen atom.

Table 10. NBO results of E1 structure in HF method

Basis Set	**R**	**Charge**			**Natural Electron Configuration**		
		N	**H**	**O**	**N**	**H**	**O**
BS1	-ph	-0.69674	0.45305	-0.73089	2s(1.22) 2p(4.47) 3p(0.01)	1s(0.54)	2s(1.71) 2p(5.02)
	-p-phOCH$_3$	-0.69545	0.45205	-0.73146	2s(1.22) 2p(4.46) 3p(0.01)	1s(0.55)	2s(1.71) 2p(5.02)
	-p-phCH$_3$	-0.69422	0.45201	-0.73149	2s(1.22) 2p(4.46) 3p(0.01)	1s(0.55)	2s(1.71) 2p(5.02)
	-p-phCl	-0.70081	0.45485	-0.72780	2s(1.22) 2p(4.47) 3p(0.01)	1s(0.54)	2s(1.71) 2p(5.01)
BS2	-ph	-0.69025	0.43558	-0.72479	2s(1.21) 2p(4.46) 3p(0.01)	1s(0.56)	2s(1.68) 2p(5.03) 3p(0.01)
	-p-phOCH$_3$	-0.69024	0.43470	-0.72568	2s(1.21) 2p(4.46) 3p(0.01)	1s(0.56)	2s(1.68) 2p(5.03) 3p(0.01) 3d(0.01)
	-p-phCH$_3$	-0.68995	0.43494	-0.72561	2s(1.21) 2p(4.46) 3p(0.01)	1s(0.56)	2s(1.68) 2p(5.03) 3p(0.01) 3d(0.01)
	-p-phCl	-0.69213	0.43671	-0.72247	2s(1.21) 2p(4.46) 3p(0.01)	1s(0.56)	2s(1.68) 2p(5.03) 3p(0.01) 3d(0.01)
BS3	-ph	-0.69808	0.44122	-0.72616	2s(1.21) 2p(4.47) 3p(0.01)	1s(0.55)	2s(1.68) 2p(5.03) 3p(0.01) 3d(0.01)
	-p-phOCH$_3$	-0.69584	0.43997	-0.72670	2s(1.21) 2p(4.47) 3p(0.01)	1s(0.56)	2s(1.68) 2p(5.03) 3p(0.01) 3d(0.01)
	-p-phCH$_3$	-0.69559	0.44021	-0.72666	2s(1.21) 2p(4.47) 3p(0.01)	1s(0.56)	2s(1.68) 2p(5.03) 3p(0.01) 3d(0.01)
	-p-phCl	-0.70089	0.44252	-0.72390	2s(1.21) 2p(4.47) 3p(0.01)	1s(0.56)	2s(1.68) 2p(5.03) 3p(0.01) 3d(0.01)
BS5	-ph	-0.70808	0.44637	-0.72764	2s(1.22) 2p(4.46) 4p(0.02)	1s(0.55)	2s(1.68) 2p(5.03) 3d(0.01)
	-p-phOCH$_3$	-0.70566	0.44662	-0.72841	2s(1.21) 2p(4.46) 4p(0.01)	1s(0.55)	2s(1.68) 2p(5.03) 3p(0.01) 3d(0.01)
	-p-phCH$_3$	-0.70506	0.44526	-0.72827	2s(1.22) 2p(4.46) 4p(0.02)	1s(0.55)	2s(1.68) 2p(5.03) 3d(0.01)
	-p-phCl	-0.71076	0.44735	-0.72546	2s(1.22) 2p(4.47) 4p(0.02)	1s(0.55)	2s(1.68) 2p(5.03) 3d(0.01)
BS7	-ph	-0.70675	0.44603	-0.72742	2s(1.22) 2p(4.46) 4p(0.02)	1s(0.55)	2s(1.68) 2p(5.03) 3d(0.01)
	-p-phOCH$_3$	-0.70416	0.44477	-0.72810	2s(1.22) 2p(4.46) 4p(0.02)	1s(0.55)	2s(1.68) 2p(5.03) 3p(0.01) 3d(0.01)

	-p-phCH$_3$	-0.70382	0.44493	-0.72806	2s(1.22) 2p(4.46) 4p(0.01)	1s(0.55)	2s(1.68) 2p(5.03) 3p(0.01) 3d(0.01)
	-p-phCl	-0.70955	0.44706	-0.72523	2s(1.22) 2p(4.47) 4p(0.02)	1s(0.55)	2s(1.68) 2p(5.03) 3d(0.01)

Table 11. NBO results of E1 structure in B3LYP method

Basis Set	**R**	**Charge**			**Natural Electron Configuration**		
		N	**H**	**O**	**N**	**H**	**O**
BS1	-ph	-0.57241	0.44148	-0.66076	2s(1.23) 2p(4.34) 3p(0.01)	1s(0.55)	2s(1.73) 2p(4.93)
	-p-phOCH$_3$	-0.57564	0.44189	-0.66056	2s(1.23) 2p(4.34) 3p(0.01)	1s(0.55)	2s(1.73) 2p(4.93)
	-p-phCH$_3$	-0.57224	0.44155	-0.66248	2s(1.23) 2p(4.34) 3p(0.01)	1s(0.55)	2s(1.73) 2p(4.93)
	-p-phCl	-0.61074	0.44528	-0.65098	2s(1.23) 2p(4.35) 3p(0.01)	1s(0.55)	2s(1.73) 2p(4.92)
BS2	-ph	-0.57340	0.42929	-0.64626	2s(1.22) 2p(4.35) 3p(0.01)	1s(0.57)	2s(1.70) 2p(4.94)
	-p-phOCH$_3$	-0.57518	0.43119	-0.65841	2s(1.22) 2p(4.35) 3p(0.01)	1s(0.56)	2s(1.70) 2p(4.95)
	-p-phCH$_3$	-0.57332	0.42936	-0.64801	2s(1.22) 2p(4.35) 3p(0.01)	1s(0.57)	2s(1.70) 2p(4.94)
	-p-phCl	-0.57400	0.42981	-0.64385	2s(1.22) 2p(4.35) 3p(0.01)	1s(0.57)	2s(1.70) 2p(4.94)
BS3	-ph	-0.61355	0.43923	-0.65113	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.56)	2s(1.70) 2p(4.94)
	-p-phOCH$_3$	-0.61242	0.43828	-0.65156	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.56)	2s(1.70) 2p(4.94)
	-p-phCH$_3$	-0.61139	0.43840	-0.65168	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.56)	2s(1.70) 2p(4.94)
	-p-phCl	-0.61691	0.44017	-0.64914	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.55)	2s(1.70) 2p(4.94)
BS5	-ph	-0.58684	0.44379	-0.66267	2s(1.22) 2p(4.34) 3p(0.01) 4p(0.01)	1s(0.55)	2s(1.70) 2p(4.95) 3p(0.01)
	-p-phOCH$_3$	-0.61969	0.44702	-0.65806	2s(1.23) 2p(4.37) 3p(0.01) 4p(0.01)	1s(0.55)	2s(1.70) 2p(4.95) 3p(0.01)
	-p-phCH$_3$	-0.61833	0.44707	-0.65829	2s(1.23) 2p(4.37) 3p(0.01) 4p(0.01)	1s(0.55)	2s(1.70) 2p(4.94) 3p(0.01)
	-p-phCl	-0.62425	0.44863	-0.65558	2s(1.23) 2p(4.38) 3p(0.01) 4p(0.01)	1s(0.55)	2s(1.70) 2p(4.94) 3p(0.01)
BS7	-ph	-0.62075	0.44724	-0.65680	2s(1.23) 2p(4.37) 3p(0.01) 4p(0.01)	1s(0.55)	2s(1.70) 2p(4.94) 3p(0.01)

	-p-phOCH$_3$	-0.61964	0.44634	-0.65728	2s(1.23) 2p(4.37) 3p(0.01) 4p(0.01)	1s(0.55)	2s(1.70) 2p(4.94) 3p(0.01)
	-p-phCH$_3$	-0.61828	0.44638	-0.65753	2s(1.23) 2p(4.37) 3p(0.01) 4p(0.01)	1s(0.55)	2s(1.70) 2p(4.94) 3p(0.01)
	-p-phCl	-0.62426	0.44798	-0.65476	2s(1.23) 2p(4.38) 3p(0.01) 4p(0.01)	1s(0.55)	2s(1.70) 2p(4.94) 3p(0.01)

Table 12. NBO results of E1 structure in B3P86 method

Basis Set	**R**	**Charge**			**Natural Electron Configuration**		
		N	**H**	**O**	**N**	**H**	**O**
BS1	-ph	-0.56916	0.44521	-0.66198	2s(1.22) 2p(4.34) 3p(0.01)	1s(0.55)	2s(1.72) 2p(4.93)
	-p-phOCH$_3$	-0.57146	0.44568	-0.66617	2s(1.22) 2p(4.34) 3p(0.01)	1s(0.55)	2s(1.73) 2p(4.94)
	-p-phCH$_3$	-0.60260	0.44799	-0.65582	2s(1.22) 2p(4.37) 3p(0.01)	1s(0.55)	2s(1.73) 2p(4.93)
	-p-phCl	-0.60908	0.44978	-0.65243	2s(1.22) 2p(4.37) 3p(0.01)	1s(0.55)	2s(1.72) 2p(4.94)
BS2	-ph	-0.60718	0.43904	-0.65054	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.56)	2s(1.70) 2p(4.94)
	-p-phOCH$_3$	-0.60611	0.43813	-0.65100	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.56)	2s(1.70) 2p(4.94)
	-p-phCH$_3$	-0.60352	0.44457	-0.63804	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.55)	2s(1.71) 2p(4.93)
	-p-phCl	-0.60913	0.44626	-0.63520	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.55)	2s(1.71) 2p(4.92)
BS3	-ph	-0.61219	0.44438	-0.65218	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.55)	2s(1.70) 2p(4.95)
	-p-phOCH$_3$	-0.61109	0.44345	-0.65258	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.55)	2s(1.70) 2p(4.95)
	-p-phCH$_3$	-0.60998	0.44358	-0.65274	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.55)	2s(1.70) 2p(4.95)
	-p-phCl	-0.61535	0.44514	-0.65018	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.55)	2s(1.70) 2p(4.94)
BS5	-ph	-0.58416	0.44679	-0.66065	2s(1.22) 2p(4.34) 3p(0.01) 4p(0.01)	1s(0.55)	2s(1.70) 2p(4.95) 3p(0.01)
	-p-phOCH$_3$	-0.61947	0.45108	-0.65642	2s(1.22) 2p(4.38) 3p(0.01) 4p(0.01)	1s(0.55)	2s(1.70) 2p(4.94) 3p(0.01)
	-p-phCH$_3$	-0.61811	0.45113	-0.65666	2s(1.22) 2p(4.37) 3p(0.01) 4p(0.01)	1s(0.55)	2s(1.70) 2p(4.94) 3p(0.01)
	-p-phCl	-0.62393	0.45252	-0.65395	2s(1.22) 2p(4.38) 3p(0.01) 4p(0.01)	1s(0.54)	2s(1.70) 2p(4.94) 3p(0.01)

BS7	-ph	-0.61689	0.45262	-0.66364	2s(1.23) 2p(4.37) 3p(0.01)	1s(0.54)	2s(1.70) 2p(4.95) 3p(0.01)
	$-p-phOCH_3$	-0.61970	0.45057	-0.65547	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.55)	2s(1.70) 2p(4.94) 3p(0.01)
	$-p-phCH_3$	-0.61836	0.45062	-0.65571	2s(1.22) 2p(4.37) 3p(0.01)	1s(0.55)	2s(1.70) 2p(4.94) 3p(0.01)
	-p-phCl	-0.62423	0.45205	-0.65296	2s(1.22) 2p(4.38) 3p(0.01)	1s(0.54)	2s(1.70) 2p(4.94) 3p(0.01)

E2 enaminone

Considering Table 2, twelve various substituents were placed in R position related to E2 structure and then were optimized. In order to select preferred basis set, we employed the length parameter of hydrogen bonding (O…H-N). In Table 13 through 15 that each table is related to one method, the values to O...H length for all substituents in five basis sets has been inserted. In each column that relates to special substituent, minimum figure has been marked. Because being low of figure is indicator of strength of O…H Hydrogen bonding. Due to marked sections in Table 13 through 15, it will be revealed that the basis set of BS1 has given the best values. So we carry out the selection of preferred method in basis set of 6-311G. Using four vital parameters of O…H length, N-H length, angle among O…H-N and distance between N and O, we select the preferred method. In Table 16 through 19 each table corresponds to special parameter the methods were compared. In Table 16, in each column, minimum value has been marked because O…H length reduction leads to increase hydrogen bonding strength. In Table 17, in each column, maximum value has been marked because increase of H-N length lead to increase hydrogen bonding strength. In Table 18, in each column, maximum value has been marked because increase of O…H-N angle lead to increase hydrogen bonding strength. In Table 19, in each column, minimum value has been marked because N, O distance reduction leads to increase hydrogen bonding strength. Due to marked points in these tables, it is revealed that the method of B3P86 has given better results. Therefore set of B3P86/6-311G will be selected for substitute selection.

Table 13. Selection of basis set in HF method and O…H length parameter

Basis set	-o-phCl	-m-phCl	-p-phCl	-o-phOH	-m-phOH	-p-phOH	$-o-phCH_3$	$-m-phCH_3$	$-p-phCH_3$	$-o-phOCH_3$	$-m-phOCH_3$	$-p-phOCH_3$
BS1	1.96300	1.95866	1.96362	1.96469	1.95834	1.97440	1.96857	1.97281	1.97539	1.96931	1.96242	1.97205
BS2	1.99880	1.98696	1.99356	2.00499	1.98623	2.00663	1.99795	2.00174	2.00582	2.00885	1.99024	2.00391
BS3	1.98730	1.97490	1.98186	1.99329	1.97460	1.99603	1.98666	1.99032	1.99523	1.99777	1.97847	1.99322
BS4	2.00161	1.99375	2.00090	2.00764	1.99252	2.01012	2.00530	2.00532	2.00973	2.01253	1.99704	2.00764
BS7	1.990	1.98180	1.98967	1.99740	1.98047	2.00044	1.99514	1.99663	2.0002	2.00216	1.98491	1.99783

Table 14. Selection of basis set in B3LYP method and O…H length parameter

Basis set	-o-phCl	-m-phCl	-p-phCl	-o-phOH	-m-phOH	-p-phOH	$-o-phCH_3$	$-m-phCH_3$	$-p-phCH_3$	$-o-phOCH_3$	$-m-phOCH_3$	$-p-phOCH_3$
BS1	1.87153	1.84059	1.84250	1.90834	1.84780	1.86125	1.85315	1.85615	1.85825	1.91404	1.85152	1.86571
BS2	1.89686	1.89636	1.87092	1.92164	1.87655	1.88917	1.87971	1.88204	1.88416	1.92408	1.87983	1.89200
BS3	1.87661	1.84673	1.84896	1.90062	1.85520	1.86929	1.85895	1.86108	1.86409	1.90606	1.85830	1.87198
BS4	1.91189	1.88132	1.88307	1.92994	1.88702	1.90216	1.89819	1.89443	1.89539	1.93371	1.89169	1.90724
BS7	1.89223	1.85850	1.86093	1.90905	1.86536	1.88086	1.87762	1.87309	1.87482	1.91611	1.87009	1.88664

Table 15. Selection of basis set in B3P86 method and O…H length parameter

Basis set	-o-phCl	-m-phCl	-p-phCl	-o-phOH	-m-phOH	-p-phOH	-o-phCH$_3$	-m-phCH$_3$	-p-phCH$_3$	-o-phOCH$_3$	-m-phOCH$_3$	-p-phOCH$_3$
BS1	1.82717	1.79836	1.79971	1.86677	1.80602	1.81544	1.81035	1.81290	1.81455	1.87259	1.80950	1.81889
BS2	1.85382	1.82884	1.82970	1.88110	1.83618	1.84572	1.83827	1.84022	1.84185	1.88364	1.83930	1.84771
BS3	1.82712	1.79907	1.80063	1.85394	1.80837	1.81937	1.81085	1.81277	1.81484	1.85978	1.81114	1.82097
BS4	1.86599	1.83807	1.83896	1.88711	1.84409	1.85485	1.85333	1.84982	1.85102	1.89073	1.84832	1.85846
BS7	1.83997	1.80853	1.81015	1.86014	1.81620	1.82760	1.82641	1.82195	1.82401	1.86723	1.82020	1.83120

Table 16. Selection of method in 6-311G basis set and O…H length parameter

Method	-o-phCl	-m-phCl	-p-phCl	-o-phOH	-m-phOH	-p-phOH	-o-phCH$_3$	-m-phCH$_3$	-p-phCH$_3$	-o-phOCH$_3$	-m-phOCH$_3$	-p-phOCH$_3$
B3P86	1.82717	1.79836	1.79971	1.86677	1.80602	1.81544	1.81035	1.81290	1.81455	1.87259	1.80950	1.81889
B3LYP	1.87153	1.84059	1.84250	1.90834	1.84780	1.86125	1.85315	1.85615	1.85825	1.91404	1.85152	1.86571
HF	1.96300	1.95866	1.96362	1.96469	1.95834	1.97440	1.96857	1.97281	1.97539	1.96931	1.96242	1.97205

Table 17. Selection of method in 6-311G basis set and N-H length parameter

Method	-o-phCl	-m-phCl	-p-phCl	-o-phOH	-m-phOH	-p-phOH	-o-phCH$_3$	-m-phCH$_3$	-p-phCH$_3$	-o-phOCH$_3$	-m-phOCH$_3$	-p-phOCH$_3$
B3P86	1.02576	1.02620	1.02592	1.02471	1.02536	1.02460	1.02492	1.02492	1.02484	1.02458	1.02515	1.02434
B3LYP	1.02279	1.02327	1.02305	1.02216	1.02263	1.02181	1.02199	1.02219	1.02207	1.02198	1.02244	1.02146
HF	0.99686	0.99684	0.99666	0.99622	0.99667	0.99597	0.99637	0.99626	0.99610	0.99606	0.99658	0.99612

Table 18. Selection of method in 6-311G basis set and O…H-N angle parameter

Method	-o-phCl	-m-phCl	-p-phCl	-o-phOH	-m-phOH	-p-phOH	-o-phCH$_3$	-m-phCH$_3$	-p-phCH$_3$	-o-phOCH$_3$	-m-phOCH$_3$	-p-phOCH$_3$
B3P86	136.888	139.161	139.034	135.366	139.222	138.096	138.736	138.565	138.378	135.320	138.977	137.920
B3LYP	135.966	138.374	138.216	134.695	138.449	137.067	137.886	137.704	137.511	134.681	138.198	136.836
HF	131.696	132.093	131.834	132.320	132.519	131.783	132.083	131.756	131.718	132.223	132.334	131.811

Table 19. Selection of method in 6-311G basis set and O and N distance parameter

Method	-o-phCl	-m-phCl	-p-phCl	-o-phOH	-m-phOH	-p-phOH	-o-phCH$_3$	-m-phCH$_3$	-p-phCH$_3$	-o-phOCH$_3$	-m-phOCH$_3$	-p-phOCH$_3$
B3P86	2.66968	2.66075	2.66079	2.69394	2.66790	2.66729	2.66782	2.66891	2.66893	2.66905	2.66913	2.66896
B3LYP	2.70205	2.69269	2.69307	2.72589	2.69971	2.70059	2.69972	2.70130	2.70162	2.73110	2.70110	2.70266
HF	2.72955	2.72905	2.73126	2.73641	2.73253	2.74057	2.73809	2.73904	2.74103	2.73983	2.73468	2.73871

Using preferred set of B3P86/6-311G, in four vital geometric parameters, we design Table 20 in order to recognize the best substituent that generates strongest hydrogen bonding. Markings in Table 20 are based upon descriptions of part Selection of Basis set and Method. Due to marks in Table 20, it is indicated that m-substituent (-m-phCl) generate the strongest hydrogen bonding (Figure 6). This conclusion that the substituent -m-phCl create the strongest hydrogen bond in structure E2 well supports the result obtained in section of studying substituent effect on the hydrogen bond in enaminone structure E1.

Table 20. Selection of substituent in B3P86/6-311G.

Parameter	-o-phCl	-m-phCl	-p-phCl	-o-phOH	-m-phOH	-p-phOH	-o-phCH$_3$	-m-phCH$_3$	-p-phCH$_3$	-o-phOCH$_3$	-m-phOCH$_3$	-p-phOCH$_3$
O…H length	1.82717	1.79836	1.79971	1.86677	1.80602	1.81544	1.81035	1.81290	1.81455	1.87259	1.80950	1.81889
N-H length	1.02576	1.02620	1.02592	1.02471	1.02536	1.02460	1.02492	1.02492	1.02484	1.02458	1.02515	1.02434
O…H-N angle	136.888	139.161	139.034	135.366	139.222	138.096	138.736	138.565	138.378	135.320	138.977	137.920
O and N distance	2.66968	2.66075	2.66079	2.69394	2.66790	2.66729	2.66782	2.66891	2.66893	2.66905	2.66913	2.66896

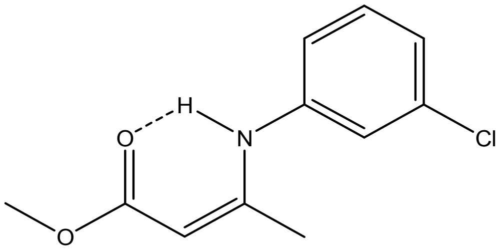


Fig. 6. The strongest hydrogen bond created in E2 structure with substituent –m-phCl.

Influence of DFT methods on the vibrational frequencies in top level of 6-311++G** were investigated. For this purpose, the desirable vibrational modes were initially drawn out and then were contrasted with equivalent experimental values [20]. In order to compare theoretic and experimental frequencies, RMS quantity was employed. The less RMS quantity, the less will be between theoretic and experimental values. In this section, three substituents –p-phCl, -p-phCH$_3$ and –p-phOCH$_3$ reviewed because only these three substituents have experimentally been synthesized among our substituents and contain experimental IR spectrum. In Table 21, three substituents were compared in two method of B3LYP and B3P86 with experimental values and RMS results has been brought to this table. In Table 21, in each substituent, minimum value of RMS has been marked because the less RMS, the less will be between theoretic and experimental value.

$$\text{RMS}=\sqrt{\frac{(Theo-Exp)^2+(Theo-Exp)^2+\cdots+N}{N}} \qquad (1)$$

Table 21. Selection of method through vibrational modes in 6-311++G** basis set

R		**vibrational modes**					**RMS**
–p-phCl	Exp [20]	3374	1652	1618	1271	1167	
	B3LYP	3380	1669	1607	1256	1188	14.69
	B3P86	3339	1680	1625	1273	1193	23.4
-p-phCH$_3$	Exp [20]	3264	1651	1598	1275	1163	
	B3LYP	3395	1666	1609	1256	1186	60.65
	B3P86	3357	1680	1627	1271	1191	47.18
–p-phOCH$_3$	Exp [20]	3264	1651	1613	1513	1246	
	B3LYP	3408	1657	1611	1523	1256	64.77
	B3P86	3367	1672	1630	1536	1192	54.38

E3 enaminone

Considering Table 2, three various substituents were placed in R position related to E3 structure and then were optimized. In order to select preferred method and basis set, we employed the length and angle parameters of R-E3 structures. In Table 22 through 24 that each table is related to one substitute, the values to lengths, angles and E$_{\text{total}}$ (E$_t$) in two methods and three basis sets has been inserted (in gas and liquid phases). The geometric parameters measured in these tables have been determined upon figure 2. As in geometric parameters and E$_t$ discussions, the results indicated that B3LYP method has more consistency than HF method with experimental values. In addition to it, the basis set 6-311++G** has yielded better results than 6-311G** or

6-311+G**. Moreover, it is clear of the results that in the liquid phase, ethanol has provided better and accurate values compared to other solutions. Generally due to the results the order of methods, basis sets and solvents preference could be showed as:

[B3LYP(BS7)□B3LYP(BS5)□B3LYP(BS3)□HF(BS7)□HF(BS5)□HF(BS3)]
[Ethanol □ chloroform □ Carbon tetrachloride]

Table 22. Geometric parameters of E3 structure

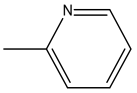
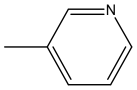
R= 		**Phase**								
		Gas						**Liquid**		
		B3LYP			**HF**			**B3LYP/BS7**		
		BS3	**BS5**	**BS7**	**BS3**	**BS5**	**BS7**	**Chloroform**	**Ethanol**	**CCl_4**
Length	H-N	1.0236	1.0240	1.0240	1.0008	1.0013	1.0013	1.0234	1.0232	1.0236
	N-C	1.3357	1.3357	1.3357	1.3250	1.3247	1.3248	1.3319	1.3306	1.3333
	C=C	1.3792	1.3805	1.3805	1.3672	1.3684	1.3684	1.3852	1.3871	1.3833
	C-C	1.4595	1.4590	1.4590	1.4593	1.4590	1.4590	1.4587	1.4586	1.4588
	C=O	1.2366	1.2385	1.2385	1.2083	1.2099	1.2100	1.2427	1.2445	1.2409
	O…H	1.9062	1.9090	1.9085	1.9900	1.9916	1.9911	1.8981	1.8911	1.9039
Angle	H-N-C	115.80	115.89	115.88	117.24	117.28	117.27	115.66	115.51	115.77
	N-C=C	126.17	126.29	126.28	127.69	127.73	127.72	126.10	125.96	126.21
	C=C-C	120.70	120.74	120.74	121.18	121.24	121.24	120.77	120.79	120.76
	C-C=O	122.23	122.03	122.02	121.57	121.44	121.43	121.81	121.74	121.90
	C=O…H	105.75	105.96	105.96	106.60	106.70	106.70	105.90	105.85	105.94
	O…H-N	129.35	129.10	129.11	125.70	125.61	125.63	129.75	130.15	129.42
E_t (ev)		-25364.30	-25364.64	-25364.65	-25208.60	-25209.00	-25209.00	-25364.93	-25365.03	-25364.82

Table 23. Geometric parameters of E3 structure

R= 		**Phase**								
		Gas						**Liquid**		
		B3LYP			**HF**			**B3LYP/BS7**		
		BS3	**BS5**	**BS7**	**BS3**	**BS5**	**BS7**	**Chloroform**	**Ethanol**	**CCl_4**
Length	H-N	1.0262	1.0265	1.0265	1.0006	1.0011	1.0011	1.025	1.0252	1.0258
	N-C	1.3359	1.3355	1.3356	1.3222	1.3217	1.3217	1.3318	1.3304	1.3333
	C=C	1.3818	1.3833	1.3832	1.3716	1.3730	1.3730	1.3874	1.3890	1.3857
	C-C	1.4571	1.4563	1.4563	1.4559	1.4554	1.4553	1.4564	1.4565	1.4563
	C=O	1.2415	1.2438	1.2438	1.2125	1.2143	1.2143	1.2460	1.2466	1.2452
	O…H	1.8274	1.8277	1.8275	1.9366	1.9391	1.9390	1.8435	1.8495	1.8375
Angle	H-N-C	113.04	113.28	113.27	115.60	115.76	115.76	113.75	113.94	113.57
	N-C=C	125.24	125.29	125.29	127.22	127.25	127.25	125.57	125.67	125.46
	C=C-C	120.54	120.52	120.53	120.81	120.86	120.86	120.57	120.57	120.55
	C-C=O	122.16	121.97	121.96	121.58	121.45	121.44	121.74	121.66	121.83
	C=O…H	104.84	105.13	105.13	106.23	106.37	106.38	105.40	105.51	105.29
	O…H-N	134.16	133.76	133.78	128.51	128.27	128.26	132.89	132.53	133.22
E_t (ev)		-25364.00	-25364.40	-25364.51	-25208.30	-25208.70	-25208.70	-25364.70	-25364.8	-25364.61

Due to results of Table 25, it is indicates that Gap $_{HO-LU}$ values in gas phase is more than liquid phase and consequently the enaminones structures are more stable in gas phase.

Table 24. Geometric parameters of E3 structure

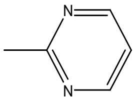
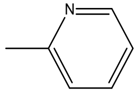
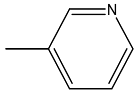
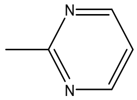
R= 		**Phase**								
		Gas						**Liquid**		
		B3LYP			**HF**			**B3LYP/BS7**		
		BS3	**BS5**	**BS7**	**BS3**	**BS5**	**BS7**	**Chloroform**	**Ethanol**	**CCl_4**
Length	H-N	1.0224	1.0229	1.0229	0.9997	1.0002	1.0002	1.0219	1.0220	1.0222
	N-C	1.3427	1.3429	1.3429	1.3347	1.3345	1.3345	1.3381	1.3360	1.3399
	C=C	1.3757	1.3772	1.3772	1.3632	1.3645	1.3645	1.3808	1.3821	1.3794
	C-C	1.4627	1.4622	1.4623	1.4622	1.4619	1.4619	1.4618	1.4620	1.4619
	C=O	1.2369	1.2389	1.2389	1.2086	1.2103	1.2103	1.2423	1.2443	1.2409
	O…H	1.8916	1.8910	1.8907	1.9754	1.9749	1.9755	1.8967	1.8951	1.8952
Angle	H-N-C	116.46	116.47	116.47	117.99	117.98	117.99	116.47	116.40	116.49
	N-C=C	125.44	125.46	125.46	126.87	126.86	126.87	125.72	125.80	125.63
	C=C-C	120.69	120.75	120.74	121.19	121.25	121.26	120.77	120.80	120.76
	C-C=O	122.23	122.04	122.04	121.58	121.46	121.45	121.78	121.70	121.89
	C=O…H	106.00	106.17	106.17	106.94	107.02	107.02	106.25	106.32	106.22
	O…H-N	129.17	129.11	129.11	125.43	125.43	125.41	129.00	129.10	129.01
E_t (ev)		-25638.00	-25801.10	-25801.20	-25644.10	-25644.00	-25644.40	-25801.00	-25802.00	-25801.01

Table 25. Gap HOMO-LUMO and E_t values for E3 structures in B3LYP/6-311++G**

R	**E_t (ev)**		**E_{HOMO} (ev)**		**E_{LUMO} (ev)**		**Gap_{HO-LU} (ev)**	
	Gas	**Liquid (Ethanol)**	**Gas**	**Liquid (Ethanol)**	**Gas**	**Liquid (Ethanol)**	**Gas**	**Liquid (Ethanol)**
	-25364.647	-25365.033	-6.280	-6.398	-2.412	-2.543	3.869	3.855
	-25364.404	-25364.817	-6.331	-6.385	-2.445	-2.499	3.888	3.887
	-25801.175	-25801.571	-6.319	-6.468	-2.464	-2.635	3.855	3.833

E4 enaminone

As the Table 2 reveals that in E4 enaminone structure which contain ferrocene group, four different substituents were placed. In Tables 26 through 29, the results related to geometrical parameters of structures from binding four substituents to E4 enaminone have been reported. In Table 26, in addition to theoretical results, experimental equivalent results have been reported which are due to experimental results existence in this structure. For the same reason in order to compare the theoretical and experimental values in this table, RMS values also have been calculated and reported. With considering the RMS results in Table 26, it could be said that B3LYP method has offered those results which approach more to the experimental results. Comparing the results reveal that in each method, taking into account the special approximations in order to solve Schrödinger equation generate minor changes in the geometrical parameters. Also through comparing the results in the various basic sets it will become clear that basic sets does not any effect on the results.

Table 26. Geometric parameters of E4 structure with–p-phBr substituent and their RMS values

Parameter		B3LYP		SVWN		EXP [21]
		BS8 / BS3	**BS8 / BS9**	**BS8 / BS3**	**BS8 / BS9**	
Length	H-N	1.04	1.04	1.10	1.10	0.76
	N-C	1.38	1.38	1.36	1.36	1.36
	C=C	1.40	1.40	1.40	1.40	1.37
	C-C	1.44	1.44	1.42	1.42	1.42
	C=O	1.29	1.29	1.30	1.30	1.26
	O…H	1.73	1.73	1.49	1.49	1.99
	RMS	0.157	0.157	0.247	0.247	
angle	H-N-C	111.52	111.50	108.85	108.84	113.41
	N-C=C	119.45	119.43	117.86	117.90	119.48
	C=C-C	123.58	123.59	121.91	121.90	125.11
	C-C=O	121.54	121.56	121.05	121.04	122.43
	C=O…H	102.51	102.49	102.91	102.94	97.05
	O…H-N	140.14	140.17	147.01	146.96	142.32
	RMS	2.62	2.61	3.91	3.91	
E_t(ev)		-41909.46	-41928.99	-41704.10	-41724.40	

Table 27. Geometric parameters of E4 structure with 3,5-dimethylphenylsubstituent

Parameter		B3LYP		SVWN	
		BS8 / BS3	**BS8 / BS9**	**BS8 / BS3**	**BS8 / BS9**
Length	H-N	1.04	1.04	1.10	1.10
	N-C	1.38	1.38	1.36	1.36
	C=C	1.40	1.40	1.40	1.40
	C-C	1.44	1.44	1.42	1.42
	C=O	1.29	1.29	1.30	1.30
	O…H	1.73	1.73	1.49	1.49
angle	H-N-C	111.36	111.33	108.70	108.67
	N-C=C	119.33	118.33	117.91	117.93
	C=C-C	123.69	123.71	121.99	121.98
	C-C=O	121.50	121.50	120.91	120.89
	C=O…H	102.48	102.47	103.03	103.07
	O…H-N	140.46	140.48	147.00	146.98
E_t (ev)		-47818.76	-47832.46	-47579.76	-47594.46

Table 28. Geometric parameters of E4 structure with –m-phCH$_3$ substituent

Parameter		B3LYP		SVWN	
		BS8 / BS3	**BS8 / BS9**	**BS8 / BS3**	**BS8 / BS9**
Length	H-N	1.04	1.04	1.10	1.10
	N-C	1.38	1.38	1.36	1.36
	C=C	1.40	1.40	1.40	1.40
	C-C	1.45	1.45	1.42	1.42
	C=O	1.29	1.29	1.30	1.30
	O…H	1.72	1.72	1.48	1.49
angle	H-N-C	111.28	111.27	108.67	108.55
	N-C=C	119.36	119.36	117.99	117.48
	C=C-C	123.65	123.66	121.92	121.95
	C-C=O	121.23	121.23	120.75	120.73
	C=O…H	102.70	102.69	103.19	103.12
	O…H-N	140.51	140.50	147.10	147.36
E_t (ev)		-42639.91	-42653.60	-42426.30	-42440.90

Table 29. Geometric parameters of E4 structure with –p-phCH$_3$ substituent.

Parameter		B3LYP		SVWN	
		BS8 / BS3	**BS8 / BS9**	**BS8 / BS3**	**BS8 / BS9**
Length	H-N	1.04	1.04	1.10	1.10
	N-C	1.38	1.38	1.36	1.36
	C=C	1.40	1.40	1.40	1.40
	C-C	1.44	1.45	1.42	1.42
	C=O	1.29	1.29	1.30	1.30
	O…H	1.72	1.29	1.48	1.48
angle	H-N-C	111.20	111.22	108.56	108.53
	N-C=C	119.29	119.25	117.89	117.89
	C=C-C	123.68	123.67	121.92	121.91
	C-C=O	121.21	121.20	120.70	120.68
	C=O…H	102.65	102.68	103.14	103.19
	O…H-N	140.74	140.71	147.32	147.31
E_t (ev)		-42639.92	-42653.61	-42426.32	-42440.91

In Table 30 through 33, the results of NBO calculation for E4 compound it has been showed that these calculations have been carried out by B3LYP method and basic series of LANL2DZ/6-311G** because DFT methods perfectly predict the electrons behaviors and properties of it due to taking into account the electron correlation effect. In these tables, atoms nomination is based on the figure 2. The reported results in these four tables show that C=O bond length is short than that of C-N because of negative charge of oxygen and nitrogen atoms, since oxygen has assigned more negative charge on itself. Also in structure of all four compounds, through creating one intramolecular hydrogen bond and creating one semi-aromatic ring, enaminone compound will reach to desirable stability and in this way that N-H bond and O atom will approach so much to each other until distance among them will become almost less than total of van der Waals radius N and O.

In Table 34 the energy values of HOMO and LUMO and Gap $_{\text{HO-LU}}$ using B3LYP and basis set LANL2DZ/-6 311G** have been shown for 4 compounds of E4 structure . Due to Gap $_{\text{HO-LU}}$ values it could be said that each four compounds have good stability because Gap value for 4 structures has been obtained more than 3 (ev). Also through comparing of Gap $_{\text{HO-LU}}$ values it could be concluded that ordering of structures stability is as follows:

-p-phBr<3,5-dimethylphenyl<-m-phCH3<-p-phCH3

Table 30. NBO results of E4 structure with –p-phBr substituent

Atom	Charge	Natural Electron Configuration
H	0.464	1s (0.53)
N	-0.620	[core] 2s (1.26) 2p (4.35) 3p (0.02)
C^3	0.305	[core] 2s (0.84) 2p (2.83) 3p (0.02)
C^2	-0.379	[core] 2s (0.97) 2p (3.40) 3p (0.02)
C^1	0.493	[core] 2s (0.85) 2p (2.62) 3p (0.02)
O	-0.679	[core] 2s (1.74) 2p (4.94) 3p (0.01)

Table 31. NBO results of E4 structure with 3,5-dimethylphenylsubstituent

Atom	Charge	Natural Electron Configuration
H	0.463	1s (0.53)
N	-0.622	[core] 2s (1.26) 2p (4.35) 3p (0.02)
C^3	0.300	[core] 2s (0.84) 2p (2.84) 3p (0.02)
C^2	-0.376	[core] 2s (0.97) 2p (3.39) 3p (0.02)
C^1	0.501	[core] 2s (0.85) 2p (2.62) 3p (0.02)
O	-0.673	[core] 2s (1.73) 2p (4.93) 3p (0.01)

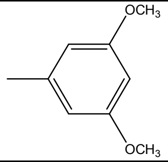
Table 32. NBO results of E4 structure with –m-phCH_3 substituent

Atom	Charge	Natural Electron Configuration
H	0.463	1s (0.53)
N	-0.623	[core] 2s (1.26) 2p (4.35) 3p (0.02)
C^3	0.299	[core] 2s (0.84) 2p (2.83) 3p (0.02)
C^2	-0.376	[core] 2s (0.97) 2p (3.39) 3p (0.02)
C^1	0.498	[core] 2s (0.85) 2p (2.62) 3p (0.02)
O	-0.680	[core] 2s (1.73) 2p (4.94) 3p (0.01)

Table 33. NBO results of E4 structure with –p-phCH_3 substituent

Atom	Charge	Natural Electron Configuration
H	0.463	1s (0.53)
N	-0.623	[core] 2s (1.26) 2p (4.35) 3p (0.02)
C^3	0.298	[core] 2s (0.84) 2p (2.83) 3p (0.02)
C^2	-0.376	[core] 2s (0.97) 2p (3.39) 3p (0.02)
C^1	0.496	[core] 2s (0.85) 2p (2.63) 3p (0.02)
O	-0.681	[core] 2s (1.73) 2p (4.94) 3p (0.01)

Table 34. Gap_{HO-LU} values for E4 structures in B3LYP method and LANL2DZ/6-311++G**

R	E_{HO} (ev)	E_{LU} (ev)	Gap_{HO-LU} (ev)
-p-phBr	-5.945	-2.530	3.415
	-5.735	-2.307	3.443
-m-phCH3	-5.796	-2.353	3.443
-p-phCH3	-5.780	-2.331	3.450

E5 enaminone

In figure 4 enaminone compound E5 and chemical reaction of complex-forming of it with molybdenum metal (Complex (1)) have been illustrated [19]. In this reaction in which enaminone plays ligand role, the end product is a binucleated complex. In Table 35 thermodynamic data of theoretical calculation related to E5 compound reaction have been indicated.

Internal and external factors are two effective factor on the complexes stability which internal factors concern to nature of central atom and ligand and external factors are those factors such as temperature, pressure, ionic strength, solvent properties, and etc. The nature of central atom is dependable to central atom oxidation number, central atom electrical charge, core effective charge and nature of ligand depend to its being bulky.

In Tables 36 and 37, the results of geometrical parameters for enaminone ligand E5 have been shown. Marking atoms in these tables is based on figure 7. With comparing theoretical and experimental results through Rsquare and SError, it could be concluded in bond length calculations, route section BPV86/6-311G** and in angles calculations, route section B3PW91/6-311G** have offered the better results. Also HF method along with basis set 6-311G possess highest deviation in respect to experimental results. One of features of density functional theory methods is taking into the account electronic correlation effect on the calculations while in HF calculations this effect has not regarded and repulsion among electrons approximately (measuring repulsion of one electron through average electronic density of other electrons) will be calculated, therefore in HF method, repulsion energy is less and as result lower values will be yielded. In figure 8 and figure 9, charts of methods and basis sets comparison with experimental results (methods and basis sets preference) based on the Rsquare test has been shown.

In Table 38 the values of Gap $_{\text{HO-LU}}$ ‘E_{LUMO}‘ E_{HOMO} and Et have been reported related to enaminone compound E5 and complex (1).

Table 35. Thermodynamic data related to reaction of complex-forming 1 using rout section B3LYP/lanl2dz in 298 K

		S (cal/mol.K)	**E (cal/mol)**
Reactants	**2[$C_{19}H_{19}O_7N$]**	358.364	479056
	$Mo_2O_3(acac)_4$	251.822	316622
	2[MeOH]	114.028	68140
	Σ_R	724.214	863818
products	**[$C_{40}H_{44}Mo_2N_2O_{20}$]**	382.319	555147
	4[acac]	372.43	293812
	Σ_P	754.749	848959
$\Delta S = \Sigma_P - \Sigma_R$		30.52	
$\Delta E = \Sigma_P - \Sigma_R$		-14859	
ΔH^o (cal/mol)= $\Delta E - \Delta nRT$		-14859	
ΔG^o (cal/mol)= $\Delta H^o - T\Delta S$		-23953.96	
$K^* = e^{-\Delta G^o/RT}$		4.27×10^{17}	

* K: Stability constant of complex

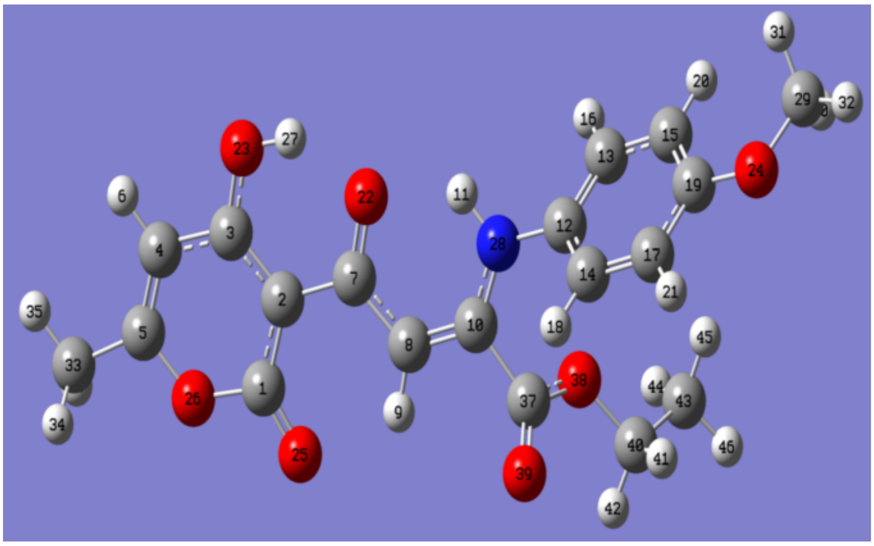


Fig. 7. E5 labeled structure
(Red: Oxygen, Blue: Nitrogen, Dark gray: Carbon, Light gray: Hydrogen).

Table 36. Bond lengths of E5 structure

bond length	**B3LYP**			**BPV86**			**B3PW91**			**HF**			**EXP [19]**
	BS1	**BS3**	**BS7**	**BS1**	**BS3**	**BS7**	**BS1**	**BS3**	**BS7**	**BS1**	**BS3**	**BS7**	
H^{11}-N	1.025	1.021	1.022	1.041	1.036	1.037	1.027	1.023	1.023	0.996	0.996	0.997	0.872
N-C^{10}	1.356	1.351	1.349	1.364	1.358	1.356	1.351	1.346	1.345	1.344	1.342	1.340	1.333
C^{10}=C^{8}	1.385	1.378	1.379	1.396	1.389	1.390	1.383	1.376	1.377	1.362	1.356	1.358	1.384
C^{8}-C^{7}	1.424	1.433	1.430	1.425	1.432	1.430	1.419	1.428	1.426	1.430	1.445	1.443	1.400
C^{7}=O^{22}	1.316	1.277	1.280	1.338	1.298	1.301	1.315	1.277	1.279	1.271	1.233	1.234	1.297
O^{22}…H^{11}	1.775	1.829	1.828	1.727	1.779	1.777	1.749	1.808	1.805	1.892	1.952	1.948	2.033
C^{7}-C^{2}	1.467	1.471	1.472	1.466	1.469	1.469	1.461	1.465	1.465	1.468	1.479	1.480	1.464
C^{2}=C^{3}	1.410	1.408	1.407	1.425	1.421	1.421	1.408	1.407	1.406	1.406	1.385	1.385	1.395
C^{3}-O^{23}	1.343	1.314	1.316	1.350	1.320	1.322	1.337	1.307	1.309	1.324	1.297	1.298	1.306
O^{23}-H^{27}	1.025	1.017	1.018	1.068	1.054	1.055	1.033	1.026	1.026	0.967	0.965	0.965	1.247
H^{27}…O^{22}	1.530	1.511	1.514	1.450	1.440	1.441	1.495	1.472	1.473	1.674	1.643	1.646	1.201
RSquare	0.9198	0.9317	0.9311	0.9311	0.9417	0.9413	0.9240	0.9379	0.9373	0.8940	0.9080	0.9050	
SError	0.142	0.134	0.134	0.128	0.120	0.120	0.136	0.126	0.126	0.173	0.166	0.167	

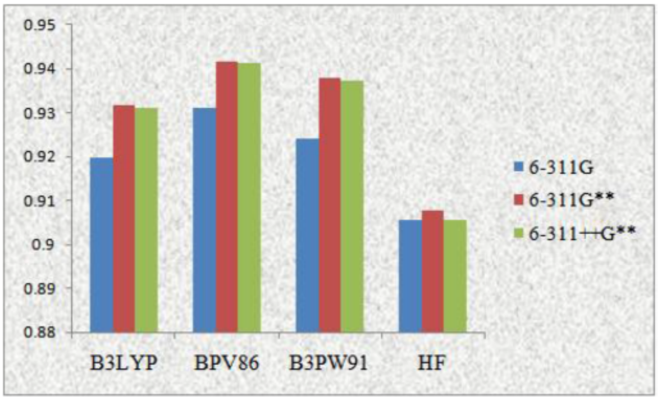


Fig. 8. Method and basis set effects on the bond length.

Table 37. Bond angles of E5 structure

bond angle	B3LYP			BPV86			B3PW91			HF			EXP
	BS1	BS3	BS7	BS1	BS3	BS7	BS1	BS3	BS7	BS1	BS3	BS7	[19]
C^7-O^{22}…H^{27}	104.81	104.98	105.11	104.49	104.62	104.75	104.91	105.06	105.18	105.89	106.06	106.08	100.80
O^{22}…H^{11}-N	136.55	134.74	134.48	138.81	137.13	136.94	137.10	135.16	134.99	130.78	129.04	129.03	133.87
H^{11}-N-C^{10}	112.13	112.34	112.54	111.26	111.41	111.57	111.92	112.18	112.33	114.46	114.61	114.69	115.15
C^3-O^{23}-H^{27}	107.53	104.95	105.19	105.49	103.36	103.55	106.95	104.25	104.43	112.06	108.09	108.27	100.31
H^{27}…O^{22}-C^7	105.94	104.41	104.59	105.20	103.75	103.91	105.84	104.19	104.31	107.79	105.77	105.86	104.94
C^{19}-O^{24}-C^{29}	119.95	118.48	118.60	118.05	117.60	117.73	118.85	118.14	118.25	121.43	119.91	120.01	116.80
C^{10}-C^{37}-O^{39}	124.49	124.01	124.00	124.65	124.14	124.17	124.46	123.97	123.99	124.15	123.60	123.49	111.56
O^{38}-C^{37}-O^{39}	123.93	124.98	125.05	124.10	125.04	125.10	124.00	125.08	125.13	123.98	125.30	125.35	126.24
C^2-C^1-O^{25}	129.84	129.74	129.47	130.51	130.32	130.04	129.70	129.61	129.38	128.56	128.45	128.24	128.37
O^{26}-C^5-C^{33}	112.46	112.51	112.57	112.38	112.49	112.54	112.44	112.49	112.55	112.38	112.26	112.31	114.56
RSquare	0.8237	0.8509	0.8511	0.8307	0.8530	0.8530	0.8270	0.8537	0.8533	0.7725	0.8119	0.8208	
SError	4.83	4.48	4.42	5.14	4.81	4.76	4.84	4.51	4.47	4.43	4.11	4.06	

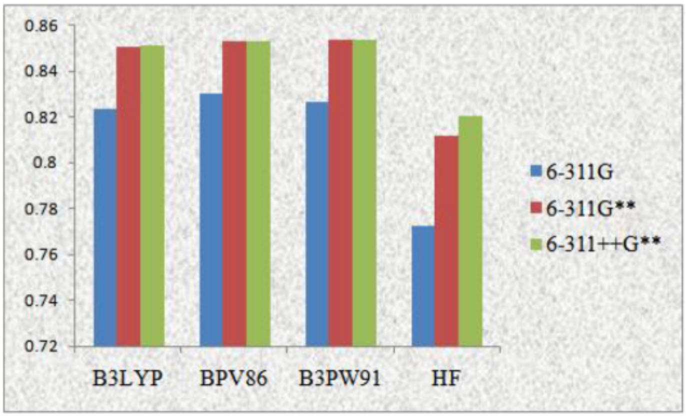


Fig.9. Method and basis set effects on the bond angles.

Table 38. Gap $_{\text{HO-LU}}$ and E_t values for E5 structure and complex (1) in B3LYP/6-311++G**, LanL2DZ

Energies	E5 Structure	Complex I
E_{HOMO} (ev)	-5.84	-5.59
E_{LUMO} (ev)	-2.38	-2.64
Gap $_{\text{HO-LU}}$ (ev)	3.46	2.95
E_t (ev)	-35827.02	-89752.11

In figure10 and 11, IR spectrums have respectively been shown related to enaminone structure E5 and complex (1). Also in Table 39 and Table 40, vibrational modes related to structure E5 and complex (1) and their equivalent experimental values have been listed respectively which has been compared by RMS quantity. Considering to results of theoretical and experimental vibrational frequencies and RMS values it could be concluded that command lines of B3LYP/6-311G and B3PW91/LANL2DZ possessed lowest deviations than experimental values respectively for E5 structure and complex (1). Also rout section of HF/6-311G** for E5 structure and rout section of HF/LANL2DZ for complex (1) have yielded highest deviation results at compared to experimental values. Difference among theoretical and experimental frequencies of ligand and complex is due to that in calculations, no interaction with surrounding space has been taken into the account while in real systems, molecules interact with each other and this affecting of various compound properties has an effect on the vibrational frequencies.

E6 enaminone

As figure 5 shows, enaminone structure E6 which contains ferrocene group, has been transformed to complex (2) in reaction to Cu metal. In figure 12 and 13, E6 enaminone structure and complex (2) has respectively been illustrated where atoms have been marked.

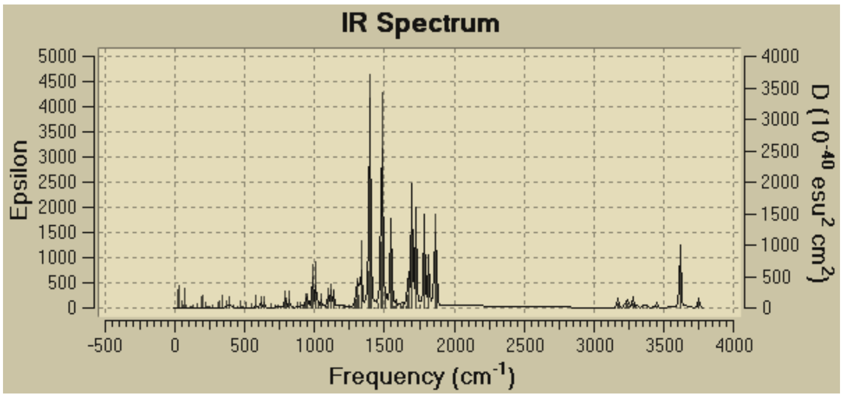


Fig. 10. IR Spectrum of E5 enaminone.

Table 39. Vibrational modes of E5 enaminone and comparison of theoretical and experimental values

Mode	HF			B3LYP			BPV86			B3PW91			EXP [19]
	BS1	**BS3**	**BS7**	**BS1**	**BS3**	**BS7**	**BS1**	**BS3**	**BS7**	**BS1**	**BS3**	**BS7**	
C=O stretch in ster	1872	2001	1988	1679	1797	1785	1616	1731	1720	1700	1818	1807	1728
C=O stretch in pyron	1861	1978	1960	1718	1815	1796	1676	1764	1748	1736	1832	1817	1646
C=O stretch in enamin	1784	1797	1787	1604	1620	1610	1549	1617	1610	1612	1631	1624	1574
C=C stretch in pyron	1697	1715	1709	1539	1566	1558	1622	1570	1568	1553	1580	1573	1512
RMS	190.6	262.1	250.4	47.99	97.92	85.38	80.81	69.17	61.03	54.79	112.4	102.0	

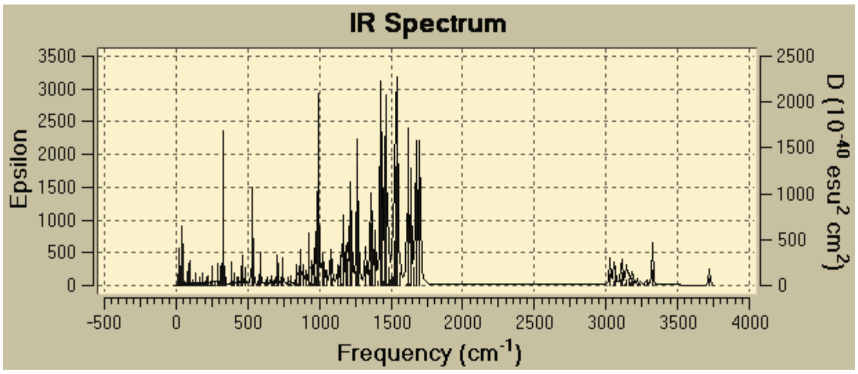


Fig. 11. IR Spectrum of complex (1).

Table 40. Vibrational modes of complex (1) and comparison of theoretical and experimental values in LANL2DZ basis set

Mode	B3LYP	BPV86	B3PW91	HF	EXP[19]
C=O stretch in ster	1674	1620	1692	1823	1721
C=O stretch in pyron	1680	1629	1696	1850	1645
C=O stretch in enamin	1525	1479	1530	1657	1578
C=C stretch in pyron	1457	1422	1469	1583	1507
Mo-O stretch	980	941	979	1072	960
O-Mo-O bending	710	689	721	806	763
RMS	54.53	79.40	51.41	123.23	

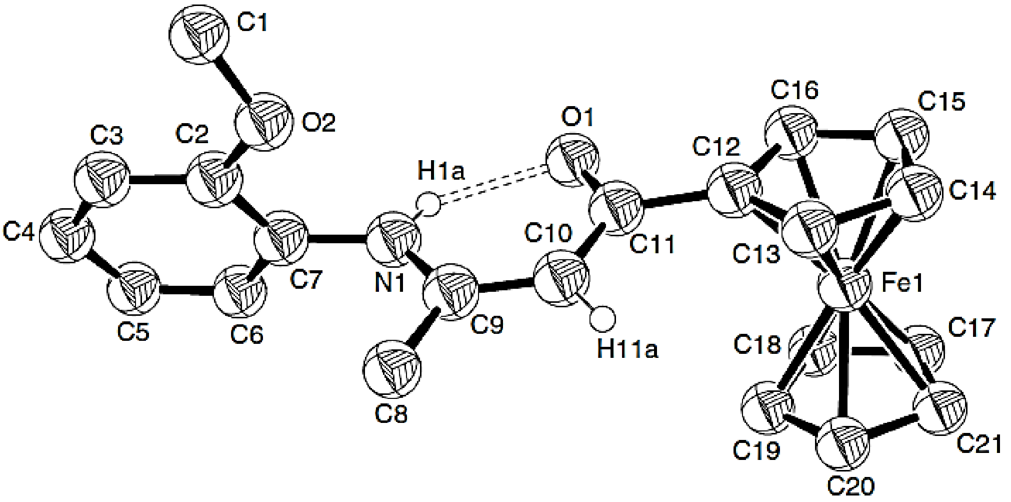


Fig. 12. Labeled structure of E6.

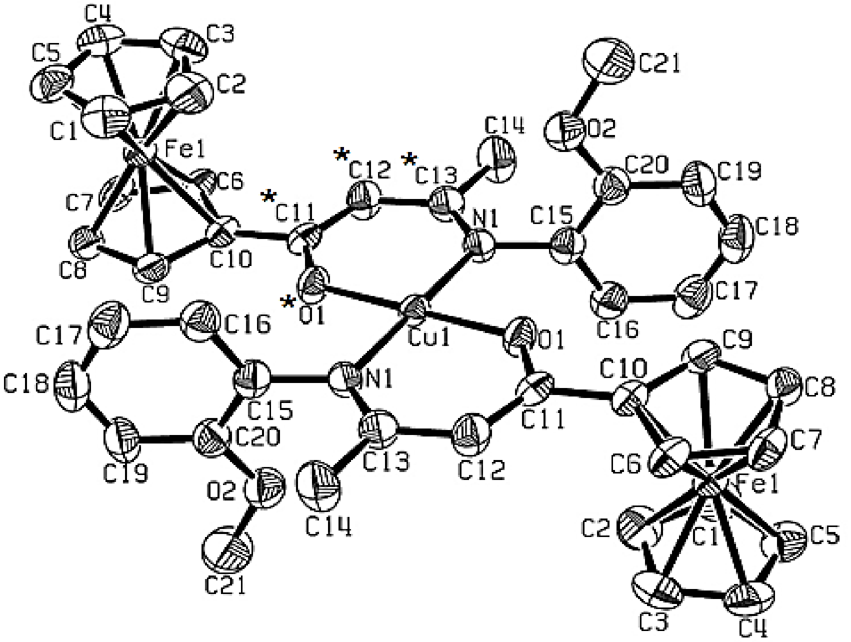


Fig. 13. Labeled structure of complex (2).

In Tables 41 and 42, results of geometrical parameters have respectively been shown for E6 enaminone and complex (2). In these tables, in addition to experimental results report (16), comparison among theoretical and experimental results by Rsquare equation has been carried out. Due to results reported for enaminone ligand E6, it could be concluded that in general, consistency pattern of method and basis sets with experimental equivalent values is as follows:
BLYP(BS8)<B3LYP(BS9)<BVWN(BS9)<HF(BS9).

Also for complex (2) results show that the following pattern indicates more agreement of theoretical results with experimental results.
BLYP(BS8)<B3LYP(BS8)<BVWN(BS8)<HF(BS9).

In general, results of E6 structure indicate that

- In all parameters of bond length, values of HF method are lower while in DFT methods the calculated values are higher.
- Consistency pattern of methods with experimental values for enaminone E6 and complex (2) is fully identical.
- HF method has offered better results than DFT methods and BLYP has offered those results which possess highest difference with experimental results.
- There is no significant difference among results of various basis sets.
- Among various methods of DFT, BVWN has offered better results.
- In E6 ligand, through basis sets shift from BS8 to BS9, it creates no significant change in results of bond length but in complex (2) through basis sets shift from BS8 to BS9, N-Cu bond length has declined and theoretical results further approach to experimental results.

In Tables 43 and 44, the results of NBO calculations have been shown for E6 enaminone structure and complex (2) using BVWN respectively. Due to the results of these tables, it could be said that in complex (2), in spite of that coördination number of Cu metal is 4 but because of difference at bonds length it has been gone out from flat square state. Also due to negative charge on the oxygen and nitrogen atoms it could be said that Cu-O bond length is lower than Cu-N bond. Also C^{12} in complex structure and C^{10} in E6

Table 41. Theoretical results of E6 structureand their experimental values.

Parameters		**HF**		**B3LYP**		**BLYP**		**BVWN**		**EXP[16]**
		BS8	**BS9**	**BS8**	**BS9**	**BS8**	**BS9**	**BS8**	**BS9**	
length	**O^1-C^{11}**	1.26	1.26	1.29	1.30	1.30	1.32	1.31	1.31	1.24
	C^{11}-C^{10}	1.44	1.44	1.44	1.44	1.44	1.45	1.45	1.45	1.44
	C^{10}-C^9	1.38	1.38	1.40	1.40	1.41	1.41	1.41	1.41	1.37
	C^9-N^1	1.36	1.36	1.37	1.37	1.38	1.38	1.38	1.38	1.35
	N^1-H^1	1.00	1.00	1.04	1.04	1.06	1.06	1.04	1.04	0.86
	H^1…O^1	1.90	1.90	1.73	1.74	1.70	1.71	1.77	1.77	1.95
	N^1-O^1	2.69	2.69	2.62	2.62	2.61	2.62	2.66	2.66	2.65
angle	**N^1-H^1…O^1**	132.99	133.01	139.95	139.94	141.01	142.33	140.66	140.86	137.64
	H^1…O^1-C^{11}	102.91	102.91	102.35	102.31	103.02	101.71	101.59	101.45	99.91
	O^1-C^{11}-C^{10}	122.46	122.45	122.07	122.08	121.67	121.93	121.99	121.99	122.27
	C^{11}-C^{10}-C^9	123.92	123.93	123.16	123.19	123.23	123.34	123.88	124.02	124.19
	C^{10}-C^9-N^1	122.35	122.34	119.97	119.96	119.35	119.19	119.76	119.69	121.27
	C^9-N^1-H^1	115.34	115.33	112.44	112.45	111.61	111.40	112.02	111.91	114.51
Rsquare		0.9913	0.9913	0.9700	0.9702	0.9604	0.9599	0.9725	0.9728	

structure possess negative charge and other carbons possess positive charge. In Table 45, values of Et and Gap $_{\text{HO-LU}}$ have been listed for enaminone E6 and complex (2).

Table 42. Theoretical results of complex (2) and their experimental values

Parameters		HF		B3LYP		BLYP		BVWN		EXP[16]
		BS8	**BS9**	**BS8**	**BS9**	**BS8**	**BS9**	**BS8**	**BS9**	
length	**O^1-C^{11}**	1.34	1.30	1.32	1.32	1.33	1.33	1.34	1.33	1.27
	C^{11}-C^{12}	1.36	1.38	1.41	1.40	1.42	1.42	1.42	1.42	1.35
	C^{12}-C^{13}	1.39	1.42	1.42	1.42	1.43	1.43	1.44	1.43	1.40
	C^{13}-N^1	1.33	1.33	1.34	1.34	1.36	1.36	1.36	1.36	1.31
	N^1-Cu^1	2.04	2.03	2.01	1.99	2.04	1.99	2.08	2.01	1.98
	Cu^1-O1	1.91	1.93	1.97	1.94	1.98	1.97	1.97	1.99	1.90
	N^1…O^1	2.74	2.82	2.88	2.86	2.91	2.91	2.90	2.93	2.79
angle	**N^1-Cu^1-O^1**	87.82	90.66	92.94	93.37	92.86	94.39	91.23	94.16	92.13
	Cu^1-O^1-C^{11}	133.09	129.99	126.58	127.38	127.19	125.89	128.56	125.82	128.16
	O^1-C^{11}-C^{12}	122.33	124.02	124.51	124.06	123.91	124.18	123.78	124.06	124.96
	C^{11}-C^{12}-C^{13}	124.77	125.54	126.91	126.41	126.88	127.23	126.78	127.80	126.43
	C^{12}-C^{13}-N^1	126.00	124.68	123.66	123.87	124.45	123.64	123.50	123.87	123.65
	C^{13}-N^1-Cu^1	125.79	124.84	124.83	124.79	124.03	124.49	124.56	123.93	124.41
Rsquare		0.9966	0.9997	0.9991	0.9989	0.9991	0.9977	0.9993	0.9981	

Table 43. NBO results of E6 structure in BVWN/SDD

Atom	Charge	Natural Electron Configuration
O^1	-0.674	[core]2S(1.75)2p(4.92)3p(0.01)
N^1	-0.615	[core]2S(1.27)2p(4.33)3p(0.02)
H^1	0.448	1S(0.55)
C^9	0.318	[core]2S(0.88)2p(2.79)3p(0.02)
C^{10}	-0.376	[core]2S(0.98)2p(3.38)3p(0.02)
C^{11}	0.460	[core]2S(0.85)2p(2.66)3p(0.03)

Table 44. NBO results of complex (2) in BVWN/Lanl2dz

Atom	Charge	Natural Electron Configuration
Cu^1	0.226	[core]4S(0.16)3d(4.97)4p(0.16)4d(0.01)
***O^1**	-0.407	[core]2S(0.85)2p(2.55)3p(0.01)
O^1	-0.402	[core]2S(0.85)2p(2.55)3p(0.01)
N^1	-0.371	[core]2S(0.68)2p(2.18)3p(0.01)
N^1	-0.376	[core]2S(0.68)2p(2.18)3p(0.01)
***C^{11}**	0.488	[core]2S(0.41)2p(1.33)3p(0.01)
C^{11}	0.492	[core]2S(0.41)2p(1.32)3p(0.01)
***C^{12}**	-0.406	[core]2S(0.48)2p(1.72)3p(0.01)
C^{12}	-0.410	[core]2S(0.48)2p(1.72)3p(0.01)
***C^{13}**	0.365	[core]2S(0.43)2p(1.37)3p(0.01)
C^{13}	0.351	[core]2S(0.43)2p(1.38)3p(0.01)

Table 45. Gap$_{HO\text{-}LU}$ and E$_t$ values for E6 and complex (2) structures

Structure	**E$_t$ (Hartree)**	**Gap$_{HO\text{-}LU}$ (ev)**
E6	-1150.758	1.360
Complex (2)	-2495.611	2.203

CONCLUSION

In the paper, six enaminone structures have been studied using computer methods. Given to enaminone structure and purpose, special methods and basis sets have been utilized and after optimizing structures by software and deriving theoretical results, has been compared to the experimental results. The studied enaminone structures in the paper have been investigated for substituent effect on the hydrogen bond, method and basis sets effect on geometrical parameters, vibrational frequencies, stability, complex-forming, NBO calculations and etc. The results of computational calculations indicate that calculation procedures could be helpful for enaminone structure. Generally data of calculations for six enaminone structures studied in the paper indicated that results in similar sections support each other.

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