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Gaussıan Calculatıons of 3-(*p*-Chlorobenzyl)-4-(3,4-Dihydroxybenzylidenamino)-4,5-Dihydro-1*H*-1,2,4-Triazol-5-One and *N*-Acetyl Derivative using B3lyp and HF Basis Sets

Gul KOTAN
Kafkas University, Kars Vocational School

Sule BAHCECI
Fatih Education Faculty, Karadeniz Technical University

Haydar YUKSEK
Kafkas University, Department of Chemistry

Abstract: 3-*p*-Chlorobenzyl-4-(3,4-dihydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one **(1)** and 1-acetyl-3-*p*-chlorobenzyl-4-(3,4-dihydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one **(2)** were described in the literature. In this study, these compounds were optimized by using the B3LYP/631G (d,p) and HF/631G (d,p) basis sets. IR absorption frequencies of analysed molecules were calculated by two methods. The veda4f program, was used in defining IR data, which were calculated theoreticall. ^{1}H-NMR and ^{13}C-NMR isotropic shift values were calculated by the method of GIAO using the program package Gaussian G09. Experimental and theoretical values were inserted into the grafic according to equatation of δ exp$_{=}$a+b. δ calc. The standard error values were found via SigmaPlot program with regression coefficient of a and b constants. The experimental and the obtained theoretical values were compared and found by regression analysis that are accurete. Furthermore, electronic, geometric and thermodynamic parameters, UV-Vis values, dipole moments, the HOMO-LUMO energy, total energy of the molecule, bond angles, bond lengths and mulliken charges from both methods were calculated.

Keywords: 4,5-Dihydro-1*H*-1,2,4-triazol-5-one, GIAO, HOMO-LUMO, UV-Vis

Introduction

1,2,4-Triazoles were reported to shown substantial antibacterial, antifungal and antihelmintic activities (Hardman et al., 1996; Gennaro et al., 1995; Richardson et al., 1984; Ammermann et al., 1991; Heindel et al., 1980). On the other hand, quantum chemical calculation methods have widely been used to theoretically predict the structural, spectroscopic, thermodynamic and electronic properties of molecular systems. The quantum chemical alculation methods provide support for experimental structural and spectroscopic studies (Yüksek et.al., 2005a; Yüksek et.al., 2005b;Yüksek et.al., 2008a;Yüksek et.al., 2008b; Gökçe ve ark., 2013; Gökçe ve ark., 2014). In this study, we report the thereotical properties of Shiff bases containing 1,2,4-triazoles. All theoretical calculations investigated for the molecule were calculated with the Gaussian 09 quantum chemistry program (Frisch et.al., 2009) on a equipped computer. Assential calculations were carried out using the Density Functional Theory (DFT) and Hatree Fock (HF) method with the restricted B3LYP (Kohn et.al., 1996; Becke et.al., 1993; Becke et.al., 1988) level of theory, using 6-31G(d,p) basis sets, for all atoms. For this, firstly, 3-*p*-Chlorobenzyl-4-(3,4-dihydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one **(1)** and 1-acetyl-3-*p*-chlorobenzyl-4-(3,4-dihydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one **(2)** were optimized by using and 6-31G(d,p) two different basis sets (Frisch et al., 2009; Wolinski, Hilton & Pulay, 1990). Thus, the most stable form of the compound were determined. The optimized structures were used to calculation of the varied theoretical properties of the compound. Then, theoretical vibrational frequency were done in gas phase. Therefore, The veda4f program was used in defining IR data (Jamróz, 2004) which are multiplied with

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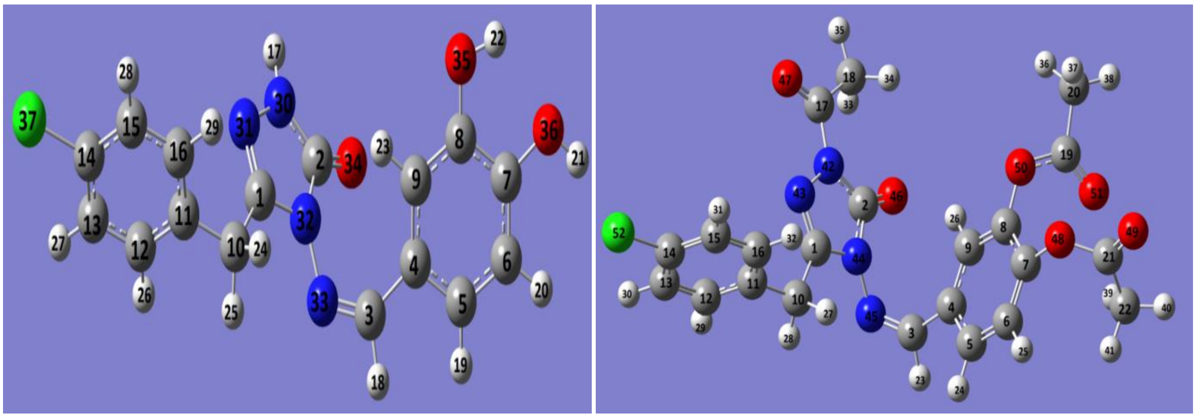
appropriate adjustment factors (Merrick et al., 2007) and result gave positive frequency values. This result, structure of compound were shown stable. Experimental data obtained from the literature (Bahçeci et al., 2002). The experimental and the calculated theoretical values were compared .The thereotical data obtained according to DFT/HF 6-31G(d,p) basis sets are formed using theoretical infrared spectrum. The experimental and theoretical IR spectra are given in Figs. 3. The ^{1}H and ^{13}C-NMR chemical shifts for the optimized molecular geometry of the molecule were calculated at B3LYP/6-31G(d,p) levels by using GIAO (the Gauge-Independent Atomic Orbital) (Pearson, 1989) approach in dimethyl sulfoxide (DMSO) solvent. Experimental and theoretical values were inserted into the graphic according to equitation of δ exp=a+b. δ calc. The standard error values were found via SigmaPlot program with regression coefficient of **a** and **b** constants. The temperature addicted thermodynamic parameters (thermal energies **E**, thermal capacity **CV**, entropy **S**) were calculated from the vibrational frequency calculations of the title compound in the gas phase using the DFT/HF 6-31G(d,p) level. In addition to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), bond lengths, mulliken charges, E_{LUMO}-E_{HOMO} energy gap (ΔEg), electronegativity (χ), electron affinity (A), global hardness (η), softness (S), ionization potential (I), chemical potential (Pi), electrophilic index(ω), Nucleophilic index (IP), total energy of the molecule, dipole moments were calculated.

Computational Details



1 2

Figure 1. The Gausview structure of the molecules 1 and 2.

Table 1. The calculated and experimental ^{13}C and ^{1}H-NMR DMSO isotropic chemical shifts of the molecule 1 and 2 (δ/ppm)

No	Exp.	DFT	Differ.	DFT/ DMSO	Differ./ DMSO	HF	Differ.	HF/ DMSO	Differ./ DMSO
C1	145.71	152.07	-6.36	153.90	-8.19	145.10	0.61	147.93	-2.22
C2	154.57	148.46	6.11	149.59	4.98	147.33	7.24	148.56	6.01
C3	151.24	160.27	-9.03	161.83	-10.59	168.16	-16.92	171.09	-19.85
C4	124.57	133.21	-8.64	131.49	-6.92	120.99	3.58	119.38	5.19
C5	121.75	129.15	-7.40	131.01	-9.26	118.74	3.01	121.80	-0.05
C6	112.86	114.99	-2.13	117.17	-4.31	107.46	5.40	110.10	2.76
C7	145.71	147.88	-2.17	149.96	-4.25	138.88	6.83	140.35	5.36
C8	149.25	148.05	1.20	147.43	1.82	138.91	10.34	137.37	11.88
C9	115.53	119.55	-4.02	117.82	-2.29	116.97	-1.44	113.76	1.77
C10	30.35	42.55	-12.20	42.09	-11.74	27.32	3.03	26.87	3.48
C11	134.72	136.69	-1.97	137.87	-3.15	128.68	6.04	130.08	4.64
C12	130.69	134.13	-3.44	134.72	-4.03	127.12	3.57	127.52	3.17
C13	128.59	131.61	-3.02	131.83	-3.24	125.00	3.59	125.16	3.43
C14	133.31	145.93	-12.62	144.73	-11.42	133.21	0.10	131.64	1.67
C15	128.59	131.63	-3.04	131.74	-3.15	124.98	3.61	125.11	3.48
C16	130.69	135.10	-4.41	135.41	-4.72	127.55	3.14	127.82	2.87
H17	11.95	7.81	4.14	8.26	3.69	7.19	4.76	7.58	4.37
H18	9.42	8.51	0.91	8.69	0.73	8.89	0.53	9.15	0.27
H19	7.05	7.56	-0.51	7.86	-0.81	7.36	-0.31	7.82	-0.77
H20	6.82	7.29	-0.47	7.76	-0.94	7.10	-0.28	7.64	-0.82
H21	7.27	8.21	-0.94	8.16	-0.89	3.63	3.64	4.59	2.68

H22	9.42	4.41	5.01	5.53	3.89	4.78	4.64	5.10	4.32
H23	9.75	5.78	3.97	6.17	3.58	8.92	0.83	8.50	1.25
H24	4.02	4.37	-0.35	4.64	-0.62	3.06	0.96	3.43	0.59
H25	4.02	4.77	-0.75	4.85	-0.83	3.58	0.44	3.78	0.24
H26	7.32	8.08	-0.76	8.30	-0.98	7.74	-0.42	8.00	-0.68
H27	7.36	8.07	-0.71	8.22	-0.86	7.78	-0.42	7.95	-0.59
H28	7.36	8.12	-0.76	8.27	-0.91	7.72	-0.36	7.90	-0.54
H29	7.32	8.20	-0.88	8.42	-1.10	7.57	-0.25	7.84	-0.52

No	Exp.	DFT	Differ.	DFT/ DMSO	Differ./ DMSO	HF	Differ.	HF/ DMSO	Differ./ DMSO
C1	144.55	152.43	-7.88	155.13	-10.58	146.04	-1.49	149.88	-5.33
C2	153.24	149.18	4.06	149.76	3.48	147.89	5.35	148.44	4.80
C3	148.20	159.51	-11.31	161.85	-13.65	168.43	-20.23	171.56	-23.36
C4	131.85	136.67	-4.82	137.09	-5.24	123.69	8.16	124.66	7.19
C5	126.82	133.08	-6.26	134.87	-8.05	123.50	3.32	126.42	0.40
C6	122.36	127.27	-4.91	128.16	-5.80	118.83	3.53	120.15	2.21
C7	148.20	153.01	-4.81	152.13	-3.93	143.25	4.95	141.84	6.36
C8	142.35	148.57	-6.22	147.67	-5.32	137.51	4.84	135.74	6.61
C9	124.38	126.79	-2.41	127.23	-2.85	123.20	1.18	121.86	2.52
C10	30.92	41.91	-10.99	41.53	-10.61	27.22	3.70	26.82	4.10
C11	130.90	134.11	-3.21	136.17	-5.27	126.57	4.33	128.89	2.01
C12	130.90	133.52	-2.62	134.64	-3.74	126.85	4.05	127.56	3.34
C13	128.34	131.56	-3.22	131.86	-3.52	125.14	3.20	125.23	3.11
C14	133.95	146.73	-12.78	144.98	-11.03	134.20	-0.25	132.04	1.91
C15	128.34	132.10	-3.76	131.65	-3.31	125.44	2.90	125.16	3.18
C16	130.90	135.83	-4.93	135.81	-4.91	127.87	3.03	128.04	2.86
C17	165.90	164.99	0.91	167.77	-1.87	156.51	9.39	160.43	5.47
C18	23.48	32.39	-8.91	32.67	-9.19	21.15	2.33	21.38	2.10
C19	168.10	171.91	-3.81	173.78	-5.68	160.96	7.14	162.99	5.11
C20	20.29	28.21	-7.92	28.44	-8.15	17.65	2.64	17.82	2.47
C21	167.98	167.84	0.14	171.54	-3.56	156.93	11.05	161.19	6.79
C22	20.29	28.40	-8.11	28.71	-8.42	17.02	3.27	17.34	2.95
H23	9.58	8.76	0.82	9.03	0.55	9.08	0.50	9.39	0.19
H24	7.76	8.08	-0.32	8.44	-0.68	7.78	-0.02	8.28	-0.52
H25	7.45	7.98	-0.53	8.28	-0.83	7.68	-0.23	8.06	-0.61
H26	7.78	8.16	-0.38	8.38	-0.60	8.93	-1.15	8.78	-1.00
H27	4.17	4.63	-0.46	4.94	-0.77	3.10	1.07	3.53	0.64
H28	4.17	4.71	-0.54	4.87	-0.70	3.57	0.60	3.84	0.33
H29	7.43	7.99	-0.56	8.28	-0.85	7.71	-0.28	8.02	-0.59
H30	7.41	8.08	-0.67	8.22	-0.81	7.81	-0.40	7.96	-0.55
H31	7.41	8.23	-0.82	8.31	-0.90	7.80	-0.39	7.92	-0.51
H32	7.43	8.46	-1.03	8.63	-1.20	7.62	-0.19	7.88	-0.45
H33	2.50	3.34	-0.84	3.42	-0.92	2.91	-0.41	3.00	-0.50
H34	2.50	3.17	-0.67	3.17	-0.67	2.79	-0.29	3.03	-0.53
H35	2.50	2.63	-0.13	2.67	-0.17	2.37	0.13	2.39	0.11
H36	2.32	3.02	-0.70	3.23	-0.91	2.48	-0.16	2.73	-0.41
H37	2.32	2.63	-0.31	2.66	-0.34	2.71	-0.39	2.77	-0.45
H38	2.32	3.31	-0.99	3.37	-1.05	2.20	0.12	2.21	0.11
H39	2.32	3.24	-0.92	3.29	-0.97	2.28	0.04	2.29	0.03
H40	2.32	2.52	-0.20	3.15	-0.83	2.07	0.25	2.18	0.14
H41	2.32	2.95	-0.63	2.56	-0.24	2.21	0.11	2.59	-0.27

The optimized R^2 values of the compound 1: B3LYP/631G(d,p) (DMSO): ^{13}C: 0.9883, ^{1}H: 0.4533; HF/631G(d,p) (DMSO): ^{13}C: 0.9762, ^{1}H: 0.5872.

The optimized R^2 values of the compound 2: B3LYP/631G(d,p) (DMSO): ^{13}C: 0.9971, ^{1}H: 0.9883; HF/631G(d,p) (DMSO): ^{13}C: 0.9916, ^{1}H: 0.9862.

There is such a relationship between R^2-values of the compound. Found standard error rate and a, b constants regression values were calculated according to formule exp =a +b. δ calc Eq. These values for compound were given in the table **2**. Theoretical and experimental carbon and proton chemical shifts ratios between acording to a, b ve R^2 values, lineer a correlation were observed.

Table 2. The correlation data for chemical shifts of the molecules 1 and 2

		^{13}C				^{1}H			
		R	**S. hata**	**a**	**b**	**R**	**S. hata**	**a**	**b**
1	**DFT**	0.9878	4.6218	1.0640	-13.0263	0.3445	2.1386	0.4761	4.2815
	HF	0.9797	5.9515	0.9483	9.0500	0.5763	1.8616	0.6130	3.5978
2	**DFT**	0.9971	3.7293	1.0388	-10.0022	0.9883	0.4190	1.0287	-0.6739
	HF	0.9916	6.3450	0.9778	4.7248	0.9862	0.4539	0.9389	0.2417

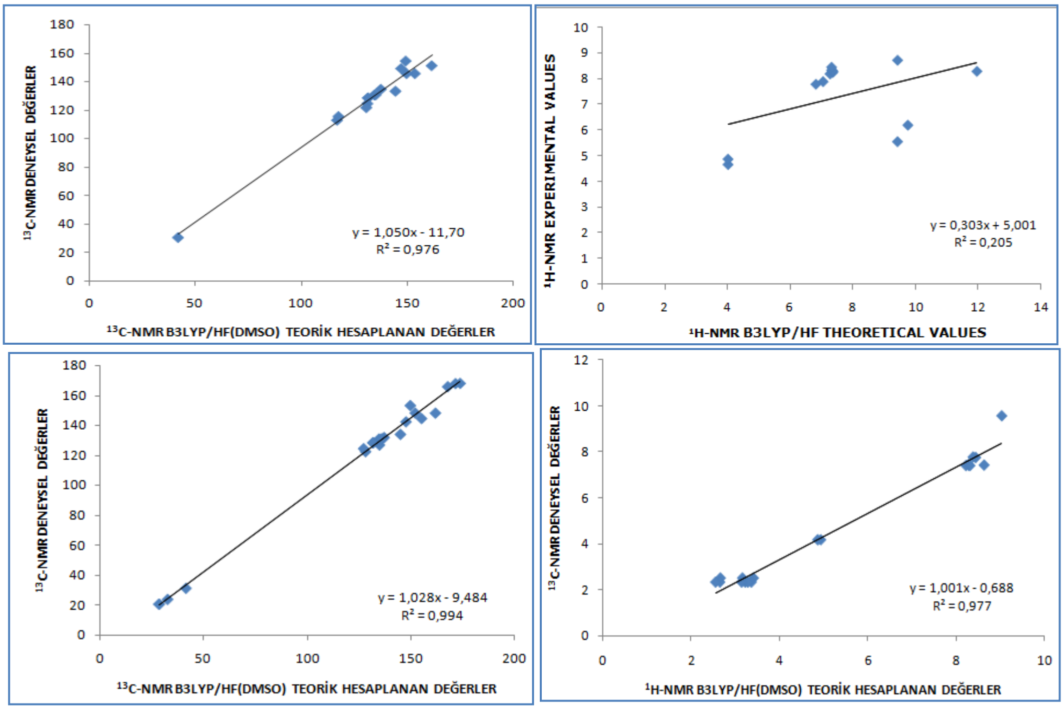
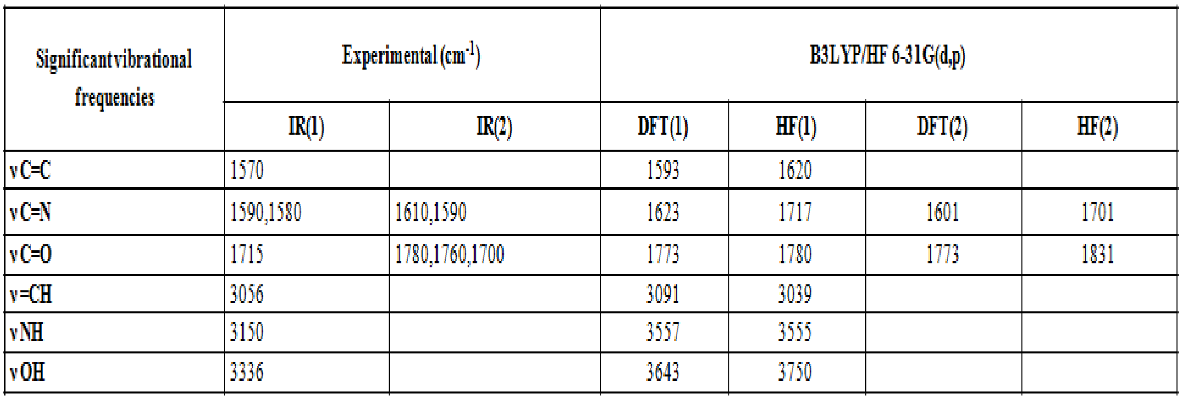


Figure 2. The correlation graphs for 6-31G(d,p) chemical shifts of the molecules 1 and 2

The Vibration Frequency of the Compound

Theoretically IR values were calculation veda 4f programme and scala values were obtain. IR spectrums were drawn with obtained values according to HF and DFT method. Theoretically IR values were compare with experimentally IR values. The result of this compare were found corresponding with each other of values. (Table 3).

Table 3. Significant vibrational frequencies (cm^{-1})of the molecules 1 and 2



Significant vibrational frequencies	Experimental (cm^{-1})		B3LYP/HF 6-31G(d,p)			
	IR(1)	IR(2)	DFT(1)	HF(1)	DFT(2)	HF(2)
νC=C	1570		1593	1620		
νC=N	1590,1580	1610,1590	1623	1717	1601	1701
νC=O	1715	1780,1760,1700	1773	1780	1773	1831
ν=CH	3056		3091	3039		
νNH	3150		3557	3555		
νOH	3336		3643	3750		

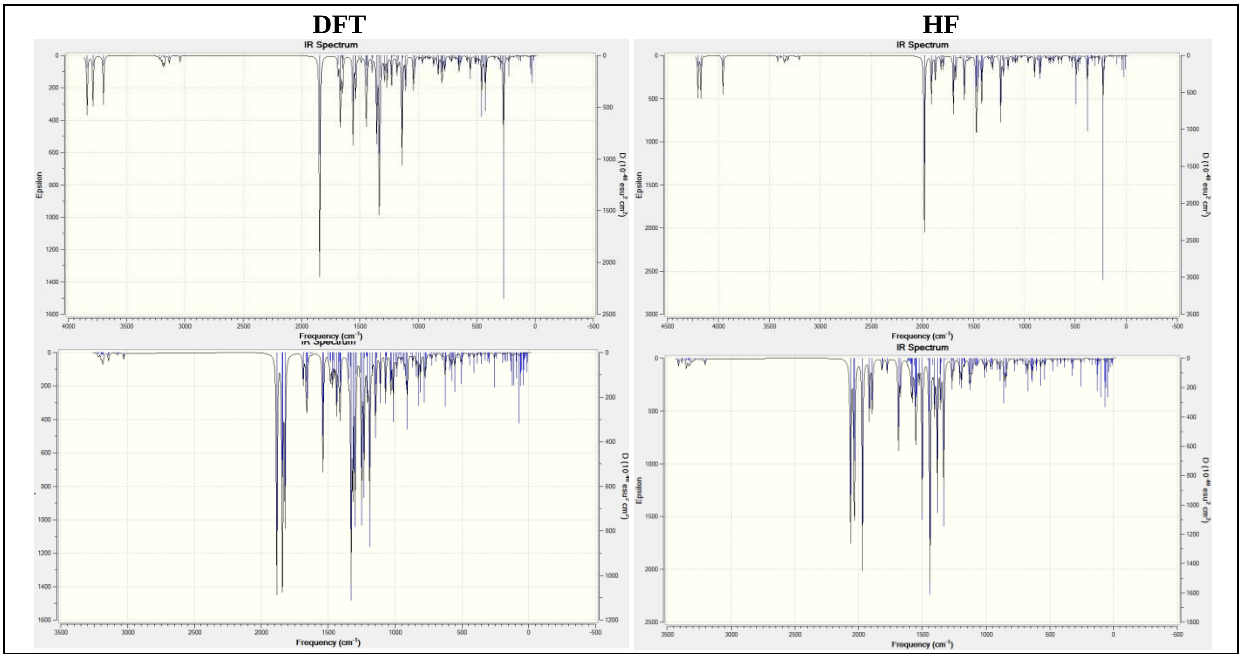


Figure 3. Experimantal and theoretical IR spectrums and simulated of the molecules 1 and 2.

Table 4. The calculated bond lengths of the molecules 1 and 2

bond length 1	**DFT**	**HF**	**bond length 1**	**DFT**	**HF**	**bond length 2**	**DFT**	**HF**	**bond length 2**	**DFT**	**HF**
C(1)-N(31)	1.300	1.267	C(15)-H(28)	1.084	1.073	C(1)-N(43)	1.294	1.263	C(16)-C(11)	1.400	1.388
C(1)-N(32)	1.388	1.380	C(15)-C(16)	1.393	1.383	C(1)-N(44)	1.398	1.384	N(45)-C(3)	1.289	1.259
C(1)-C(10)	1.499	1.498	C(16)-H(29)	1.086	1.075	C(1)-C(10)	1.501	1.498	C(3)-H(23)	1.091	1.079
N(31)-N(30)	1.381	1.370	C(16)-C(11)	1.399	1.388	N(42)-N(43)	1.394	1.381	C(3)-C(4)	1.470	1.484
N(30)-H(17)	1.006	0.990	N(33)-C(3)	1.290	1.260	N(42)-C(17)	1.429	1.410	C(4)-C(5)	1.403	1.390
N(30)-C(2)	1.374	1.349	C(3)-H(18)	1.091	1.079	C(17)-O(47)	1.207	1.183	C(4)-C(9)	1.404	1.389
C(2)-O(34)	1.217	1.199	C(3)-C(4)	1.466	1.481	C(17)-C(18)	1.508	1.506	C(5)-H(24)	1.085	1.075
C(2)-N(32)	1.422	1.383	C(4)-C(5)	1.404	1.388	C(18)-H(33)	1.092	1.081	C(5)-C(6)	1.391	1.381
N(32)-N(33)	1.393	1.397	C(4)-C(9)	1.408	1.394	C(18)-H(34)	1.094	1.082	C(6)-H(25)	1.084	1.073
C(1)-C(10)	1.499	1.498	C(5)-H(19)	1.085	1.075	C(18)-H(35)	1.089	1.079	C(6)-C(7)	1.395	1.382
C(10)-H(24)	1.098	1.086	C(5)-C(6)	1.392	1.385	N(42)-C(2)	1.399	1.374	C(7)-O(48)	1.375	1.358
C(10)-H(25)	1.096	1.084	C(6)-H(20)	1.087	1.076	C(2)-O(46)	1.215	1.197	O(48)-C(21)	1.398	1.362
C(10)-C(11)	1.513	1.512	C(6)-C(7)	1.390	1.378	C(2)-N(44)	1.410	1.373	C(21)-O(49)	1.199	1.177
C(11)-C(12)	1.398	1.386	C(7)-O(36)	1.370	1.355	N(44)-N(45)	1.391	1.399	C(21)-C(22)	1.507	1.505
C(12)-H(26)	1.086	1.076	O(36)-H(21)	0.965	0.942	C(10)-H(27)	1.091	1.086	C(22)-H(39)	1.093	1.080
C(12)-C(13)	1.394	1.384	C(7)-C(8)	1.409	1.394	C(10)-H(28)	1.095	1.084	C(22)-H(40)	1.092	1.083
C(13)-H(27)	1.084	1.073	C(8)-O(35)	1.361	1.345	C(10)-C(11)	1.513	1.512	C(22)-H(41)	1.089	1.079
C(13)-C(14)	1.393	1.381	O(35)-H(22)	0.968	0.944	C(11)-C(12)	1.397	1.386	C(7)-C(8)	1.402	1.387
C(14)-Cl(37)	1.760	1.744	C(8)-C(9)	1.386	1.377	C(12)-H(29)	1.086	1.076	C(8)-O(50)	1.390	1.371
C(14)-C(15)	1.393	1.382	C(9)-H(23)	1.081	1.071	C(12)-C(13)	1.395	1.384	O(50)-C(19)	1.374	1.343
						C(13)-H(30)	1.084	1.073	C(19)-O(51)	1.207	1.184
						C(13)-C(14)	1.392	1.380	C(19)-C(20)	1.503	1.498
						C(14)-Cl(52)	1.759	1.743	C(20)-H(36)	1.092	1.083
						C(14)-C(15)	1.394	1.382	C(20)-H(37)	1.089	1.083
						C(15)-H(31)	1.084	1.073	C(20)-H(38)	1.094	1.079
						C(15)-C(16)	1.392	1.382	C(8)-C(9)	1.384	1.378
						C(16)-H(32)	1.085	1.075	C(9)-H(26)	1.082	1.071

Table 5. The calculated bond angles with B3LYP/HF 631G(d,p) of the molecule1 and 2.

	bond angles	**B3LYP**	**HF**		**bond angles**	**B3LYP**	**HF**
1	C(1)-N(31)-N(30)	104.314	104.822	**27**	H(28)-C(15)-C(16)	120.825	120.690
2	C(1)-N(32)-C(2)	107.989	107.670	**28**	C(14)-C(15)-C(16)	119.031	119.162
3	N(31)-C(1)-N(32)	111.741	111.506	**29**	C(15)-C(16)-H(29)	119.153	119.091
4	N(31)-N(30)-H(17)	120.090	120.790	**30**	H(29)-C(16)-C(11)	119.667	119.825
5	H(17)-N(30)-C(2)	124.717	125.429	**31**	C(1)-N(32)-N(33)	121.389	122.020
6	N(31)-N(30)-C(2)	114.513	113.416	**32**	N(32)-N(33)-C(3)	118.973	117.547
7	N(30)-C(2)-O(34)	130.513	129.838	**33**	N(33)-C(3)-H(18)	110.921	112.173
8	O(34)-C(2)-N(32)	128.522	127.998	**34**	H(18)-C(3)-C(4)	113.594	114.513
9	C(2)-N(32)-N(33)	125.612	123.480	**35**	C(3)-C(4)-C(5)	116.446	115.879
10	C(1)-C(10)-C(11)	113.794	113.863	**36**	C(3)-C(4)-C(9)	124.515	124.561
11	C(1)-C(10)-H(24)	108.475	107.910	**37**	C(4)-C(5)-H(19)	119.654	120.283
12	C(1)-C(10)-H(25)	107.581	107.738	**38**	H(19)-C(5)-C(6)	119.438	119.283
13	H(24)-C(10)-H(25)	105.470	106.127	**39**	C(4)-C(5)-C(6)	120.905	120.431
14	H(24)-C(10)-C(11)	110.273	110.340	**40**	C(5)-C(6)-C(7)	119.590	119.704
15	H(25)-C(10)-C(11)	110.868	110.524	**41**	C(5)-C(6)-H(20)	120.486	120.325
16	C(10)-C(11)-C(12)	120.708	120.683	**42**	H(20)-C(6)-C(7)	119.922	119.969
17	C(10)-C(11)-C(16)	120.780	120.724	**43**	C(6)-C(7)-O(36)	124.746	124.043
18	C(11)-C(12)-H(26)	119.647	119.863	**44**	C(6)-C(7)-C(8)	120.333	120.294
19	H(26)-C(12)-C(13)	119.148	119.046	**45**	C(7)-O(36)-H(21)	110.141	111.829
20	C(12)-C(13)-H(27)	120.818	120.664	**46**	O(36)-C(7)-C(8)	114.918	115.658
21	H(27)-C(13)-C(14)	120.185	120.190	**47**	C(7)-C(8)-O(35)	120.294	120.601
22	C(12)-C(13)-C(14)	118.996	119.146	**48**	C(8)-O(35)-H(22)	107.807	110.084
23	C(13)-C(14)-Cl(37)	119.473	119.563	**49**	O(35)-C(8)-C(9)	119.915	119.423
24	Cl(37)-C(14)-C(15)	119.450	119.512	**50**	C(8)-C(9)-H(23)	117.848	118.418
25	C(13)-C(14)-C(15)	121.077	120.925	**51**	H(23)-C(9)-C(4)	121.645	121.507
26	C(14)-C(15)-H(28)	120.145	120.148				

bond angles 2	**B3LYP**	**HF**	**bond angles 2**	**B3LYP**	**HF**
C(1)-N(43)-N(42)	105.214	105.578	N(42)-C(2)-O(46)	130.406	129.835
C(1)-N(44)-C(2)	108.033	107.757	C(2)-N(44)-N(45)	126.350	122.967
N(43)-C(1)-N(44)	111.945	111.768	N(44)-N(45)-C(3)	118.801	117.333
N(43)-N(42)-C(17)	119.321	119.327	N(45)-C(3)-H(23)	111.634	112.577
N(43)-C(1)-C(10)	126.535	126.852	H(23)-C(3)-C(4)	114.648	115.066
N(44)-C(1)-C(10)	121.460	121.342	C(3)-C(4)-C(5)	117.883	116.809
C(1)-C(10)-H(27)	107.932	107.654	C(3)-C(4)-C(9)	123.408	123.860
C(1)-C(10)-H(28)	107.437	107.596	C(4)-C(5)-H(24)	119.602	120.135
H(27)-C(10)-C(11)	110.428	110.437	H(24)-C(5)-C(6)	119.499	119.269
H(28)-C(10)-C(11)	110.713	110.525	C(4)-C(5)-C(6)	120.893	120.583
H(27)-C(10)-H(28)	105.314	106.180	C(5)-C(6)-H(25)	120.867	120.668
C(1)-C(10)-C(11)	114.550	114.088	H(25)-C(6)-C(7)	119.046	119.357
C(10)-C(11)-C(16)	121.075	120.719	C(5)-C(6)-C(7)	120.079	119.973
C(10)-C(11)-C(12)	120.339	120.573	C(6)-C(7)-O(48)	121.873	121.752
C(11)-C(12)-H(29)	119.755	119.959	C(7)-O(48)-C(21)	122.962	125.018
H(29)-C(12)-C(13)	119.047	119.011	O(48)-C(21)-O(49)	116.867	117.203
C(11)-C(12)-C(13)	121.198	121.030	O(49)-C(21)-C(22)	125.764	124.346
C(12)-C(13)-H(30)	120.783	120.656	C(21)-C(22)-H(39)	111.321	111.211
H(30)-C(13)-C(14)	120.231	120.203	C(21)-C(22)-H(40)	110.187	110.371
C(13)-C(14)-Cl(52)	119.502	119.557	C(21)-C(22)-H(41)	107.680	107.215
Cl(52)-C(14)-C(15)	119.459	119.502	H(39)-C(22)-H(40)	108.034	108.943
C(12)-C(13)-C(14)	118.987	119.141	H(40)-C(22)-H(41)	110.344	110.115
C(14)-C(15)-H(31)	120.130	120.149	H(39)-C(22)-H(41)	109.280	108.952
H(31)-C(15)-C(16)	120.728	120.671	O(48)-C(7)-C(8)	118.706	118.659
C(14)-C(15)-C(16)	119.142	119.180	C(7)-C(8)-O(50)	120.293	120.789
C(15)-C(16)-H(32)	119.132	119.071	C(8)-O(50)-C(19)	118.423	119.972
H(32)-C(16)-C(11)	119.806	119.925	O(50)-C(19)-O(51)	123.306	122.963
C(15)-C(16)-C(11)	121.057	121.003	O(51)-C(19)-C(20)	126.534	126.217
N(42)-C(17)-O(47)	119.616	119.760	C(19)-C(20)-H(36)	110.560	109.892
O(47)-C(17)-C(18)	124.610	123.550	C(19)-C(20)-H(37)	109.418	109.387
N(42)-C(17)-C(18)	115.766	116.690	C(19)-C(20)-H(38)	109.059	109.012
C(17)-C(18)-H(33)	111.249	110.996	H(36)-C(20)-H(37)	107.537	107.940
C(17)-C(18)-H(34)	111.158	111.020	H(37)-C(20)-H(38)	109.657	110.088
C(17)-C(18)-H(35)	107.208	106.956	H(36)-C(20)-H(38)	110.573	110.494
H(33)-C(18)-H(34)	106.425	107.064	C(8)-C(9)-H(26)	118.178	118.863
H(34)-C(18)-H(35)	110.221	110.382	H(26)-C(9)-C(4)	121.436	121.313

Frontier Molecular Orbital Analysis

Frontier molecular orbitals (FMO) (Figs. 4,5) determines the electric, electronic transitions, optical properties and kinetic stability (Fukui et al., 1952). HOMO-LUMO energy of compound was calculated using 6-31G (d,p) level of theory. Using HOMO-LUMO energy gap electronegativity (χ), electron affinity (A), global hardness (η), softness (S), chemical potential (μ), ionization potential (I), chemical potential (Pi), electrophilic index(ω), Nucleophilic index (IP) for the compound was calculated. These all properties are calculated as follows (Parr, 1989; Parr et al., 1999; Özdemir et al., 2013):

$$\eta = (I - A)/2,\ \ \mu = -(I + A)/2,\ \ \chi = (I + A)/2,\ Pi = \chi,\ \omega = \mu^2 / 2\eta$$

In this formule, I and A symbolised ionization potential and electron affinity of the compound, which are virtually obtained from HOMO and LUMO energies. Where $I = -E_{HOMO}$ and $A = -E_{LUMO}$ showed as per Janak theorem (Janak, 1978) and Perdew et al. (Perdew et al., 1982). The HOMO-LUMO energy gap in compounds is 4.29; 11,18 e.v. All these parameters such as global hardness (η) chemical potential (μ), the global electrophilicity index (ω), electronegativity (χ), ionization potential (I), chemical potential (Pi), electrophilic index(ω), Nucleophilic index (IP) have been calculated for the target compound using 6-31G (d,p) basis set and are showed in Tables 6,7.

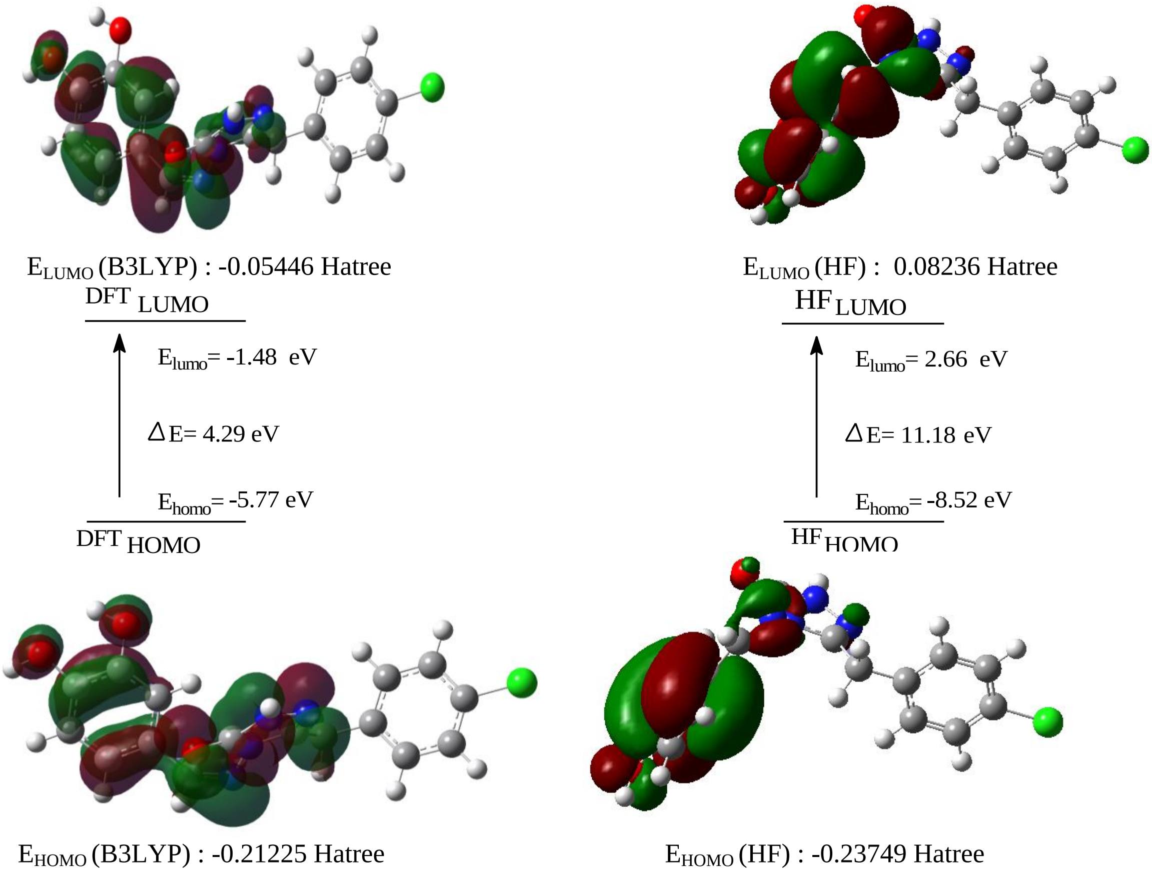
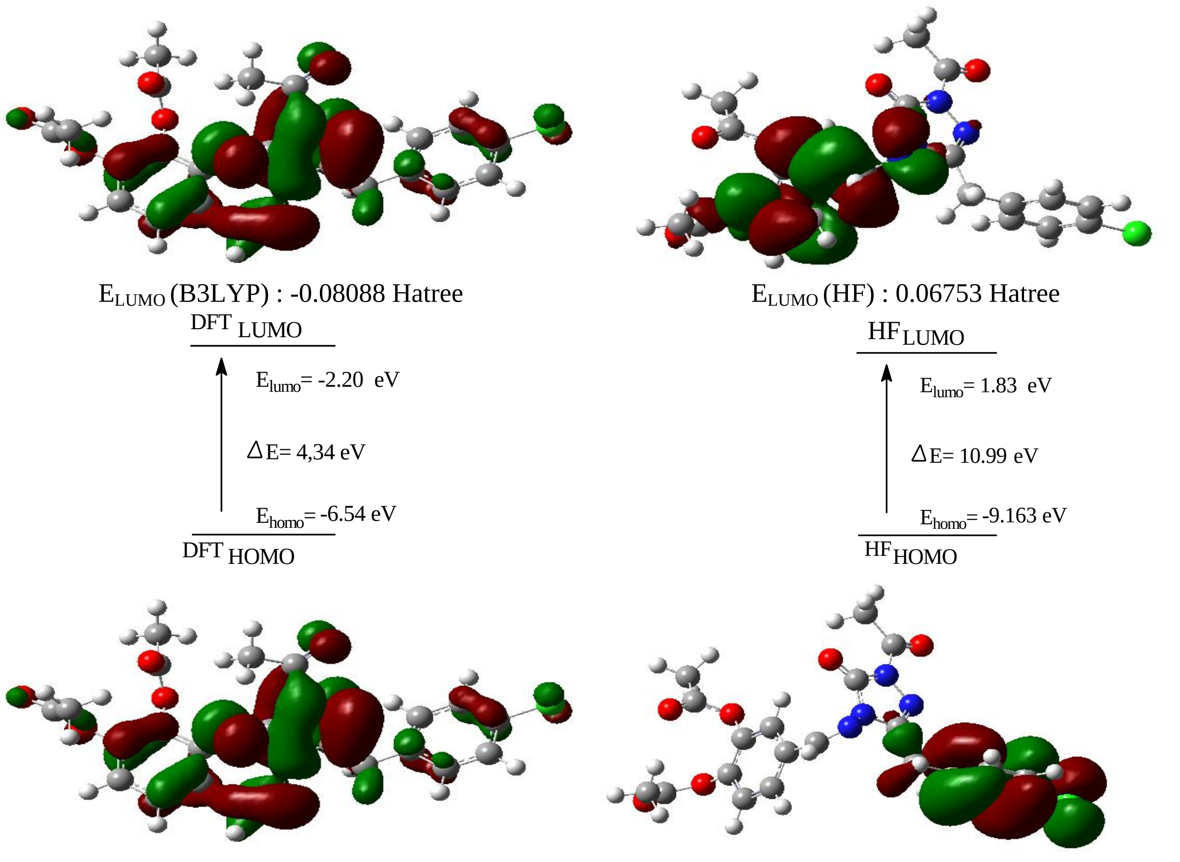


Figure 4. HOMO-LUMO energy calculated with DFT/HF 6-31G(d,p) levels of the molecule 1

Table 6. The calculated electronic structure parameters of the molecule 1

		Hatree	**ev**	**kcal/mol**	**KJ/mol**
	LUMO	-0,05446	-1,48189	-34,1738	-142,985
	HOMO	-0,21225	-5,77547	-133,188	-557,262
A	electron affinity	0,05446	1,48189	34,1738	142,985
I	ionization potential	0,21225	5,77547	133,188	557,262
ΔE	energy gap	0,15779	4,29358	99,0137	414,278
χ	electronegativity	0,133355	3,62868	83,6807	350,124
Pi	chemical potential	-0,133355	-3,62868	-83,6807	-350,124
ω	electrophilic index	0,000701517	0,01909	0,4402	1,84183
IP	Nucleophilic index	-0,01052104	-0,28628	-6,60199	-27,623
S	molecular softness	12,6751	344,898	7953,65	33278,4
η	molecular hardness	0,078895	2,14679	49,5068	207,139



E_{LUMO} (B3LYP) : -0.08088 Hatree

E_{LUMO} (HF) : 0.06753 Hatree

E_{HOMO} (B3LYP) : -0.24155 Hatree

E_{HOMO} (HF) : -0.33380 Hatree

Figure 5. HOMO-LUMO energy calculated of the molecule 2

Table 7. The calculated electronic structure parameters of the molecule 2

		Hatree	**ev**	**kcal/mol**	**KJ/mol**
	LUMO	-0,08088	-2,2008	-50,7524	-212,35
	HOMO	-0,24155	-6,57274	-151,573	-634,19
A	electron affinity	0,08088	2,2008	50,7524	212,35
I	ionization potential	0,24155	6,57274	151,573	634,19
ΔE	energy gap	0,16067	4,37194	100,821	421,839
χ	electronegativity	0,161215	4,38677	101,163	423,27
Pi	chemical potential	-0,161215	-4,38677	-101,163	-423,27
ω	electrophilic index	0,001043964	0,02841	0,65509	2,74093
IP	Nucleophilic index	-0,01295121	-0,35241	-8,12692	-34,0034
S	molecular softness	12,4479	338,715	7811,08	32681,9
η	molecular hardness	0,080335	2,18597	50,4105	210,92

Thermodynamics Properties of Compound

Table 8. The calculated thermodynamics properties of the molecule 1.

Rotational temperatures (Kelvin)	**DFT**	**HF**
A	0.02986	0.01930
B	0.00363	0.00439
C	0.00353	0.00406
Rotational constants (GHz)		
A	0.62224	0.40219
B	0.07555	0.09141
C	0.07348	0.08467
Thermal Energies E (kcal/mol)		
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	183.677	196.381
Total	185.455	198.159

Thermal Capacity CV (cal/mol-K)		
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	73.753	68.087
Total	79.715	74.048
Entropy S (cal/mol-K)		
Translational	43.401	43.401
Rotational	35.785	35.889
Vibrational	81.320	75.340
Total	160.507	154.630
Zero-point correction (Hartree/Particle)	0.274631	0.296125
Thermal correction to Energy	0.295541	0.315786
Thermal correction to Enthalpy	0.296485	0.316730
Thermal correction to Gibbs Free Energy	0.220223	0.243260
Sum of electronic and zero-point Energies	-1522.105640	-1515.008945
Sum of electronic and thermal Energies	-1522.084730	-1514.989284
Sum of electronic and thermal Enthalpies	-1522.083786	-1514.988340
Sum of electronic and thermal Free Energies	-1522.160048	-1515.061810
Zero-point vibrational energy (Kcal/Mol)	172.33359	185.82126

Table 9. The calculated thermodynamics properties of the molecule 2

Rotational temperatures (Kelvin)	**DFT**	**HF**
A	0.01278	0.00903
B	0.00242	0.00261
C	0.00229	0.00235
Rotational constants (GHz)		
A	0.26638	0.18817
B	0.05035	0.05433
C	0.04782	0.04900
Thermal Energies E (kcal/mol)		
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	260.146	277.814
Total	261.924	279.592
Thermal Capacity CV (cal/mol-K)		
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	107.833	99.762
Total	113.794	105.724
Entropy S (cal/mol-K)		
Translational	44.332	44.332
Rotational	37.458	37.704
Vibrational	129.793	123.222
Total	211.583	205.257
Zero-point correction (Hartree/Particle)	0.386315	0.416320
Thermal correction to Energy	0.417402	0.445558
Thermal correction to Enthalpy	0.418346	0.446502
Thermal correction to Gibbs Free Energy	0.317816	0.348977
Sum of electronic and zero-point Energies	-1979.955917	-1970.231524
Sum of electronic and thermal Energies	-1979.924831	-1970.202287
Sum of electronic and thermal Enthalpies	-1979.923887	-1970.201343
Sum of electronic and thermal Free Energies	-1980.024417	-1970.298867
Zero-point vibrational energy (Kcal/Mol)	242.41655	261.24488

Table 10. The calculated mulliken charges datas of the molecule 1 and 2

1	DFT	HF	1	DFT	HF	2	DFT	HF	2	DFT	HF
C1	0.536	0.605	**H18**	0.086	0.156	**C1**	0.547	0.622	**H27**	0.142	0.163
C2	0.768	1.024	**H19**	0.331	0.361	**C2**	0.817	1.094	**H28**	0.152	0.179
C3	0.077	0.195	**H20**	0.336	0.371	**C3**	0.072	0.195	**H29**	0.092	0.160
C4	0.142	-0.098	**H21**	0.112	0.240	**C4**	0.131	-0.107	**H30**	0.111	0.180
C5	-0.140	-0.156	**H22**	0.134	0.161	**C5**	-0.122	-0.144	**H31**	0.113	0.181
C6	-0.128	-0.192	**H23**	0.149	0.176	**C6**	-0.113	-0.167	**H32**	0.097	0.161
C7	0.298	0.342	**H24**	0.094	0.161	**C7**	0.317	0.371	**H33**	0.154	0.168
C8	0.313	0.354	**H25**	0.110	0.178	**C8**	0.329	0.362	**H34**	0.160	0.157
C9	-0.117	-0.151	**H26**	0.109	0.177	**C9**	-0.123	-0.139	**H35**	0.136	0.161
C10	-0.321	-0.288	**H27**	0.093	0.160	**C10**	-0.322	-0.291	**H36**	0.148	0.160
C11	0.131	0.001	**N28**	-0.412	-0.543	**C11**	0.128	-0.001	**H37**	0.151	0.174
C12	-0.109	-0.138	**N29**	-0.341	-0.344	**C12**	-0.119	-0.139	**H38**	0.165	0.167
C13	-0.069	-0.112	**N30**	-0.438	-0.638	**C13**	-0.068	-0.110	**H39**	0.138	0.189
C14	50.094	-0.164	**N31**	-0.279	-0.274	**C14**	-0.093	-0.162	**H40**	0.184	0.142
H15	0.288	0.340	**O32**	-0.584	-0.681	**C15**	-0.071	-0.110	**H41**	0.150	0.175
H16	0.114	0.169	**Cl33**	-0.028	-0.006	**C16**	-0.083	-0.121	**N42**	-0.423	-0.667
H17	0.093	0.162				**C17**	0.560	0.743	**N43**	-0.315	-0.286
						C18	-0.387	-0.409	**N44**	-0.462	-0.661
						C19	0.586	0.763	**N45**	-0.252	-0.258
						C20	-0.389	-0.414	**O46**	-0.520	-0.646
						C21	0.567	0.759	**O47**	-0.424	-0.511
						C22	0.418	-0.454	**O48**	-0.511	-0.671
						H23	0.128	0.181	**O49**	-0.414	-0.510
						H24	0.107	0.175	**O50**	-0.517	-0.667
						H25	0.116	0.184	**O51**	-0.450	-0.560
						H26	0.115	0.242	**Cl 52**	-0.023	-0.001

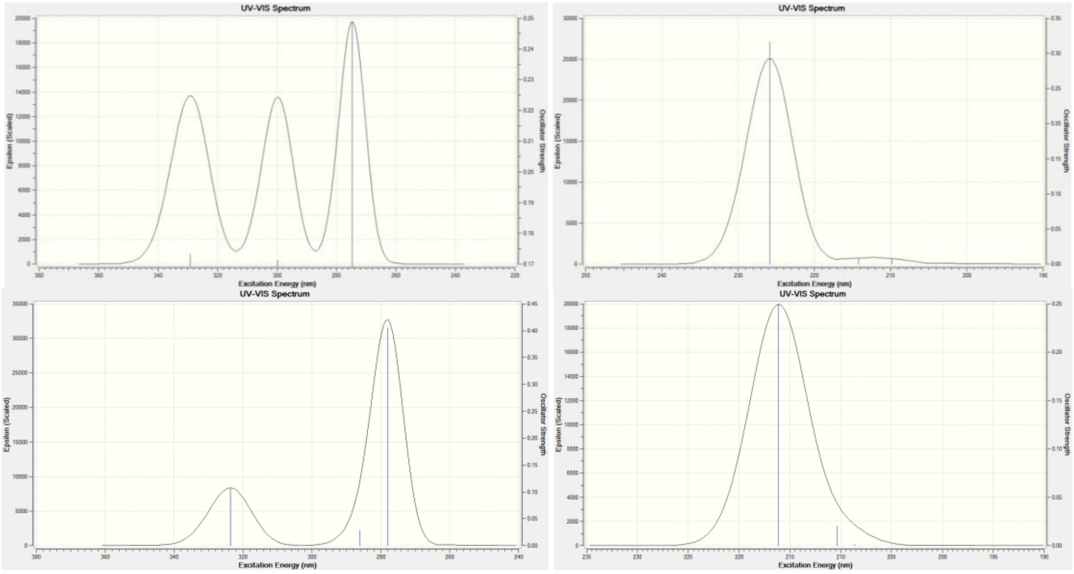


Figure 6. The UV-vis spectrum of the molecules 1 and 2

λ (nm)B3LYP/HF	Excitation energy (eV) B3LYP/HF	λ (nm)B3LYP/HF	Excitation energy (eV) B3LYP/HF
329.11/225.85	3.7673/5.4898	323.65/216.16	3.8308/5.7357
299.75/214.20	4.1362/5.7883	286.10/210.31	4.3336/5.8952
274.69/209.87	4.5137/5.9076	278.04/208.65	4.4592/5.9422

Table 11. The calculated dipole moments datas of the molecule

Dipole moments	B3LYP 1	HF 1	B3LYP 2	HF 2
μ_x	-1.4678	-0.6046	2.4975	2.7535
μ_y	-5.2882	-6.5842	-4.5046	-6.5222
μ_z	1.4558	1.9100	2.3302	2.3489
μ_{Toplam}	5.6779	6.8823	5.6532	7.4591

Table 12. The calculated total energy datas of the molecule

Energy	**B3LYP**	**HF**
1	-1522.380	-1515.305
2	-1980.342	-1970.647

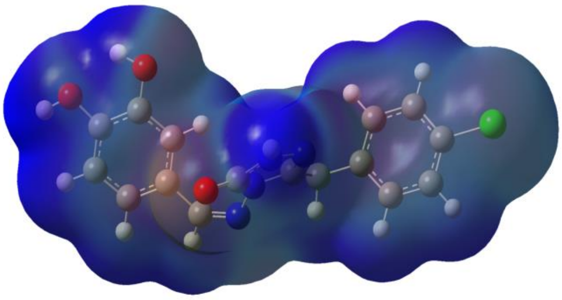


Figure 7. The total density of the molecule

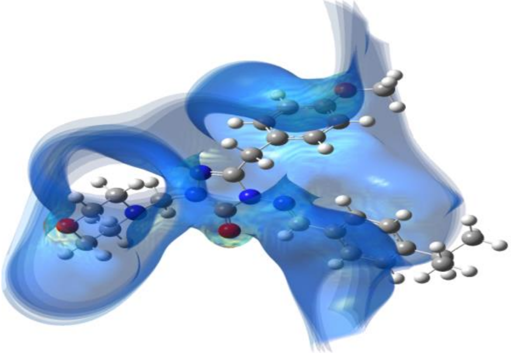


Figure 8. The MEP of the molecule

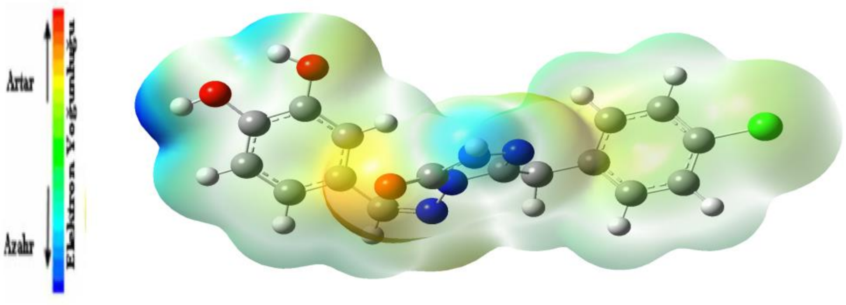


Figure 9. The ESP of the molecule

Conclusion

In this work, geometrical parameters and spectroscopic parameters such as IR, ^{1}H-NMR and ^{13}C-NMR spectra of molecule are calculated by Density Functional Theory (DFT) and Hartree-Fock (HF) methods with the 631G(d,p) basis sets of the program package Gaussian G09W. Obtained spectroscopic parameters are compared with experimental data. Otherwise, calculated theoretical properties of the compound according to two different basis sets were compared. In the result, the obtained data with B3LYP/HF 631G (d,p) basis sets were found to be closer to the experimental data. The chemical shifts in the calculations ^{1}H-NMR and ^{13}C-NMR and IR vibrational frequencies are found to be compatible with the experimental data. Theoretical and experimental carbon and proton chemical shifts ratios between acording to R^2 and a, b values, lineer a correlation were observed. The possitive frequency in the IR data was found. This result, structure of compound were shown stable. In addition, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), bond lengths, mulliken charges, E_{LUMO}-E_{HOMO} energy gap (ΔE_g), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), total energy of the molecule, thermodynamics properties (thermal energies (E), entropy (S), thermal capacity (CV), dipole moments were calculated B3LYP/HF 631G (d,p) basis sets.

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Author Information

Gul Kotan
Kafkas University Kars Vocational School
Kars, Turkey
Contact e-mail: *gulkemer@hotmail.com*

Sule BAHCECI
Fatih Education Faculty, Karadeniz Technical University,
Trabzon, Turkey

Haydar Yuksek
Kafkas University, Department of Chemistry
Kars, Turkey