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The Investigation of Spectral and Theoretical Properties of 2-(3-Cyclopropyl-4,5-dihydro-1H-1,2,4-triazol-5-yl-iminomethyl) Benzoic Acid by Using B3LYP/HF 6-31g (d,p) Basis Set

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ABSTRACT

1H-1,2,4-triazole has been theoretically studied. All theoretical calculations have been carried out by using Density Functional Theory (DFT) and Hartree-Fock (HF) methods. The vibrational frequencies were calculated by using HF/6-31G(d,p) and DFT(B3LYP)/6-31G(d,p) basis sets in ground state. The UV-vis (ethanol), Proton Nuclear Magnetic Resonance (¹H-NMR) and Carbon-13 Nuclear Magnetic Resonance (¹³C-NMR) spectra of title molecule have been recorded. The ¹H and ¹³C-NMR chemical shifts of the title molecule were calculated by the GIAO method and compared with experimental results. Using gauge independent atomic orbital method ¹H and ¹³C-NMR chemical shifts have been calculated and correlated with the experimental chemical shifts. The polarizability (α), hyperpolarizability (β), dipole moment along with molecular electrostatic potential surface have been calculated. The molecular electrostatic potential (MEP) map was calculated to assign reactive site on the surface of the molecule. The calculated electronic, structural (bond lengths and bond angles) and several thermodynamic parameters, molecular electrostatic potential (MEP) map of the compound were performed using the Hartree-Fock (HF) and density functional method (DFT/B3LYP) with 6-31G(d,p) basis set.

Keywords: 1H-1,2,4-triazol-5-one, GIAO, DFT/HF, 6-31G(d,p) basis set

INTRODUCTION

4-Amino-1H-1,2,4-triazole and their derivatives are reported to possess a wide spectrum of biological activities such as antifungal, antibacterial, anticancer, anti-inflammatory and antitumor properties [1-13]. During the past two decades, considerable attention has been paid to the chemistry and computational chemical calculations of 1,2,4-triazole and their derivatives. That's why these methods have been commonly used the prediction of many properties in the chemical systems. The computational chemical models are widely used design of functional materials. Also, many authors have studied the structure, spectroscopic, electronic and thermodynamic parameters of many organic compounds by using theoretical calculation methods [13-18].

The derivatives of 1,2,4-triazole are known to exhibit many biological activities. Hence, various 1,2,4-triazole and their derivatives have been theoretically analyzed [18-21]. Reliable results consistent with experimental results have been obtained for 1,2,4-triazole and their derivatives [21-25]. For this purpose, firstly, all quantum chemical calculations of target compound have been carried out by using B3LYP/6-31G(d,p) and HF/6-31G(d,p) methods. The DFT/B3LYP and HF methods are known to be the most widely used methods in many reported references [26,27]. Also, the vibrational frequencies and calculated structural parameters (bond lengths and bond angles), electronic, thermodynamic parameters, gauge including atomic orbital (GIAO) ¹H and ¹³C chemical shift values, UV-vis, HOMO-LUMO energies, charge distributions, total static dipole moment (μ), the mean polarizability ($\langle\alpha\rangle$), the anisotropy of the polarizability ($\Delta\alpha$), the mean first-order hyperpolarizability ($\langle\beta\rangle$), electronegativity(χ), hardness(η), molecular electrostatic potential maps (MEP) of target molecule were calculated by using the optimized structures with B3LYP/6-31G(d,p) and HF/6-31G(d,p) basis sets in ground state. The vibrational frequencies of the title molecule were related with the spectral data obtained with DFT/B3LYP and HF 6-31G(d,p) basis sets. In the identification of calculated IR data was used the veda4f program [28]. The calculated vibrational frequencies were compared with their experimental data.

MATERIAL AND METHODS

Theoretical

The quantum chemical calculations of target molecule were performed by using Gaussian 09W [29] and GaussView [30] software. The molecular geometry of title compound was optimized using density functional theory (DFT/B3LYP) and hartree fock (HF) methods with the 6-31G(d,p) basis set in ground state. From the optimized geometry, structural (bond lengths and bond angles), ¹H and ¹³C-NMR chemical shift values, UV-Vis values, total energy, molecular electrostatic potential (MEP) map, dipole moment and Mulliken atomic charges, vibrational

frequencies and HOMO–LUMO energies of the molecule were calculated with B3LYP/ HF 6-31G(d,p) levels. The IR, Proton Nuclear Magnetic Resonance ($^1\text{H-NMR}$), Carbon-13 Nuclear Magnetic Resonance ($^{13}\text{C-NMR}$) and UV-vis (ethanol) spectra of target molecule have been recorded. The veda4f program was used for the identification of the calculated IR data [28]. The gauge independent atomic orbital (GIAO) ^1H and $^{13}\text{C-NMR}$ chemical shift values was calculated at B3LYP/6-31G(d,p) and HF/6-31G(d,p) levels [31,32]. The theoretical UV-vis spectral values were carried out using TD-DFT method in ethanol solvent. The experimental spectra values of this compound obtained from ^1H and $^{13}\text{C-NMR}$ spectra were compared to the calculated results from the DFT/B3LYP and HF 6-31G(d,p) basis sets.

Optimized geometries

2-(3-Cyclopropyl-4,5-dihydro-1*H*-1,2,4-triazol-5-on-4-yl-iminomethyl) benzoic acid was optimized by means of DFT(B3LYP)/HF methods with 6-31G(d,p) basis set. The optimized geometric structure of 2-(3-cyclopropyl-4,5-dihydro-1*H*-1,2,4-triazol-5-on-4-yl-iminomethyl) benzoic acid is shown in Figure 1. The geometric parameters (bond angles and bond lengths), Mulliken atomic charges of 2-(3-cyclopropyl-4,5-dihydro-1*H*-1,2,4-triazol-5-on-4-yl-iminomethyl) benzoic acid were calculated using the DFT(B3LYP)/HF 6-31G(d,p) method. The calculated parameters are given in Tables 1-3 and Chart 1.

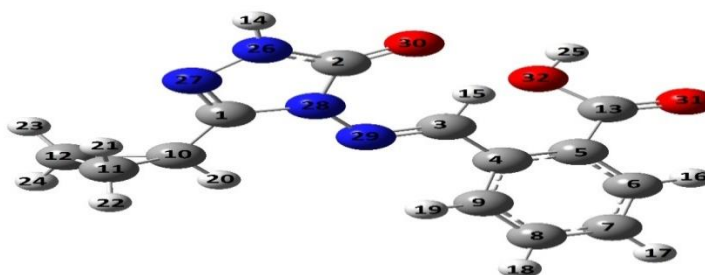


Figure 1: The computed geometric structure of 2-(3-cyclopropyl-4,5-dihydro-1*H*-1,2,4-triazol-5-on-4-yl-iminomethyl) benzoic acid (DFT (B3LYP)/6-31G(d,p))

Table 1: The calculated bond angles ($^\circ$) of title compound (6-31G(d,p) B3LYP/HF)

S. No.	Bond Angles ($^\circ$)	B3LYP 6-31G(d,p)	HF 6-31G(d,p)
1	C(1)-N(27)-N(26)	104.633	105
2	C(1)-N(28)-N(29)	121.645	121.404
3	C(1)-N(28)-C(2)	108.268	108.133
4	C(1)-C(10)-H(20)	113.423	113.89
5	C(1)-C(10)-C(11)	119.225	119.18
6	C(1)-C(10)-C(12)	119.217	108.291
7	H(20)-C(10)-C(11)	118.069	118.209
8	C(10)-C(11)-H(21)	116.357	117.218
9	C(10)-C(11)-H(22)	117.21	116.905
10	H(21)-C(11)-H(22)	115.188	114.952
11	H(21)-C(11)-C(12)	117.677	117.938
12	H(22)-C(11)-C(12)	118.913	118.487
13	C(11)-C(12)-C(10)	60.578	60.65
14	C(11)-C(12)-H(23)	117.683	117.745
15	C(11)-C(12)-H(24)	118.99	118.984
16	H(23)-C(12)-H(24)	115.2	114.868
17	H(23)-C(12)-C(10)	116.383	117.231
18	H(24)-C(12)-C(10)	117.216	117.183
19	C(12)-C(10)-H(20)	117.578	116.731
20	N(27)-C(1)-N(28)	111.284	111.155
21	N(27)-N(26)-H(14)	120.438	120.939
22	N(26)-C(2)-O(30)	129.935	129.398
23	H(14)-N(26)-C(2)	124.993	125.2
24	O(30)-C(2)-N(28)	128.814	128.625
25	C(2)-N(28)-N(29)	130.053	130.392
26	N(28)-N(29)-C(3)	118.64	119.431

27	N(29)-C(3)-H(15)	122.026	122.026
28	N(29)-C(3)-C(4)	118.482	118.482
29	H(15)-C(3)-C(4)	119.489	119.489
30	C(3)-C(4)-C(5)	122.991	122.991
31	C(4)-C(5)-C(13)	126.052	126.052
32	C(3)-C(4)-C(9)	118.891	118.891
33	C(5)-C(13)-O(31)	123.874	123.874
34	C(5)-C(13)-O(32)	114.44	114.44
35	O(31)-C(13)-O(32)	121.65	121.65
36	C(13)-O(32)-H(25)	106.072	106.072
37	C(4)-C(5)-C(6)	119.621	119.621
38	C(13)-C(5)-C(6)	114.322	114.322
39	C(5)-C(6)-H(16)	117.747	117.747
40	C(5)-C(6)-C(7)	121.264	121.264
41	H(16)-C(6)-C(7)	120.987	120.987
42	C(6)-C(7)-H(17)	120.073	120.073
43	C(6)-C(7)-C(8)	119.396	119.396
44	H(17)-C(7)-C(8)	120.531	120.987
45	C(7)-C(8)-H(18)	120.246	120.073
46	C(7)-C(8)-C(9)	120.019	119.396
47	H(18)-C(8)-C(9)	119.727	119.727
48	C(8)-C(9)-C(4)	121.634	121.634
49	C(8)-C(9)-H(19)	120.385	120.385
50	H(19)-C(9)-C(4)	117.973	117.973

Table 2: The calculated bond lengths (Å⁰) of title compound (6-31G(d,p) B3LYP/HF)

S. No.	Bond Lengths	B3LYP 6-31G(d,p)	HF 6-31G(d,p)
1	C(1)-N(28)	1.39	1.38
2	C(1)-N(27)	1.31	1.27
3	C(1)-C(10)	1.47	1.48
4	C(10)-H(20)	1.08	1.07
5	C(10)-C(11)	1.52	1.5
6	C(11)-H(21)	1.09	1.07
7	C(11)-H(22)	1.08	1.08
8	C(11)-C(12)	1.5	1.49
9	C(12)-H(23)	1.09	1.08
10	C(12)-H(24)	1.09	1.08
11	C(12)-C(10)	1.52	1.51
12	N(27)-N(26)	1.38	1.37
13	N(26)-H(14)	1.01	1
14	N(26)-C(2)	1.37	1.35
15	C(2)-O(30)	1.22	1.22
16	C(2)-N(28)	1.42	1.42
17	N(28)-N(29)	1.37	1.37
18	N(29)-C(3)	1.29	1.26
19	C(3)-H(15)	1.08	1.08
20	C(3)-C(4)	1.48	1.49

21	C(4)-C(5)	1.42	1.4
22	C(5)-C(13)	1.5	1.5
23	C(13)-O(31)	1.22	1.19
24	C(13)-O(32)	1.35	1.33
25	O(32)-H(25)	0.97	0.95
26	C(5)-C(6)	1.4	1.39
27	C(6)-H(16)	1.08	1.07
28	C(6)-C(7)	1.39	1.38
29	C(7)-H(17)	1.09	1.07
30	C(7)-C(8)	1.39	1.38
31	C(8)-H(18)	1.09	1.08
32	C(8)-C(9)	1.39	1.38
33	C(9)-H(19)	1.08	1.07
34	C(9)-C(4)	1.41	1.39

Table 3: The calculated Mulliken atomic charges of title compound

Atoms	DFT	HF	Atoms	DFT	HF
C1	0.59	0.65	H17	0.10	0.17
C2	0.82	1.05	H18	0.10	0.16
C3	0.13	0.18	H19	0.11	0.18
C4	-0.05	-0.04	H20	0.13	0.18
C5	-0.17	-0.15	H21	0.14	0.17
C6	-0.10	-0.11	H22	0.12	0.14
C7	-0.09	-0.15	H23	0.14	0.15
C8	-0.08	-0.13	H24	0.12	0.14
C9	-0.10	-0.13	H25	0.33	0.37
C10	-0.14	-0.20	N26	-0.43	-0.56
C11	-0.21	-0.25	N27	-0.37	-0.37
C12	-0.21	-0.24	N28	-0.45	-0.65
C13	0.53	0.79	N29	-0.32	-0.30
H14	0.29	0.34	O30	-0.54	-0.66
H15	0.18	0.24	O31	-0.47	-0.56
H16	0.13	0.20	O32	-0.49	-0.61

The calculated C4-C5, C5-C6, C6-C7, C7-C8, C8-C9, C9-C4 bond lengths of benzene rings in this compound are [1.42/1.40 Å], [1.40/1.39 Å], [1.39/1.38 Å], [1.39/1.39 Å], [1.39/1.38 Å] and [1.41/1.38 Å], respectively. The Ar(C)-Ar(C) bond lengths of benzene rings are generally observed at 1.34-1.53 Å in literature [33,34]. The calculated C-H bond lengths of the compound are about 1.08 Å and the C-H bond lengths in literature are 1.09 Å [33,34]. Also, the calculated N26-C2 bond length in 1,2,4-triazole-5-one ring is [1.37/1.35 Å]. It has been recorded that it has bond length between single bonded N-N and double bonded N=N due to resonance. The same bond length in literature is recorded as between 1.29-1.47 Å [33,34]. Compared with the bond lengths in the literature, the results show that the molecular structure is very well.

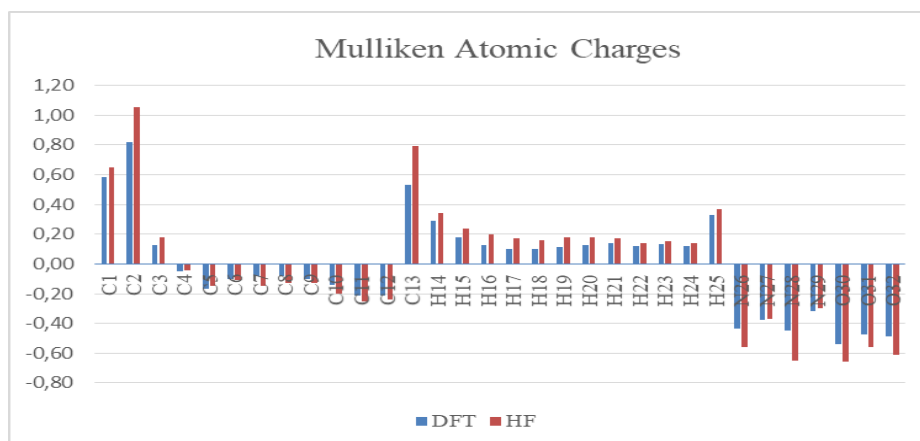


Chart 1: Graphics of the calculated Mulliken atomic charges of title compound

It has been recorded that the electronegative N and O atoms have negative atomic charge values in gas phase. The carbon atoms surrounded with electronegative atoms have positive atomic charge values in gas phase. The C1 atom which is surrounded with two electronegative atoms (N, N), C1 atom surrounded with three electronegative atoms (N, N, O) have the highest positive charges values. All hydrogen atoms of the compound have positive atomic charge values (Table 3 and Chart 1).

NMR, IR and UV-vis spectra

The GIAO ^1H and ^{13}C chemical shift, experimental and calculated IR, UV-vis values were determined by employing DFT(B3LYP)/HF 6-31G(d,p) method. The calculational and experimental results are given in Figures 2 and 3, Tables 4-7 and Chart 2.

Table 4: The calculated ^1H and ^{13}C -NMR isotropic chemical shifts of title compound (with respect to TMS, all values in ppm) (6-31G(d,p))

	$\delta_{\text{Exp.}}$	$\delta_{\text{cal. HF}}$ (Vacum)	$\delta_{\text{cal. HF}}$ (DMSO)	Different	Different (DMSO)	$\delta_{\text{cal. B3LYP}}$ (Vacum)	$\delta_{\text{cal. B3LYP}}$ (DMSO)	Different	Different (DMSO)
C1	148.25	154.23	155.38	-5.98	-7.13	148.1	149.65	0.15	-1.40
C2	151.15	151.77	152.56	-0.62	-1.41	145.78	146.57	5.37	4.58
C3	152.86	154.85	155.14	-1.99	-2.28	149.76	150.43	3.10	2.43
C4	133.67	140.95	140.35	-7.28	-6.68	134.61	133.81	-0.94	-0.14
C5	130.73	134.4	133.92	-3.67	-3.19	124.83	124.27	5.90	6.46
C6	132.05	138.14	137.83	-6.09	-5.78	131.73	131.34	0.32	0.71
C7	130.21	132.43	133.8	-2.22	-3.59	124.57	125.8	5.64	4.41
C8	131.52	135.01	136.61	-3.49	-5.09	130.4	131.91	1.12	-0.39
C9	126.76	129.91	130.34	-3.15	-3.58	123.67	124.02	3.09	2.74
C10	5.46	16.52	16.55	-11.06	-11.09	1.7	1.81	3.76	3.65
C11	6.38	20.52	20.72	-14.14	-14.34	4.07	4.44	2.31	1.94
C12	6.38	22.43	22.66	-16.05	-16.28	5.38	5.22	1.00	1.16
C13	167.75	167.95	169.2	-0.20	-1.45	157.52	158.95	10.23	8.80
H14	11.78	7.84	8.35	3.94	3.43	7.1	7.56	4.68	4.22
H15	10.40	12.01	12	-1.61	-1.60	10.92	10.87	-0.52	-0.47
H16	8.03	9.28	9.25	-1.25	-1.22	9.13	9.11	-1.10	-1.08
H17	7.63	8.36	8.62	-0.73	-0.99	8.09	8.37	-0.46	-0.74
H18	7.65	8.42	8.71	-0.77	-1.06	8.23	8.54	-0.58	-0.89
H19	7.92	9.24	9.35	-1.32	-1.43	8.55	8.69	-0.63	-0.77
H20	2.12	3.17	3.25	-1.05	-1.13	2.16	2.29	-0.04	-0.17
H21	0.96	2.01	1.93	-1.05	-0.97	1.64	1.5	-0.68	-0.54
H22	0.96	1.85	2.08	-0.89	-1.12	0.94	1.16	0.02	-0.20
H23	0.96	1.82	1.78	-0.86	-0.82	0.75	0.79	0.21	0.17
H24	0.96	1.88	2.09	-0.92	-1.13	1.01	1.2	-0.05	-0.24
H25	11.78	7.06	7.6	4.72	4.18	6.2	6.75	5.58	5.03

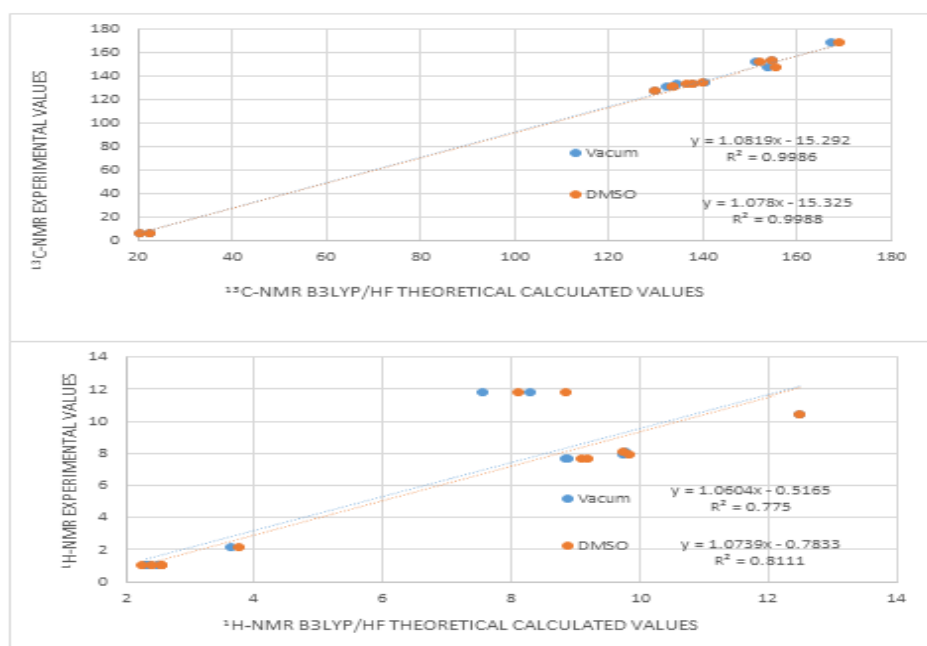


Chart 2: Comparison of experimental/theoretical ^1H and ^{13}C -NMR chemical shifts values of title compound with 6-31G(d,p) B3LYP/HF (Vacum/DMSO) methods

The GIAO ^1H and ^{13}C chemical shift values in gas phase/DMSO solvent (with respect to TMS) of title compound were calculated using the DFT (B3LYP) and Hartree Fock (HF) methods with 6-31G(d,p) basis set. The calculated and experimental data are shown in Table 4.

The calculated ^1H chemical shift values are observed to be 0.94-10.92/1.82-12.01 ppm in gas phase and 0.79-10.87/1.78-12.00 in DMSO solvent at DFT (B3LYP)/HF methods, while the experimental parameters are calculated 0.96-11.78 ppm with 6-31G(d,p) basis set. Aromatic C-H signals were observed at 7.63-8.03 ppm. These signals were calculated 8.09-9.13/8.36-9.28 in gas phase and 8.37-9.11/8.62-9.25 ppm in DMSO solvent at B3LYP/HF levels. The cyclopropyl protons of this compound were observed at 0.96 ppm. These were calculated as 0.72-1.64/1.82-2.01 ppm in gas phase and 0.79-1.50/1.78-2.09 ppm in DMSO solvent at B3LYP/HF levels. The O-H signal was observed at 11.78 ppm. This signal was calculated as 6.20/7.06 ppm at gas phase and 6.75/7.60 ppm in DMSO solvent at B3LYP/HF levels. The N-H signal was observed at 11.78 ppm but these signals were observed at 7.1/7.84 ppm in gas phase and 7.56-7.84 ppm in DMSO solvent at B3LYP/HF levels. There is a slight difference between theoretical and experimental N-H signal because N-H proton of 4,5-dihydro-1H-1,2,4-triazol-5-one ring was displayed the acidic character.

The ^{13}C -NMR chemical shift values of the title compounds are observed to be 1.70-157.72/20.52-167.95 ppm in gas phase and 1.81-158.95/20.72-169.20 in DMSO solvent at DFT (B3LYP)/HF methods, while the experimental parameters are calculated 5.46-167.75 ppm with 6-31G(d,p) basis set. As a result of, the R^2 values of title compound were evaluated and ^{13}C and ^1H -NMR chemical shift values of title compound were plotted graphs (Chart 2). Theoretical and experimental between ^{13}C and ^1H -NMR chemical shifts ratios of title compound were observed a linear correlation. It is such a relationship between R-values of title compound; B3LYP(DFT)/HF 6-31G(d,p)_{vacum.}: ^1H : 0.7750, ^{13}C : 0.9986, B3LYP(DFT)/HF 6-31G(d,p)_{DMSO}: ^1H : 0.8111 ^{13}C : 0.9988.

Table 5: The calculated IR frequencies of title compound (6-31G(d,p))

S. No.	Vibration Frequencies	HF	B3LYP
1	τ NCCC (18), τ CCCN(28)	11	13
2	τ NCCC(41), τ CCCN(25)	21	29
3	τ OCCC(45)	39	39
4	τ NNCN(13), τ NCNN(31),	57	55
5	δ NCC(15)	67	71
6	τ CNNC(39)	100	94
7	δ CCC(11), δ CCN(11), τ OCCC(11), τ CCCC(12)	116	121
8	τ CNNC(17)	139	137
9	δ CCN(21), τ CNNC(12), τ CCCC(12)	152	166
10	δ CNN(13), τ CCCC(17)	202	202
11	δ NCC(10), δ CCC(21), τ CCCN(11)	211	217
12	τ CNNC(32)	227	236
13	τ NCNN(21), τ CCCC(10)	249	263
14	δ CCC(17), δ OCC(29)	279	284
15	τ NCNN(11), τ NNCN(28), τ CCCC(18)	323	334
16	δ CCC(10)	360	385
17	ν CC(13), δ CCC(13), δ OCO(11)	377	389
18	τ CCCN(12), τ HNNC(10), τ NNCN(30)	379	396
19	δ NNC(10), τ CCCC(24)	412	435
20	δ CCC(11), τ CCCC(21)	443	466
21	τ HNNC(54)	470	491
22	δ OCC(17), τ CCCC(14)	516	533
23	δ OCC(10), τ CCCC(14), τ HCCC(10)	543	570
24	δ CCC(19)	581	598
25	τ HOCC(75)	604	608
26	δ OCN(17), δ CCC(16)	620	644
27	δ CCC(26), δ OCO(36)	632	661
28	ν CC(12), δ CCN(18)	671	684
29	τ CNNC(17), τ ONNC(15)	694	748
30	τ CCCC(29), τ ONNC(30)	715	751
31	τ NNCN(15), τ ONNC(39)	722	774
32	ν CC(12), δ OCO(11), δ CCC(16)	745	801

33	τ CCCC(12), τ HCCC(47)	765	808
34	ν NC(11), δ CNN(26)	787	821
35	δ HCC(46)	797	823
36	τ HCCC(28), τ ONNC(20)	802	852
37	δ CCC(17), τ HCCN(36)	821	859
38	ν NN(14), δ CCC(17), δ NCN(10)	824	863
39	ν CC(12), δ NNC(19), δ NCC(13), δ CCC(13)	877	915
40	ν CC(33), δ CCC(12), τ HCCC(11)	897	931
41	τ HCCC(69)	903	965
42	ν CC(28), δ CCC(15), τ HCCN(35)	909	978
43	τ HCCC(87)	978	1054
44	τ CCCC(13), τ HCNN(26), τ HCCC(44)	996	1078
45	τ HCNN(59), τ HCCC(20)	1003	1081
46	ν CC(10), δ NNC(22)	1026	1087
47	ν NN(10), τ HCCN(36)	1054	1092
48	ν CC(46), δ HCC(17)	1060	1115
49	τ HCCC(33), τ HCCN(10)	1070	1133
50	τ HCCC(28), τ HCCN(45)	1083	1136
51	ν CC(10), δ CCC(25), δ HCC(16)	1095	1161
52	τ HCCN(33)	1125	1164
53	ν OC(30), δ HCC(15), ν CC(11)	1127	1181
54	ν NN(24), τ HCCN(13)	1136	1183
55	ν CC(10), δ HCC(76)	1180	1192
56	ν CC(10), δ HOC(41)	1198	1248
57	δ HCC(72)	1202	1251
58	ν NC(18), δ HCC(13)	1203	1255
59	ν CC(53)	1215	1264
60	ν CC(12), ν NC(10)	1235	1279
61	ν NN(10), δ CNN(11)	1271	1292
62	δ HCC(40)	1291	1343
63	ν NC(18), ν NN(10), δ HCN(16)	1326	1358
64	ν CC(49)	1339	1420
65	ν OC(20), ν CC(11), δ HOC(26), δ OCO(14)	1370	1440
66	ν NC(12), δ HNN(65)	1383	1471
67	δ HCN(52)	1421	1484
68	δ HCH(97)	1462	1521
69	δ HCC(18), δ HCH(16)	1472	1535
70	ν CC(11), δ HCC(23), δ HCH(12)	1475	1537
71	ν CC(13), δ HCC(11), δ HCH(45)	1506	1577
72	δ HCC(25), δ HCH(13), δ CCC(13)	1513	1587
73	ν CC(29), δ CCC(10)	1600	1681
74	ν NC(45)	1624	1716
75	ν NC(31), ν CC(12)	1633	1774
76	ν NC(39), ν CC(16)	1655	1810
77	ν OC(44)	1794	1878
78	ν OC(39), ν NC(12)	1808	1909
79	ν CH(58)	3117	3140

80	v CH(56)	3120	3149
81	v CH(30)	3159	3190
82	v CH(61)	3175	3207
83	v CH(39)	3188	3208
84	v CH(58)	3194	3222
85	v CH(55)	3197	3232
86	v CH(53)	3203	3236
87	v CH(26)	3212	3238
88	v CH(27)	3217	3274
89	v NH(100)	3664	3763
90	v OH(100)	3720	3926

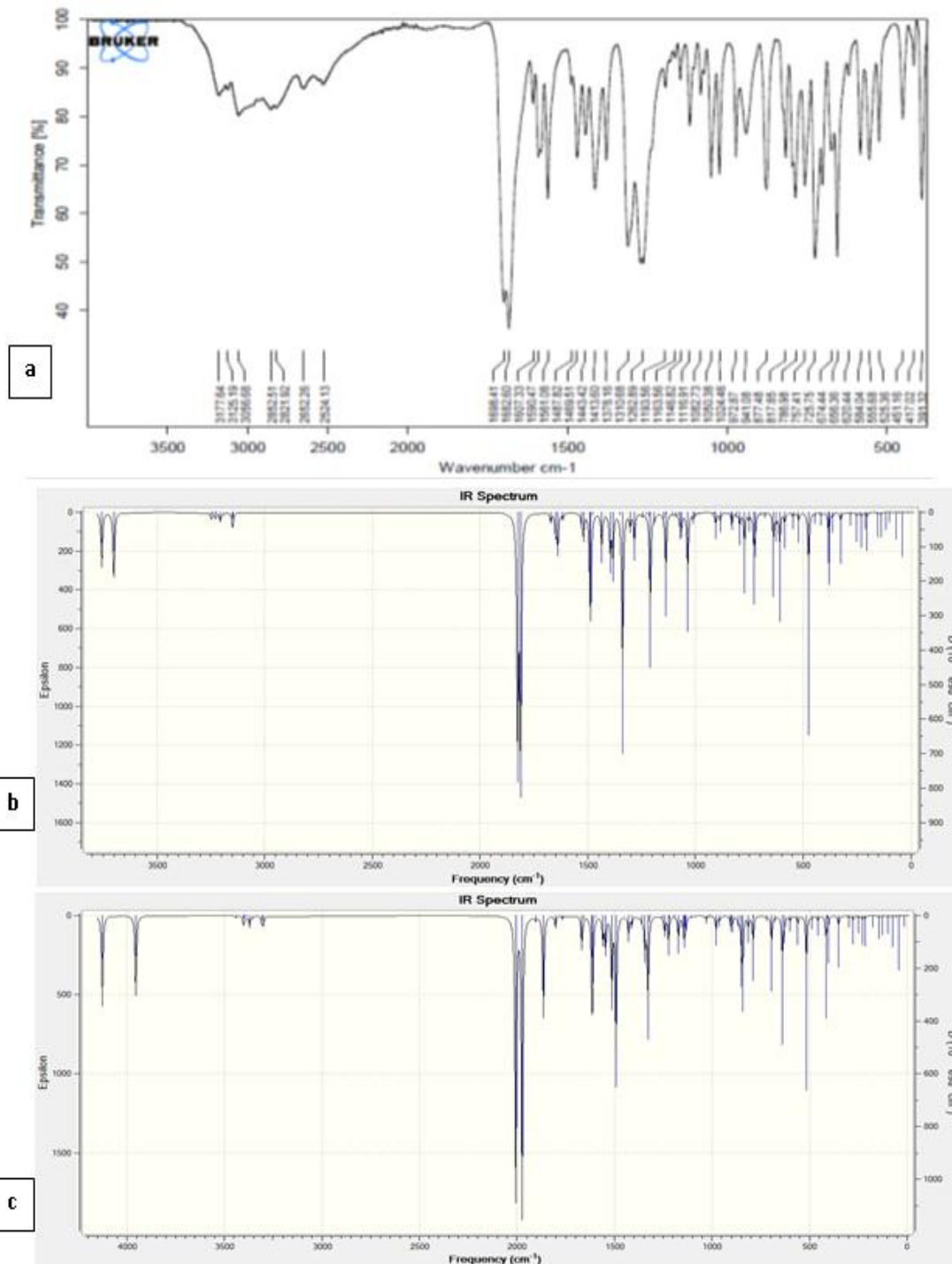


Figure 2: Experimental (a) and theoretical (6-31G(d,p) DFT (b)/HF (c) IR spectra of title compound

The experimental O-H, N-H, C-H, C=O stretching vibrations were given in Table 6. There is a slight difference between theoretical vibrational and experimental frequencies. Theoretical vibrational frequencies for title compound are generally closer to the experimental frequencies.

Table 6: The experimental IR frequencies of title compound

Experimental Vibrations	IR (cm ⁻¹)
ν OC	1263
ν C=C	1591
ν C=N	1607
ν C=O	1683
ν C=O	1698
ν =CH	3057
ν NH	3125
ν OH	3178

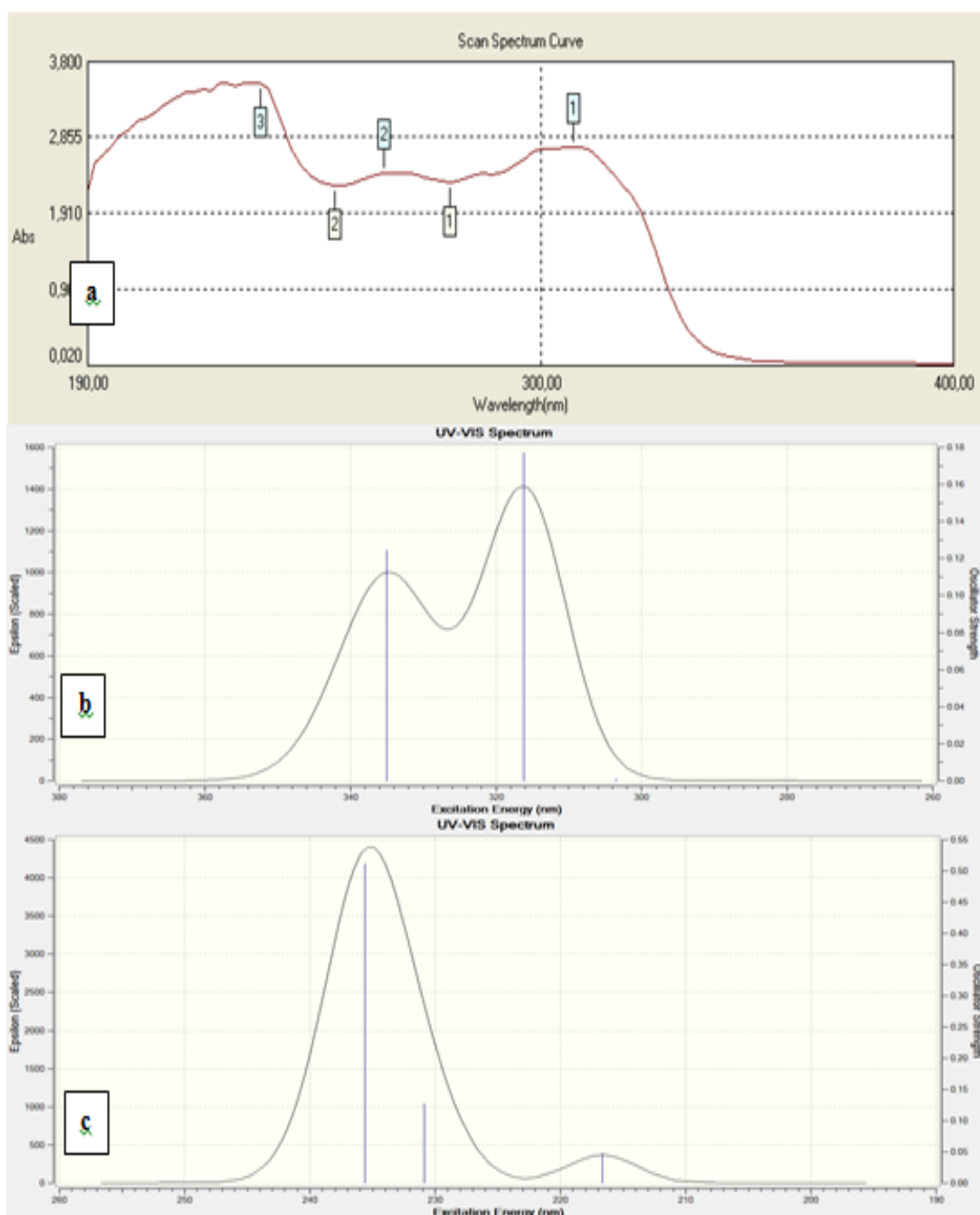


Figure 3: Experimental (a) and theoretical (6-31G(d,p) DFT/HF) UV-vis spectra of title compound

Table 7: The experimental and calculated UV-vis values (HF/B3LYP 6-31G(d,p)) of title compound

Experimental (nm)	λ (nm) HF/B3LYP 6-31G(d,p)	Excitation Energy (eV) HF/B3LYP 6-31G(d,p)	f (osillatör strengths) HF/B3LYP 6-31G(d,p)
308	235.61/335.03	5.2622/3.7007	0.5106/0.1245
262	230.87/316.19	5.3702/3.9211	0.1272/0.1771
232	216.64/303.51	5.7232/4.0850	0.0467/0.0010

The experimental absorption wavelenghts in ethanol solvent of title compound were recorded as 308, 262, 232 nm respectively. The excitation energies, oscillator strengths (f) and absorption wavelenghts (λ) of UV-vis electron absorption spectroscopy in ethanol solvent of title molecule have been calculated by using B3LYP/HF methods with 6-31G(d,p) basis set and were given in Figure 3 and Table 7. The calculated UV-vis values of title compound are in a very good agreement with the experimental values.

Electronic and thermodynamics properties, homo-lumo energies

The energy levels and distributions of HOMO and LUMO were calculated at DFT(B3LYP)/HF 6-31G(d,p) level for title compound. Energies of HOMO, LUMO were recorded as -7.649 -5.275 and 7.852 -5.201 eV B3LYP and HF/6-31G(d,p), respectively. Also, The molecular softness (S), hardness (η), electronegativity (χ), chemical potential (Pi), ionization potential (I), electron affinity (A), electrophilic (ω) and nucleophilic index (IP) were calculated by using HOMO and LUMO energies (Table 8). The ΔE_{H-L} (energy gap) energies are 2.235/2.651 eV at B3LYP/HF level, respectively (Figure 4).

Table 8: The calculated electronic properties of title compound (6-31G(d,p) B3LYP/HF)

	B3LYP (6-31G(d,p))	Hartree	Ev	Kcal/mol	Kj/mol
	LUMO	-0.194	-5.275	-121.635	-508.927
	HOMO	-0.281	-7.649	-176.404	-738.083
A	Electron Affinity	0.194	5.275	121.635	508.927
I	Ionization Potential	0.281	7.649	176.404	738.083
ΔE	Energy Gap	0.087	2.375	54.769	229.156
χ	Electronegativity	0.237	6.462	149.020	623.505
Pi	Chemical Potential	-0.237	-6.462	-149.020	-623.505
ω	Electrophilic Index	0.001	0.033	0.772	3.231
IP	Nucleophilic Index	-0.010	-0.282	-6.503	-27.210
S	Molecular Softness	22.914	623.519	14.378.914	60.162.005
η	Molecular Hardness	0.044	1.187	27.385	114.578
	HF (6-31G(d,p))	Hartree	Ev	Kcal/mol	Kj/mol
	LUMO	-0.191	-5.201	-119.947	-501.864
	HOMO	-0.289	-7.852	-181.072	-757.614
A	Electron Affinity	0.191	5.201	119.947	501.864
I	Ionization Potential	0.289	7.852	181.072	757.614
ΔE	Energy Gap	0.097	2.651	61.125	255.750
χ	Electronegativity	0.240	6.527	150.510	629.739
Pi	Chemical Potential	-0.240	-6.527	-150.510	-629.739
ω	Electrophilic Index	0.001	0.038	0.879	3.678
IP	Nucleophilic Index	-0.012	-0.318	-7.331	-30.671
S	Molecular Softness	20.532	558.684	12.883.749	53.906.170
η	Molecular Hardness	0.049	1.325	30.563	127.875

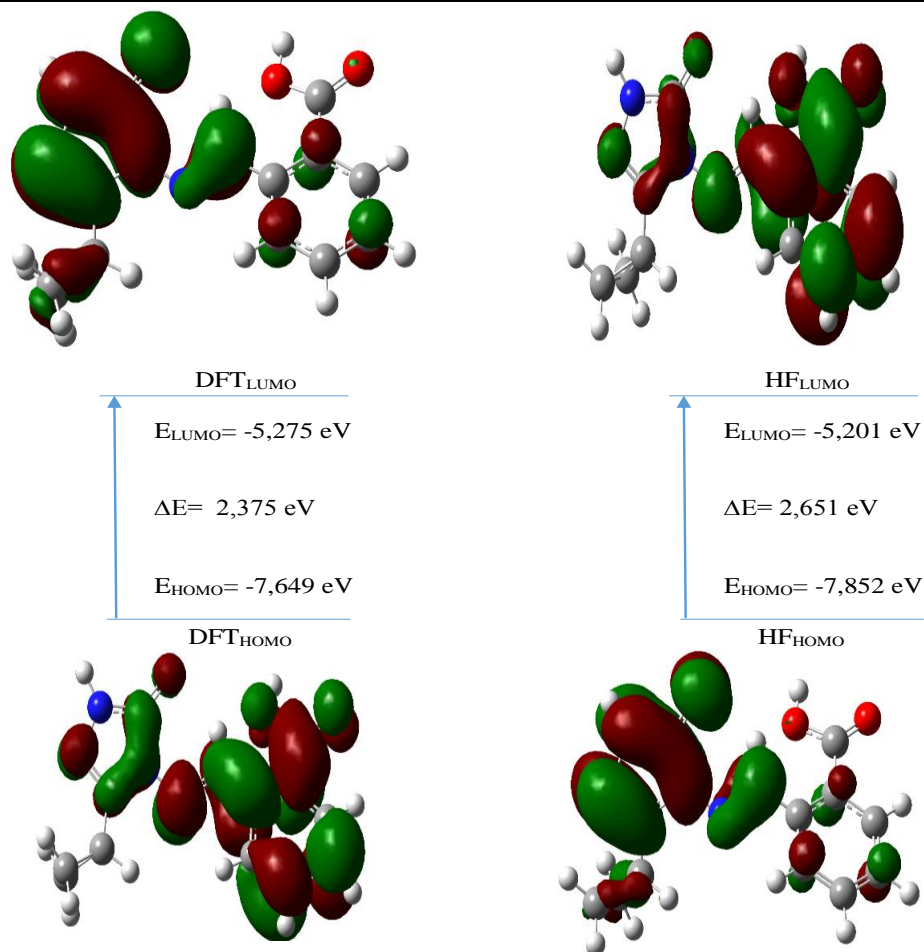


Figure 4: 3D plots of HOMO-LUMO energies of title compound at the B3LYP/HF 6-31G(d,p)

The dipole moment values of title compound were computed as 0.581/0.606 D for DFT(B3LYP)/HF methods with the 6-31G(d,p) basis set. The results were given in Table 9. The highest dipole moment is recorded as μ_z component. The mean polarizability ($\langle\alpha\rangle$) and the mean first-order hyperpolarizability ($\langle\beta\rangle$) are calculated -47.160×10^{-24} esu/ $23,088 \times 10^{-24}$ esu and 8.107×10^{-30} esu/ 3.169×10^{-30} esu for B3LYP/HF, respectively. It was found that the β values at B3LYP/HF methods of title compound is higher than that of urea.

Table 9: The mean polarizability ($\langle\alpha\rangle$), the anisotropy of the polarizability ($\Delta\alpha$), the mean first-order hyperpolarizability ($\langle\beta\rangle$), dipole moment values of title compound

	B3LYP (6-31G(d,p))	HF(6-31G(d,p))
μ_x	-1.558 Debye	1.141 Debye
μ_y	2.599 Debye	3.240 Debye
μ_z	0.581 Debye	0.606 Debye
μ_{Toplam}	3.085 Debye	3.488 Debye
α_{xx}	-116.52 a.u.	31.522 a.u.
α_{yy}	-26.19 a.u.	24.379 a.u.
α_{zz}	1.24 a.u.	13.362 a.u.
A	-47.160×10^{-24} esu	23.088×10^{-24} esu
$\Delta\alpha$	106.71810^{-24} esu	15.846×10^{-24} esu
Bx	-7850.88 a.u.	3071.51 a.u.
β_y	1966.29 a.u.	409.35 a.u.
β_z	-463.44 a.u.	-663.47 a.u.
β_{xxx}	-2361.58 a.u.	189.72 a.u.
β_{xxy}	-125.85 a.u.	89.16 a.u.
β_{xyy}	-9.83 a.u.	189.72 a.u.
β_{yyy}	-137.92 a.u.	-20.12 a.u.
β_{xxz}	76.32 a.u.	6.64 a.u.
β_{xyz}	-13.01 a.u.	9.71 a.u.
β_{yyz}	17.39 a.u.	-40.84 a.u.
β_{xzz}	-90.96 a.u.	-12.44 a.u.
β_{yzz}	-40.22 a.u.	-20.12 a.u.

β_{zzz}	62.80 a.u.	-45.08 a.u.
β	8.107×10^{-30} esu	3.169×10^{-30} esu

The MEP map of title compound is shown in Figure 5. The MEP map shows that the positive potential sites are around the hydrogen as well as the negative potential sites on electronegative oxygen, nitrogen atoms. Also, thermodynamic properties of title compound are given in Table 10.

Table 10: The calculated thermodynamics parameters of title compound (6-31G(d,p) B3LYP/HF)

Rotational temperatures (Kelvin)	DFT	HF
A	0.02847	0.02796
B	0.00917	0.00936
C	0.00721	0.00773
Rotational constants (GHZ)		
A	0.59328	0.5826
B	0.19116	0.19497
C	0.1503	0.16112
Zero-point vibrational energy (Kcal/Mol)	153.21673	165.36306
Thermal correction to Energy	0.261506	0.279787
Thermal correction to Enthalpy	0.26245	0.280731
Thermal correction to Gibbs Free Energy	0.195555	0.216273
Sum of electronic and zero-point Energies	-947.016165	-941.378701
Sum of electronic and thermal Energies	-946.998826	-941.362437
Sum of electronic and thermal Enthalpies	946.997882	-941.361493
Sum of electronic and thermal Free Energies	-947.064777	941.42595
Thermal Energies E (Kcal/mol)		
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	162.320	173.791
Total	164.097	175.569
Thermal Capacity CV (Cal/Mol-Kelvin)		
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	59.289	54.379
Total	65.251	60.34
Entropy S (Cal/Mol-Kelvin)		
Translational	42.702	42.702
Rotational	34.199	34.129
Vibrational	63.891	58.833
Total	140.792	135.663

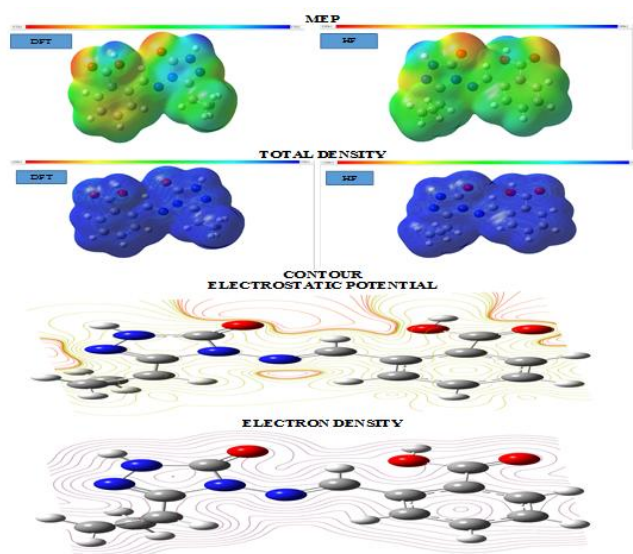


Figure 5: The calculated molecular surfaces of title compound

CONCLUSION

In this study, the geometric, thermodynamics, spectroscopic and electronic values of title compound have been calculated by using DFT (B3LYP) and HF methods with the 6-31G(d,p) basis sets. The UV-vis, IR, ¹H- and ¹³C- NMR spectra have been obtained and compared with the experimental spectroscopic values. The theoretical calculated spectra values were found good agreement with experimental UV-vis, IR, ¹H- and ¹³C- NMR spectra values. The value of the energy gap between the HOMO-LUMO energies was determined. Geometric parameters; bond angles and bond lengths were compared with experimental values obtained from literature [33,34]. All results showed that the calculated spectroscopic, geometric, thermodynamics and electronic parameters obtained by B3LYP/6-31G(d,p) method had a better agreement with the experimental values than HF/6-31G(d,p) method.

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