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SPECTROSCOPIC PROPERTIES OF 3-BENZYL-4-[3-(3-NITROBENZOXY)-4-METHOXYBENZYLIDENEAMINO]-4,5-DIHYDRO-1H-1,2,4-TRIAZOL-5-ONE MOLECULE

Fevzi Aytemiz[1], Haydar Yüksek[1], Murat Beytur[1]

[1] Kafkas University Department of Chemistry, 36100 Kars, Turkey.

muratbeytur83@gmail.com

Abstract

3-Benzyl-4-[3-(3-nitrobenzoxy)-4-methoxybenzylideneamino]-4,5-dihydro-1H-1,2,4-triazol-5-one were synthesized by the reaction of 3-benzyl-4-amino-4,5-dihydro-1H-1,2,4-triazol-5-one with 3-nitrobenzoxy-4-methoxybenzaldehyde. The molecule has been optimized using B3LYP/631G (d,p) and HF/631G (d,p) basis set. Starting from this optimized structure with ^{1}H-NMR and ^{13}C-NMR and IR spectral data values according to GIAO method was calculated using the method of Gaussian G09W program package in gas phase. Theoretically and experimentally values were plotted according to exp =a +b. δ calc Eq. a and b constants regression coefficients with a standard error values were found using the SigmaPlot program. Theoretically calculated IR data are multiplied with appropriate adjustment factors and the data obtained according to HF and DFT method are formed using theoretical infrared spectrum. The identification of calculated IR data was used in veda4f program. Experimentally and theoretically UV-vis values in ethanol were calculated and compared. Additionally, the HOMO-LUMO energy of the molecule obtained from both methods was described.

Key words: Theoretical, HOMO-LUMO, 1,2,4-Triazol-5-one.

Introduction

3-Benzyl-4-[3-(3-nitrobenzoxy)-4-methoxybenzylideneamino]-4,5-dihydro-1H-1,2,4-triazol-5-one [1] was optimized by using the B3LYP/6-31G(d,p) and HF/6-31G (d,p) basis set [2, 3]. Vibrational frequencies, UV–Vis spectroscopic parameters, atomic charges and frontier molecule orbitals (HOMO and LUMO) of the title compound have been calculated by using DFT/B3LYP and HF method with 6-31G(d,p) basis set from the optimized molecular structure. All quantum chemical calculations were carried out by using Gaussian 09W [2, 3] program package and the GaussView molecular visualization program [2]. The molecular structure and vibrational calculations of the molecule was computed by using Becke-3-Lee

Yang Parr (B3LYP) [4] density functional method with 6-31G(d,p) basis set in ground state. IR absorption frequencies of analyzed molecule were calculated by two methods. Then, they were compared with experimental data [1] which are shown to be accurate. Infrared spectrum was composed by using the data obtained from both methods. The assignments of fundamental vibrational modes of the title molecule were performed on the basis of total energy distribution (TED) analysis by using veda4f program [5].

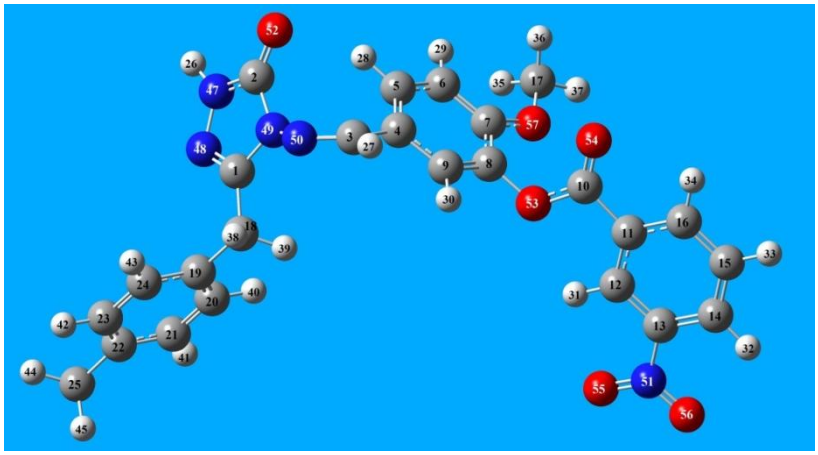


Figure 1. Optimized molecular structure of title compound with DFT/B3LYP/6-31G(d,p) level.

Methods

The molecular structure of the title compound in the ground state (in vacuo) was computed by performing both Hartree-Fock (HF) and the density functional theory (DFT) by a hydrid functional B3LYP functional (Becke's three parameter hybrid functional using the LYP correlation functional) methods at 6-31G(d,p) level.

Results and Findings

Vibrational frequencies

The 3-benzyl-4-[3-(3-nitrobenzoxy)-4-methoxybenzylideneamino]-4,5-dihydro-1H-1,2,4-triazol-5-one have 57 atoms and the number of the normal vibrations were 165. This result shows that the structure of compound was shown to be stable. IR spectrums were drawn with obtained values according to HF and DFT method. The observed and calculated vibrational frequencies, the calculated IR intensities and assignments of vibrational frequencies for title compound were summarized in Table **1**.

Table 1. The Calculated Frequencies Values of the Molecule

	Vibration Frequencies	Scaled DFT	Scaled HF
1	τ CCCN(17), τ NCCN(14)	4	6
2	τ HCCC(36), τ CCCC(11)	9	9
3	τ CCCC(13), τ (CCOC(12), τ CCCN(14)	14	10
4	τ OCCC(11), τ CCOC(11), τ CCCN(28)	21	15
5	τ OCCC(14), τ CCOC(38)	23	22
6	τ HCCC(31), τ CCOC(14)	34	25
7	τ CCCN(25)	38	35
8	τ CCCC(11)	44	39
9	τ ONCC(73)	48	44
10	τ ONNC (65)	49	47
11	τ CCCC(16), τ COCC(30)	64	60
12	τ CCCC(12)	74	61
13	τ COCC(14), τ NCCN(11)	76	79
14	δ OCC(10)	102	92
15	τ OCCC(13)	112	113
16	τ COCC(10), τ NCCN(12)	128	119
17	τ NCCC(12)	140	142
18	τ NCNN(16), τ CNNC(10)	143	144
19	δ CCN(12), τ CCCC(11)	145	147
20	ν OC(88), δ CCN(11)	171	181
21	τ CCCC(28), τ NCCC(17)	185	191
22	τ NNCC (22)	192	195
23	δ NCC (12)	225	225
24	τ HCOC(26)	227	234
25	δ NCC (14), τ HCOC (23), τ OCCC (13)	242	246
26	δ OCC (13), δ COC (10)	251	257
27	δ CCC (12)	264	267
28	δ CCC (46), τ HCCC (16), τ NNCC (10)	279	287
29	δ CCC (38), τ HCCC (27)	292	302
30	τ CCCC (25)	310	314
31	δ CCC(11), τ CCCC(13)	316	319
32	δ COC(25)	331	335
33	τ CCCN(12), τ OCCC(12)	340	353
34	NC(30), δ ONO(11), δ CCC(13)	357	366
35	δ CCC(40)	366	368
36	τ HCCC(19), τ CCCC(80)	402	410
37	τ HCCC(11), τ CCCC(18)	418	424
38	δ ONC(13), CCC(22)	429	433
39	δ ONC(13), CCC(22)	430	436
40	δ OCN(10), τ HNNC(26)	440	448
41	τ CCCC(14)	454	453
42	τ OCCC(15), τ CCOC(25)	460	466
43	τ CCCC(23)	462	471
44	τ CCNN(12), τ CCCC(15)	482	486
45	δ CCC(11),CCCC(22)	509	516
46	δ ONC(27)	524	529
47	δ ONC(21)	535	544
48	τ CCNN(126), τ CCCC(18)	550	573
49	τ CCCN(11)	578	581
50	δ OCC(12)	605	610
51	δ CCC(10), τ HNNC(12), τ NNCC(10), τ NCNC(29)	623	631
52	ν CC(18), δ CCC(39), δ HCC(10)	635	642
53	δ OCN(10)	637	648
54	δ CCC(30)	645	650
55	τ CCCC(19)	649	655

56	δ NCN(10)	668	674
57	τ CCCN(12)	686	697
58	τ CCCN(16), τ CCCC(11)	689	712
59	τ HCCC(15), τ OCON(36), τ OCOC(25)	698	726
60	τ ONNC(73)	702	739
61	ν CC(22), NN(12)	721	745
62	ν NO(17), δ CCC(12)	728	759
63	τ OCON(33), τ OCOC(36)	743	769
64	ν CC(14), τ HCCC(38)	749	770
65	ν CC(15)	760	787
66	ν NC(15), δ CNN(33)	776	787
67	τ HCCC(36)	798	813
68	ν CC(18), τ HCCC(25)	806	835
69	δ OCO(12), δ ONO(20)	807	839
70	δ OCO(12), δ ONO(20)	815	851
71	τ HCCC(99)	821	853
72	δ NCN(15), δ CCN(19)	832	853
73	ν CC(18), τ HCCC(17)	835	869
74	δ ONO(11), τ HCCC(13), τ CCOC(10)	868	903
75	τ CCOC(10)	893	916
76	ν CC(11), δ HCC(30), τ HCCC(29)	902	932
77	τ HCCC(40)	918	938
78	τ HCCC(30)	920	969
79	τ HCCC(40), τ CCCC(14)	925	974
80	τ HCCC(32), τ HCNN(20)	927	975
81	τ HCCC(32), τ CCCC(14)	929	983
82	τ HCCC(70)	940	983
83	τ HCCC(13), τ HCNN(29)	942	985
84	τ HCCC(73)	975	992
85	δ HCH(17), τ HCCC(36)	976	1004
86	ν CC(21), δ CCC(29)	980	1025
87	δ CCC(49), δ HCC(12)	1000	1027
88	δ NNC(29), τ HCNN(13)	1007	1042
89	ν OC(63)	1021	1045
90	δ HCH(18), τ HCCC(42)	1025	1048
91	ν OC(10)	1043	1064
92	ν NC(13), ν NN(35)	1061	1072
93	δ HCC(32)	1070	1084
94	δ HCC(13)	1089	1088
95	ν CC(23), δ HCC(52)	1102	1105
96	ν OC(19), δ CCO(10)	1111	1117
97	δ HCH(25), τ HCOC(26)	1131	1125
98	ν NC(14), ν NN(11), δ HCC(24)	1142	1141
99	δ HCC(52)	1145	1149
100	δ HCH(25), τ HCOC(28)	1155	1156
101	ν CC(21), δ HCC(75)	1165	1174
102	ν CC(10), δ HCH(10), τ HCOC(18)	1168	1174
103	ν CC(38)	1169	1178
104	ν NC(25), ν NN(11)	1181	1186
105	ν CC(16), δ CCC(14), δ HCC(22)	1191	1196
106	ν CC(18), δ HCC(27)	1198	1206
107	ν CC(12), δ HCC(13)	1224	1211
108	ν CC(10), δ HCC(40), τ HCCC(12)	1227	1220
109	ν OC(20), δ HCC(19)	1262	1226
110	ν NC(15), δ CNN(10), τ HCCC(20)	1265	1270
111	ν CC(10), δ HCC(12)	1267	1273
112	δ HCC(25)	1282	1289
113	δ HCC(28)	1295	1295

114	ν OC(37)	1306	1313
115	δ HCC(80)	1309	1317
116	ν NN(10), δ HCN(10), δ NNC(10), τ HCCC(26)	1326	1323
117	ν NC (11), δ HNN (71)	1342	1371
118	δ HNN(19), δ HCH(62)	1347	1394
119	δ HNN(46), δ HCH(62)	1372	1395
120	ν CC(18), δ HCC(40)	1375	1412
121	τ HCCC(11)	1384	1417
122	ν CC(39), δ HCC(20)	1400	1429
123	δ HCN (16), δ CCC (11)	1412	1430
124	δ HCH(89)	1414	1447
125	δ HCH(80), τ HCCC(11)	1430	1455
126	δ HCH(80), τ HCCC(11)	1433	1455
127	δ HCH(69), τ HCCC(10)	1444	1459
128	δ HCH(65), τ HCOC(15)	1448	1468
129	δ HCH(70), τ HCOC(14)	1451	1475
130	ν ON(57)	1458	1476
131	ν ON(20), δ HCC(29), δ CCC(11)	1461	1487
132	δ HCC(59)	1501	1522
133	ν CC(18), ν OC(10), δ HCC(25)	1503	1528
134	ν CC(21), δ CCC(11)	1557	1595
135	ν CC(27)	1565	1598
136	ν CC(30)	1570	1600
137	ν ON(17)	1576	1618
138	ν CC(35)	1615	1635
139	ν CC(56)	1596	1642
140	ν ON(69)	1612	1682
141	ν NC(43)	1615	1683
142	ν NC(43)	1625	1718
143	ν OC(72)	1755	1773
144	ν OC(88)	1759	1817
145	ν CH(78)	2916	2861
146	ν CH(91)	2920	2872
147	ν CH(96)	2924	2881
148	ν CH(41)	2957	2914
149	ν CH(96)	2978	2917
150	ν CH (51)	2983	2935
151	ν CH (53)	3005	2937
152	ν CH(99)	3006	2979
153	ν CH(48)	3042	2983
154	ν CH(17)	3048	2995
155	ν CH(82)	3048	2996
156	ν CH (98)	3063	3007
157	ν CH(99)	3067	3015
158	ν CH(27)	3080	3023
159	ν CH(77)	3085	3035
160	ν CH(44)	3104	3052
161	ν CH(67)	3104	3056
162	ν CH(42)	3122	3070
163	ν CH(67)	3141	3076
164	ν CH(25)	3142	3098
165	ν NH(100)	3556	3554

ν, stretching; δ, bending; δs, scissoring; ρ, rocking; γ, out-of-plane bending; τ, torsion

NMR spectral analysis

In nuclear magnetic resonance (NMR) spectroscopy, the isotropic chemical shift analysis allows us to identify relative ionic species and to calculate reliable magnetic properties which provide the accurate predictions of molecular geometries [6-8]. In this framework, the optimized molecular geometry of title compound was obtained by using B3LYP and HF methods with 6-31G(d,p) basis level in DMSO solvent. By considering the optimized molecular geometry of the title compound the ^{1}H and ^{13}C NMR chemical shift values were calculated at the same level by using Gauge-Independent Atomic Orbital (GIAO) method. Theoretical and experimental values were plotted according to δ exp=a. δ calc.+ b, Eq. a and b constants regression coefficients with a standard error values were found using the SigmaPlot program [6-8].

Table 2. The Calculated and Experimental ^{13}C and ^{1}H NMR Isotropic Chemical Shift Values of the Molecule

	Deneysel	**DFT/631d**	**Fark**	**HF/631d**	**Fark**
C1	148,10	155,20	-7,10	148,87	-0,77
C2	152,31	152,91	-0,60	149,05	3,26
C3	151,24	167,88	-16,64	170,20	-18,96
C4	121,05	127,45	-6,40	116,64	4,41
C5	126,53	133,27	-6,74	125,24	1,29
C6	139,37	144,13	-4,76	130,72	8,65
C7	153,29	158,24	-4,95	149,76	3,53
C8	113,15	116,94	-3,79	105,97	7,18
C9	130,31	135,64	-5,33	129,27	1,04
C10	162,27	165,37	-3,10	155,53	6,74
C11	128,92	135,32	-6,40	123,10	5,82
C12	124,21	130,03	-5,82	128,79	-4,58
C13	146,34	152,93	-6,59	138,91	7,43
C14	128,43	133,41	-4,98	131,81	-3,38
C15	128,69	133,72	-5,03	122,10	6,59
C16	135,85	142,40	-6,55	140,60	-4,75
C17	56,28	61,75	-5,47	46,43	9,85
C18	30,69	42,55	-11,86	27,05	3,64
C19	132,71	134,93	-2,22	125,95	6,76
C20	128,93	133,38	-4,45	127,00	1,93
C21	128,62	132,13	-3,51	124,62	4,00
C22	135,69	141,51	-5,82	134,28	1,41

C23	128,62	132,12	-3,50	124,62	4,00
C24	128,93	133,18	-4,25	127,00	1,93
C25	20,55	29,87	-9,32	17,05	3,50
H26	11,95	8,47	3,48	7,50	4,45
H27	9,64	9,12	0,52	9,20	0,44
H28	7,75	8,32	-0,57	8,27	-0,52
H29	7,34	8,01	-0,67	7,58	-0,24
H30	7,78	9,44	-1,66	9,15	-1,37
H31	8,82	10,15	-1,33	10,31	-1,49
H32	8,63	9,65	-1,02	9,75	-1,12
H33	7,96	8,82	-0,86	8,43	-0,47
H34	8,60	9,63	-1,03	9,64	-1,04
H35	3,87	4,74	-0,87	4,00	-0,13
H36	3,87	4,70	-0,83	3,89	-0,02
H37	3,87	4,96	-1,09	4,32	-0,45
H38	4,02	4,74	-0,72	3,82	0,20
H39	4,02	4,22	-0,20	3,44	0,58
H40	7,08	8,12	-1,04	7,77	-0,69
H41	7,20	8,18	-0,98	7,86	-0,66
H42	7,20	8,23	-1,03	7,89	-0,69
H43	7,08	8,24	-1,16	7,93	-0,85
H44	2,23	3,09	-0,86	2,52	-0,29
H45	2,23	2,96	-0,73	2,53	-0,3
H46	2,23	3,38	-1,15	2,8	-0,57

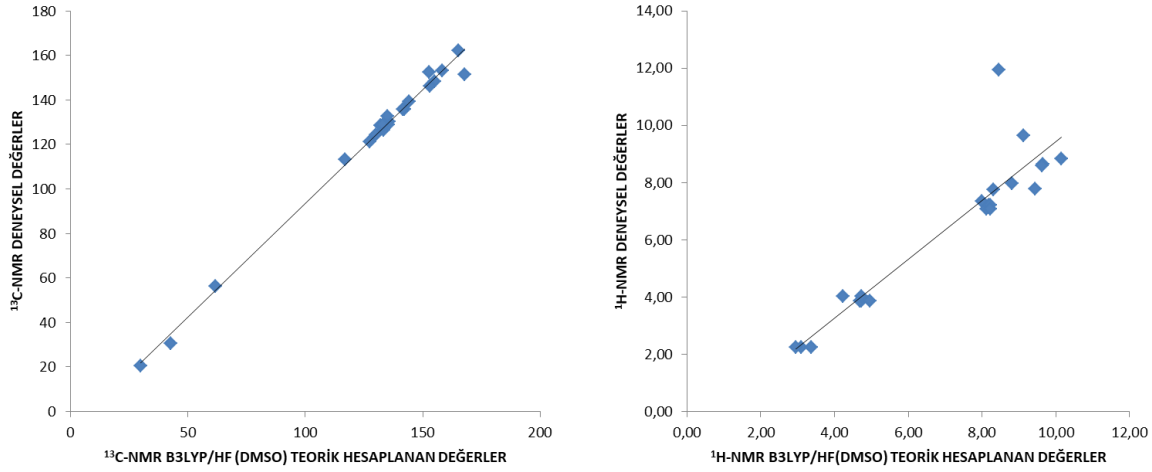
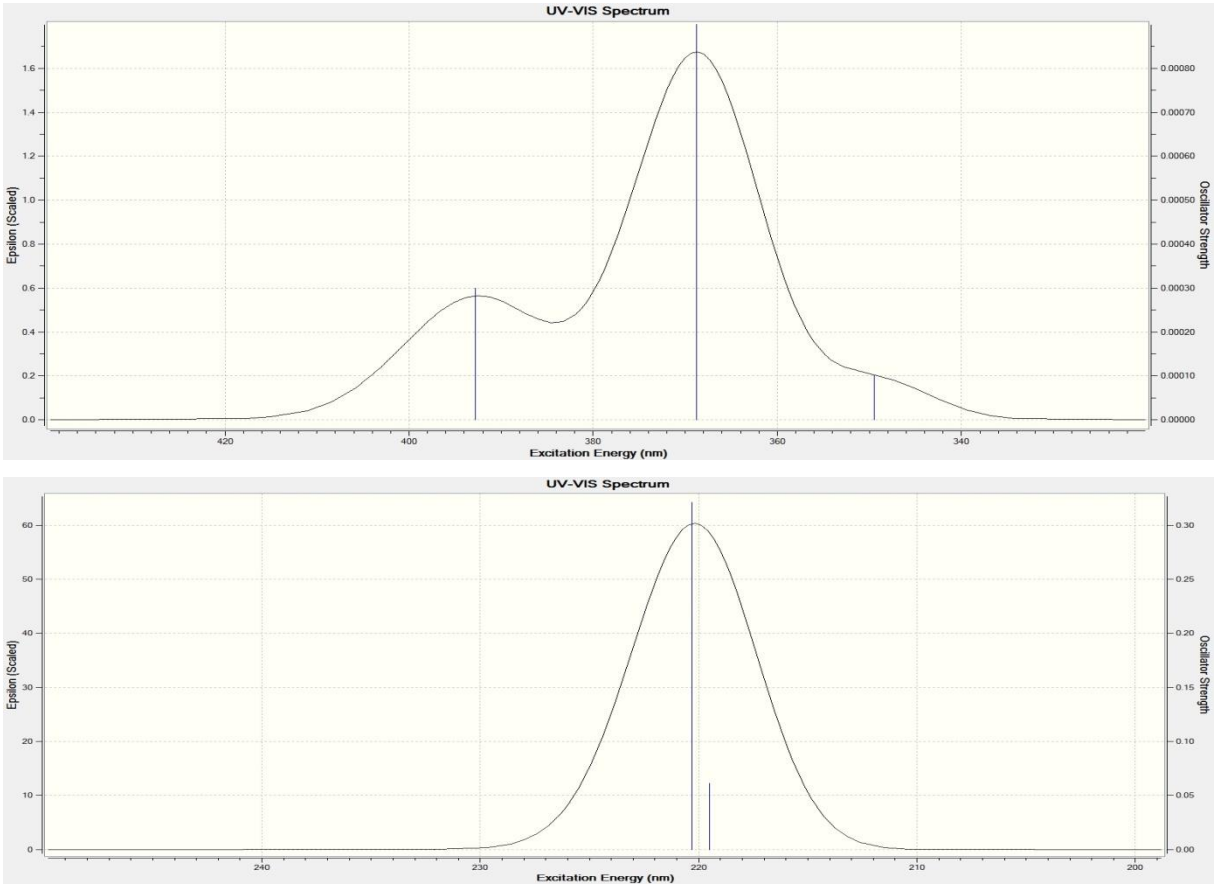


Figure 1. The correlation graphics for 13C-NMR (DMSO) and 1H-NMR (DMSO) chemical shifts of the molecule

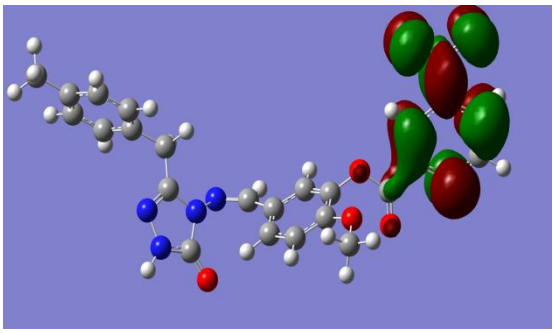
Table 3. The Correlation Data for Chemical Shifts of the Molecule

	^{13}C (DMSO)				^{1}H (DMSO)			
	R	S. hata	a	b	R	S. hata	a	b
DFT	0,9845	6,3158	1,0114	5,0076	0,9247	1,0660	1,0284	0,7196
HF	0,9744	8,1002	0,9296	5,6408	0,9018	1,2094	0,9133	0,7131

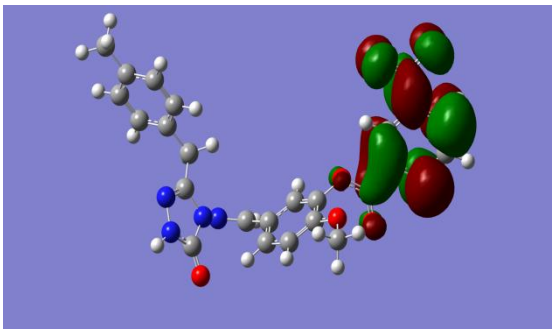


λ (nm)B3LYP/HF	**excitation Energy(eV) B3LYP/HF**	***f* (oscillator values) B3LYP/HF**
392.79/232.12	3.1565/5.3413	0.0003/0.0000
368.76/220.31	3.3622/5.6278	0.0009/0.3211
349.45/219.51	3,5480/5.6482	0.0001/0.0612

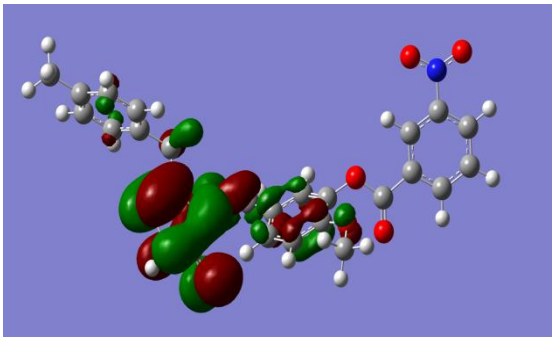
Figure 2. The Absorption Wavelength (λ), Excitation Energies and Oscillator Strengths (*f*) of the Molecule.



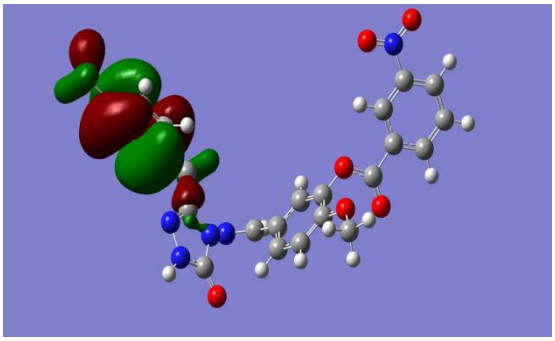
E_{LUMO} (B3LYP) : -0.07831 Hatree



E_{LUMO} (HF) : 0.04878 Hatree



E_{HOMO} (B3LYP) : -0.20962 Hatree



E_{HOMO} (HF) : -0.31706 Hatree

Figure 3. HOMO-LUMO Energy Calculated With DFT/B3LYP/631G(d,p) and HF/B3LYP/6311G(d,p) Levels of the Molecule.

Conclusion

In this work, geometrical and spectroscopic parameters such as IR, ^{1}H-NMR, ^{13}C-NMR and UV–vis values spectra of 3-benzyl-4-[3-(3-nitrobenzoxy)-4-methoxybenzylideneamino]-4,5-dihydro-1H-1,2,4-triazol-5-one is calculated by density functional theory (DFT) and Hartree-Fock (HF) methods with the 631G(d,p) basis set. Obtained spectroscopic parameters are compared with 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 according to a, b ve R^2 values, a linear correlation were observed. Furthermore, HOMO-LUMO energy was also calculated theoretically by using the B3LYP/631G(d,p) and HF/631G(d,p) basis sets.

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