Comparison of 6-311G(d) and 3-21G(Dft/Hf) Methods of 3-Methyl-4-[3-(3-methoxybenzoxy)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one

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ABSTRACT

3-Methyl-4-[3-(3-methoxybenzyl)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one was synthesized by the reaction of 3-methyl-4-amino-4,5-dihydro-1*H*-1,2,4-triazole-5-one with 3-(3-methoxybenzyl)-benzaldehyde which was synthesized by the reaction of 3-hydroxybenzaldehyde with 3-methoxybenzoyl chloride by using triethylamine. This compound was optimized by using B3LYP/6-311G(d) HF/6-311G(d) and B3LYP/3-21G, HF/3-21G basis sets. Electronic properties (total energy, dipole moment), thermodynamic parameters, geometric properties (bond angles and bond lengths), the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), Mulliken atomic charges, the molecular electrostatic potential (MEP) of 3-methyl-4-[3-(3-methoxybenzyl)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one have been performed. ^{1}H-NMR and ^{13}C-NMR isotropic shift values of 3-methyl-4-[3-(3-methoxybenzyl)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one in the ground state and in DMSO solvent were calculated by using the gauge-including atomic orbital (GIAO) method. The structural and spectroscopic data of the molecule in the ground state have been calculated by using density functional method (DFT/B3LYP) and Hartree–Fock method (HF) with the 6-311G(d) and 3-21G basis sets. The veda4f program was used for the identification of calculated IR data. The UV-vis values in ethanol were found and compared with experimental results. All experimental data were compared with theoretical data.

Keywords: 4,5-Dihydro-1*H*-1,2,4-triazol-5-on, Gaussian 09W, GIAO, B3LYP, HF, 6-311G(d), 3-21G basis sets.

1. INTRODUCTION

1,2,4-triazole and its derivatives play an important role in numerous biological activities such as antimicrobial, antitumor, anticancer, antifungal, anti-HIV, antiviral, anti-inflammatory, analgesic and antioxidant properties [1-4]. *N*-arylidenamino-4,5-dihydro-1*H*-1,2,4-triazole-5-one derivatives have attracted considerable attention due to these properties. In recent years, theoretical calculation methods have been commonly used the design of functional materials. The development of computational chemistry has widely used the prediction of many properties in the chemical systems. Moreover, the theoretical calculations are largely contributed to the spectroscopic studies performing by experimentally [5-10]. The Hartree Fock (HF) and Density Functional Theory (DFT) has been intensively employed for the calculation of many properties of some 4,5-dihydro-1*H*-1,2,4-triazole-5-one derivatives such as molecular structure, FT-IR, UV-Vis, and ^{1}H and ^{13}C NMR spectra, HOMO-LUMO energies, charge distributions and thermodynamics properties. The reliable results consistent with experimental data have been attained for 1,2,4-triazole derivatives [11-15].

In this present study, new 3-methyl-4-[3-(3-methoxybenzyl)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**3**) were obtained from the reaction of the compound **(2)** with 3-(3-methoxybenzyl)-benzaldehyde (**1**) which was synthesized by the reaction of 3-hydroxybenzaldehyde with 3-methoxybenzoyl chloride by using triethylamine (Scheme **1**). The structural characterization of the compound (**3**) was experimentally accomplished by ^{1}H NMR and ^{13}C NMR, FTIR and UV-Vis spectroscopic methods.

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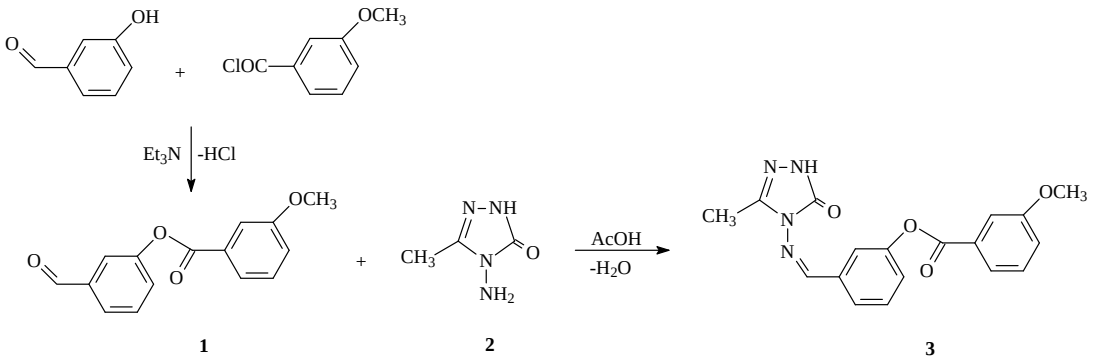


Scheme1. Synthetic pathway of compound **3**

3-Methyl-4-[3-(3-methoxybenzyl)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**3**) has been optimized by using B3LYP/6-311G(d), HF/6-311G(d) and B3LYP/3-21G, HF/3-21G basis sets [16]. The optimized molecular geometry, IR frequencies, ^{1}H and ^{13}C NMR chemical shifts, UV-Vis spectra, the bond angles, bond lengths, dipole moments, HOMO-LUMO energies, molecular electrostatic potential (MEP) map, dipole moment and atomic charges of the compound (**3**) were investigated using B3LYP/6-311G (d), HF/6-311G (d) and B3LYP/3-21G, HF/3-21G basis sets. The experimental data [16] of the compound (**3**) obtained from IR, UV-Vis, ^{1}H and ^{13}C NMR spectra were compared to the calculated results from the DFT and HF methods.

2. MATERIAL AND METHODS

2.1. Experimental

Chemistry

Chemical reagents and all solvents used in this study were purchased from Merck AG (Darmstadt, Germany), Sigma (Sigma-Aldrich GmbH, Sternheim, Germany) and Fluka (Buchs, Switzerland). The starting compound 3-methyl-4-amino-4,5-dihydro-1*H*-1,2,4- triazole-5-one **2** were prepared from the reactions of the corresponding ester ethoxycarbonylhydrazones with an aqueous solution of hydrazine hydrate as described in the literature [30]. Melting points were determined in open glass capillaries using a WRS-2A Microprocessor melting-point apparatus (Liaoning, mainland China) and are uncorrected. The IR spectra were obtained on an ALPHA-P BRUKER FT-IR (Germany) spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in deuterated dimethyl sulfoxide with TMS as an internal standard using a Bruker (Germany) spectrometer at 400 MHz and 100 MHz, respectively. UV absorption spectra were measured in 10 mm quartz cells between 200 and 400 nm using a PG Instruments Ltd T80 UV/VIS (Leicestershire, United Kingdom) spectrometer. Extinction coefficients (ε) are expressed in L mol^{-1} cm^{-1}.

*The synthesis of compound **3***

The compound **2** (0.01 mol) was dissolved in acetic acid (20 mL) and treated with 3-(3 methoxybenzoxybenzaldehyde) **1** (0.01 mol). The mixture was refluxed for 2 h and subsequently evaporated at 50-55 °C *in vacuo*. Several recrystallizations of the residue from ethanol gave pure compound **3** as colourless crystals.

3-Methyl-4-[3-(3-methoxybenzoxy)-benzylidenamino]-4,5-dihydro-1H-1,2,4-triazol-5-one

Yield: 3.48 g (98%); mp: 187.8-188.3 ºC; IR (KBr, *u*, cm^{-1}): 3169 (NH), 1735, 1700 (C=O), 1601, 1578 (C=N), 1268 (COO), 776, 681 (1,3-disubstituted benzenoid ring); ^{1}H NMR (400 MHz, DMSO-d6): δ 2.29 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 7.33-7.36 (m, 1H, Ar-H), 7.46-7.48 (m, 1H, Ar-H), 7.55 (t, 1H, Ar-H, *J*=7.84), 7.60-7.64(m, 2H), 7.75-7.79(m, 3H), 9.79 (s, 1H, N=CH), 11.87 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d6): δ 11.08 (CH_3), 55.43 (OCH_3), 120.22 (2C), 122.13, 124.94, 125.94, 130.03, 130.16, 130.25, 135.21, 151.01, 159.39, 144.31 (triazole C3), 151.15 (N=CH), 152.40 (triazole C5), 164.33 (COO); UV λ_{max} (ε): 296 (16.750), 242 (13.213), 220 (23.654) nm.

2.2. Theoretical

All the calculations for title compound were performed by using Gaussian G09W program [17]. Firstly, the geometry of the compound (**3**) was obtained at the HF and DFT/B3LYP levels of theory along with standard 6-311G(d) and 3-21G basis sets. The obtained results were visualized by the aid of GaussView program [18]. The GIAO (Gauge-Including Atomic Orbital) method is the most widely used technique for calculating NMR shielding values [19]. The veda4f program was used for the identification of the calculated IR data [20].

The theoretical UV-vis spectra data were performed using time dependent-density functional theory (TD-DFT) method in ethanol solvent [21-23]. The optimized molecular geometry, bond lengths, bond angles, ^{1}H and ^{13}C NMR chemical shifts, UV-Vis values, IR frequencies HOMO-LUMO energies, total energy, molecular electrostatic potential (MEP) map, dipole moment and atomic charges of the compound (**3**) were investigated using HF and DFT/B3LYP levels of theory along with

standard 6-311G(d) and 3-21G basis sets. The experimental data [16] of the compound (**3**) obtained from ^{1}H and ^{13}C NMR FTIR, UV-Vis spectra were compared to the calculated results from the HF and DFT/B3LYP levels of theory along with standard 6-311G(d) and 3-21G basis sets.

3. RESULTS AND DISCUSSION

3.1. Molecular Geometry

The optimized molecular structure of 3-methyl-4-[3-(3-methoxybenzyl)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one are shown in (Figure **1**). The calculated molecular geometric parameters (bond angles, bond lengths, Mulliken atomic charges) by using the Hartree Fock (HF) and DFT/B3LYP methods with 6-311G(d) and 3-21G basis sets are given in Table **1-3**. The N35-N36, N36=C1, C2=O39 and N2-C35 bond lengths in the triazole ring according to HF/DFT methods with 6-311G(d) and 3-21G basis sets are computed as 1.3695/1.3798, 1.4278/1.4390 Å, 1.2661/1.2957, 1.2786/1.3125 Å, 1.1960/1.2156, 1.2185/1.2372 Å, and 1.3460/1.3686, 1.3543/1.3778 Å, respectively. In the literature, the N=C, N-N, C=O bond lengths are measured as 1.280, 1.404 [24], . 1.212 Å [25], respectively. The calculated molecular geometric parameters for triazole rings in the title molecule are in a good agreement with in the literature [24, 25]. The calculated Mulliken atomic charges [26] and results of the thermodynamic parameter by using the Hartree Fock (HF) and DFT/B3LYP methods with 6-311G(d) and 3-21G basis sets of the compound (**3)** in the gas phase are listed in (Table **3**), respectively. The electronegative nitrogen (N), oxygen (O) atoms have negative atomic charge values. The carbon atoms surrounded by electronegative atoms have positive atomic charge values for compound (3). The C1 atom surrounded by two electronegative atoms (N, N) and C2 atom which is surrounded by three electronegative atoms (N, N, O) have the highest positive charges values. All hydrogen atoms of the compound (**3**) have positive atomic charge values (Table **3**).

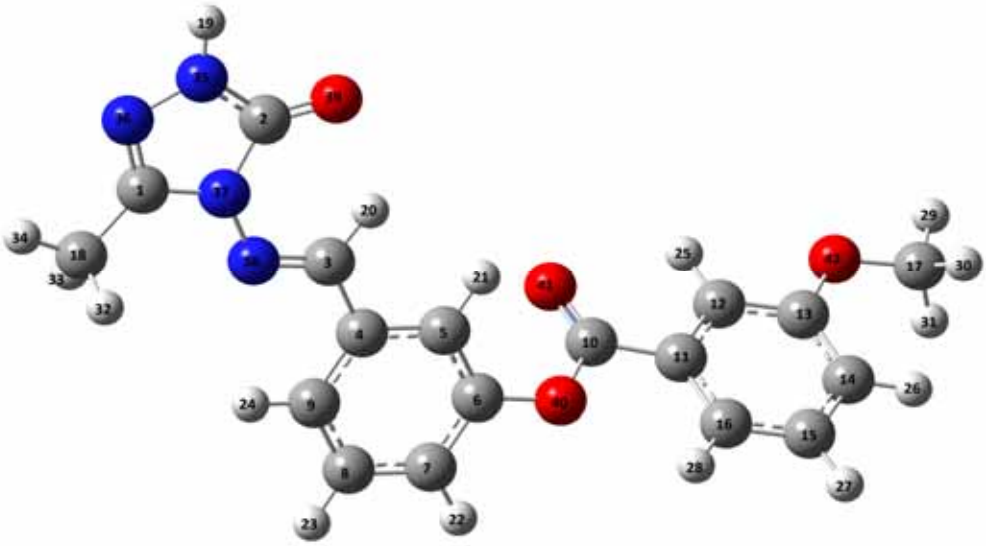


Figure 1. The optimized molecular structure of 3-methyl-4-[3-(3-methoxybenzoxy)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one

Table 1. The calculated bond angles (^{0}) of the compound 3 (6-311G(d) HF/B3LYP, 3-21G HF/B3LYP)

	Bond Angles	HF 6-311G(d)	B3LYP 6-311G(d)	HF 3-21G	B3LYP 3-21G
1	C(1)-N(37)-N(38)	121.062	121.276	120.430	120.701
2	C(1)-N(36)-N(35)	105.020	104.750	104.094	103.327
3	C(1)-N(37)-C(2)	108.082	108.260	109.216	109.287
4	C(1)-C(18)-H(32)	110.647	111.137	110.144	110.380
5	C(1)-C(18)-H(33)	110.649	111.158	110.144	110.380
6	C(1)-C(18)-H(34)	108.624	108.723	108.983	108.909
7	H(32)-C(18)-H(34)	109.546	109.258	109.799	109.765
8	H(33)-C(18)-H(32)	107.814	107.259	107.962	107.632
9	H(33)-C(18)-H(34)	109.548	109.270	109.799	109.765
10	N(36)-C(1)-N(37)	111.302	111.401	111.725	112.206
11	N(36)-N(35)-H(19)	120.841	120.313	120.148	119.487
12	N(36)-N(35)-C(2)	113.777	114.490	112.860	113.973
13	N(37)-C(1)-C(18)	123.272	123.480	122.367	122.485
14	H(19)-N(35)-C(2)	125.382	125.197	126.992	126.540
15	N(35)-C(2)-N(37)	101.818	101.098	102.105	101.206
16	N(35)-C(2)-O(39)	129.582	130.112	130.222	130.859
17	O(39)-C(2)-N(37)	128.600	128.790	127.673	127.934
18	C(2)-N(37)-N(38)	130.854	130.462	130.354	130.013
19	N(37)-N(38)-C(3)	120.006	119.209	118.992	117.229
20	N(38)-C(3)-H(20)	122.340	122.029	122.540	122.475

21	N(38)-C(3)-C(4)	120.404	117.948	120.047	119.613
22	H(20)-C(3)-C(4)	117.259	117.762	117.413	117.911
23	C(3)-C(4)-C(5)	119.033	119.572	117.828	119.082
24	C(3)-C(4)-C(9)	122.564	122.481	121.645	121.572
25	C(4)-C(5)-H(21)	120.989	120.233	120.936	121.089
26	C(4)-C(5)-C(6)	119.885	119.572	119.061	119.167
27	H(21)-C(5)-C(6)	119.125	120.190	120.004	119.744
28	C(5)-C(6)-O(40)	117.928	122.321	124.881	125.371
29	C(5)-C(6)-C(7)	121.117	121.037	120.820	120.661
30	O(40)-C(6)-C(7)	120.872	116.532	114.299	113.968
31	C(6)-C(7)-H(22)	120.051	119.242	118.721	118.559
32	C(6)-C(7)-C(8)	118.950	119.278	119.694	119.793
33	H(22)-C(7)-C(8)	120.998	121.480	121.585	121.648
34	C(7)-C(8)-H(23)	119.425	119.481	119.583	119.507
35	C(7)-C(8)-C(9)	120.709	120.519	120.328	120.343
36	H(23)-C(8)-C(9)	119.866	120.000	120.089	120.150
37	C(8)-C(9)-H(24)	120.516	120.851	121.131	121.542
38	C(8)-C(9)-C(4)	119.934	120.021	119.570	119.689
39	H(24)-C(9)-C(4)	119.549	119.129	119.300	118.769
40	C(9)-C(4)-C(5)	119.404	119.571	120.527	120.347
41	C(6)-O(40)-C(10)	120.030	120.567	128.248	125.479
42	O(40)-C(10)-O(41)	123.395	123.565	123.483	124.181
43	O(40)-C(10)-C(11)	111.899	111.211	111.449	110.232
44	O(41)-C(10)-C(11)	124.706	125.224	125.068	125.587
45	C(10)-C(11)-C(16)	122.175	122.641	122.033	122.615
46	C(10)-C(11)-C(12)	117.239	117.015	116.966	116.550
47	C(11)-C(12)-H(25)	120.464	120.163	120.618	120.120
48	C(11)-C(12)-C(13)	120.285	120.321	120.061	120.243
49	H(25)-C(12)-C(13)	119.251	119.517	119.321	119.637
50	C(12)-C(13)-O(42)	115.788	115.688	116.044	115.806
51	C(12)-C(13)-C(14)	119.428	119.522	119.360	119.196
52	C(13)-O(42)-C(17)	119.946	118.659	120.963	118.207
53	O(42)-C(13)-C(14)	124.784	124.790	124.596	124.998
54	O(42)-C(17)-H(29)	106.190	105.746	105.464	104.864
55	O(42)-C(17)-H(30)	111.459	111.547	111.308	111.613
56	O(42)-C(17)-H(31)	111.465	111.553	111.308	111.613
57	H(29)-C(17)-H(30)	109.105	109.243	109.618	109.684
58	H(29)-C(17)-H(31)	109.099	109.236	111.308	109.683
59	H(30)-C(17)-H(31)	109.430	109.419	109.445	109.293
60	C(13)-C(14)-C(15)	119.785	119.682	120.128	120.122
61	C(13)-C(14)-H(26)	121.116	120.999	120.696	120.618
62	C(14)-C(15)-C(16)	121.132	119.682	120.795	120.907
63	H(26)-C(14)-C(15)	119.099	119.319	119.176	119.260
64	C(14)-C(15)-H(27)	119.033	119.057	119.259	119.175
65	H(27)-C(15)-C(16)	119.835	119.814	119.946	119.918
66	C(15)-C(16)-H(28)	120.743	120.874	121.400	121.677
67	C(15)-C(16)-C(11)	118.784	119.002	118.655	118.697
68	H(28)-C(16)-C(11)	120.472	120.123	119.945	119.626
69	C(16)-C(11)-C(12)	120.586	120.344	121.001	120.835

Table 2. The calculated bond lengths (A^0) of the compound 3 (6-311G(d) HF/B3LYP, 3-21G HF/B3LYP)

	Bond Lenghts	HF 6-311G(d)	HF 3-21G	B3LYP 6-311G(d)	B3LYP 3-21G
1	C(1)-N(36)	1.2661	1.2786	1.2957	1.3125
2	C(1)-N(37)	1.3793	1.3816	1.3889	1.3890
3	C(1)-C(18)	1.4875	1.4840	1.4852	1.4861
4	C(18)-H(32)	1.0827	1.0824	1.0927	1.0948
5	C(18)-H(33)	1.0827	1.0824	1.0926	1.0948
6	C(18)-H(34)	1.0800	1.0749	1.0894	1.0911
7	N(37)-C(2)	1.3884	1.3971	1.4209	1.4328
8	C(2)-O(39)	1.1960	1.2185	1.2156	1.2372
9	N(35)-C(2)	1.3460	1.3543	1.3686	1.3778
10	N(35)-H(19)	0.9885	0.9919	1.0053	1.0087
11	N(35)-N(36)	1.3695	1.4278	1.3798	1.4390
12	N(37)-N(38)	1.3629	1.3985	1.3692	1.4099
13	N(38)-C(3)	1.2572	1.2669	1.2846	1.2972
14	C(3)-H(20)	1.0741	1.0701	1.0866	1.0848
15	C(3)-C(4)	1.4767	1.4716	1.4664	1.4653
16	C(4)-C(5)	1.3876	1.3884	1.4005	1.4032

17	C(4)-C(9)	1.3916	1.3866	1.4038	1.4036
18	C(5)-H(21)	1.0748	1.0657	1.0824	1.0778
19	C(5)-C(6)	1.3797	1.3807	1.3905	1.3949
20	C(6)-O(40)	1.3786	1.3957	1.3937	1.4100
21	C(6)-C(7)	1.3767	1.3814	1.3892	1.3974
22	C(7)-H(22)	1.0736	1.0694	1.0840	1.0817
23	C(7)-C(8)	1.3872	1.3817	1.3958	1.3949
24	C(8)-H(23)	1.0747	1.0713	1.0849	1.0834
25	C(8)-C(9)	1.3799	1.3811	1.3869	1.3916
26	C(9)-H(24)	1.0726	1.0695	1.0830	1.0820
27	O(40)-C(10)	1.3400	1.3572	1.3733	1.3940
28	C(10)-O(41)	1.1782	1.2048	1.2018	1.2277
29	C(10)-C(11)	1.4921	1.4787	1.4891	1.4807
30	C(11)-C(12)	1.3802	1.3772	1.3926	1.3923
31	C(11)-C(16)	1.3933	1.3884	1.4026	1.4027
32	C(12)-H(25)	1.0722	1.0687	1.0829	1.0812
33	C(12)-C(13)	1.3902	1.3859	1.3972	1.3986
34	C(13)-O(42)	1.3455	1.3689	1.3611	1.3825
35	C(13)-C(14)	1.3851	1.3821	1.3986	1.3397
36	C(14)-H(26)	1.0726	1.0695	1.0827	1.0815
37	C(14)-C(15)	1.3902	1.3879	1.3966	1.3990
38	C(15)-H(27)	1.0750	1.0715	1.0851	1.0836
39	C(15)-C(16)	1.3770	1.3769	1.3872	1.3903
40	C(16)-H(28)	1.0713	1.0673	1.0815	1.0794
41	O(42)-C(17)	1.3977	1.4368	1.4193	1.4603
42	C(17)-H(29)	1.0785	1.0772	1.0882	1.0899
43	C(17)-H(30)	1.0849	1.0831	1.0954	1.0968
44	C(17)-H(31)	1.0850	1.0831	1.0954	1.0968

Table 3. The calculated Mulliken atomic charges of compound 3 (6-311G(d) HF/B3LYP, 3-21G HF/B3LYP)

	HF 6-311G(d)	**HF 3-21G**	**B3LYP 6-311G(d)**	**B3LYP 3-21G**
C1	0.515	0.756	0.405	0.626
C2	0.787	1.249	0.583	0.940
C3	0.036	0.192	0.055	0.108
C4	-0.042	-0.164	-0.023	-0.056
C5	-0.272	-0.246	-0.209	-0.212
C6	0.327	0.383	0.231	0.301
C7	-0.211	-0.254	-0.193	-0.192
C8	-0.207	-0.227	-0.201	-0.183
C9	-0.194	-0.205	-0.159	-0.172
C10	0.647	1.008	0.430	0.708
C11	-0.203	-0.246	-0.157	-0.107
C12	-0.241	-0.199	-0.203	-0.166
C13	0.368	0.417	0.272	0.322
C14	-0.300	-0.267	-0.259	-0.207
C15	-0.195	-0.227	-0.193	-0.182
C16	-0.211	-0.209	-0.168	-0.183
C17	-0.416	-0.273	-0.454	-0.336
C18	-0.670	-0.618	-0.670	-0.596
C19	0.406	0.404	0.371	0.353
H20	0.306	0.330	0.261	0.262
H21	0.240	0.324	0.229	0.247
H22	0.238	0.266	0.209	0.206
H23	0.227	0.251	0.200	0.195
H24	0.241	0.271	0.209	0.207
H25	0.264	0.305	0.230	0.230
H26	0.242	0.255	0.216	0.196
H27	0.224	0.251	0.199	0.195
H28	0.244	0.274	0.213	0.205
H29	0.233	0.239	0.233	0.227
H30	0.208	0.200	0.211	0.199
H31	0.207	0.200	0.211	0.199
H32	0.244	0.251	0.235	0.231
H33	0.245	0.251	0.236	0.231
H34	0.251	0.250	0.239	0.226
H35	-0.496	-0.760	-0.496	-0.592

N36	-0.266	-0.389	-0.198	-0.337
N37	-0.468	-0.849	-0.363	-0.622
N38	-0.271	-0.358	-0.206	-0.320
N39	-0.532	-0.670	-0.389	-0.520
O40	-0.509	-0.815	-0.373	-0.600
O41	-0.436	-0.616	-0.317	-0.481
O42	-0.461	-0.735	-0.336	-0.550

3.2. Vibrational spectral analysis

3-Methyl-4-[3-(3-methoxybenzyl)-benzylidenamino]-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule has 42 atoms and the normal vibrational number is 120. The observed and calculated vibrational frequencies for compound (**3**) are summarized by using of 6-311G(d) and 3-21G basis sets of HF and B3LYP methods (Table **4** and **5**).

3.2.1. NH vibrations

In the experimental IR spectrum of the title compound, ν(N-H) appeared at 3169 cm^{-1} whereas the calculated values appeared at 3540/3515 and 3771/3656 cm^{-1} according to 6-311G(d) and 3-21G basis sets of HF and B3LYP methods, respectively.

3.2.2. Aromatic Ring vibrations

In the titled compound, the band ν(C-H) is observed 3029 cm^{-1} in the experimental IR spectrum and the calculated values lie in the region 2900-3250 cm^{-1}. The aromatic C=C stretching vibrations 1583-1319 cm^{-1} in the experimental IR in the region whereas their calculated value were in the region 1671-1310 cm^{-1}. The band observed at 681 and 776 cm^{-1} were assigned to C=C in-plane bending vibration of aromatic rings, whereas the calculated were 692/658, 694/683 and 779/739, 784/744 cm^{-1}, respectively.

3.2.2. C=O vibrations

In the titled compound, two bands in the region 1750-1650 cm^{-1} due to the presence of two carbonyl (C=O) group in the molecule. the two bands ν(C=O) are observed 1735 and 1700 cm^{-1} in the experimental IR spectrum. Their calculated values were 1903/1793, 1864/1787 cm^{-1} and 1745/1710, 1733/1675 cm^{-1}, respectively.

Table 4. The calculated IR frequencies of compound 3 (6-311G(d))

	Vibration Frequencies	HF	B3LYP
1	τ NCCC(18), τ CCCC(20), τ COCC(80)	7	10
2	τ NCCC(23), τ COCC(21), τ CNNC(34), τ CCCN(28)	14	15
3	τ COCC(38), τ NCCC(12), τ CCOC(63)	18	19
4	τ COCC(14), τ CCCC(16), δ COC(11)	41	41
5	τ CCCC(10), τ COCC(28), τ CCNN(20), τ NCCN(27)	56	50
6	δ COC(17), τ CCNN(10), τ NCCN(11), τ NCNN(26),τ NNCN(11), τ COCC(11)	62	63
7	δ NCC(13), τ COCC(17), τ HCOC(11)	70	82
8	τ COCC(53), δ CNN(22), δ CCN(26)	78	83
9	τ NCNN(10), τ CNNC(33), τ CCCN(15)	110	115
10	δ CCC(10), δ COC(17), δ CCO(13)	152	134
11	τ HCCN(15), τ CNNC(37)	163	162
12	τ HCCN(41), τ CNNC(10), τ CCCC(10), δ COC(12)	169	166
13	τ CNNC(25), τ HCCN(55)	181	173
14	ν CC(10), δ COC(10), δ CCC(11), τ CCCC(13)	185	191
15	δ CNN(14), δ CCC(10),δ NNC(17)	206	204
16	τ HCOC(18), τ CCCC(12), τ COCC(13), τ OCCC(25), τ CCCN(14), τ NCCN(31)	225	214
17	τ NCCC(11), τ NCNN(17), τ CCCC(30), τ HCOC(19), τ OCCC(11)	226	237
18	ν CC(12), δ CCN(22), δ COC(11), δ CCO(12)	245	240
19	δ COC(23)	271	263
20	τ HCOC(45), τ CCCC(25), τ COCC(10)	293	280
21	τ HNNC(17), τ HCCN(11), τ CNNC(33), τ NCNN(26)	293	290
22	δ COC(21), δ OCO(13)	307	296
23	δ CCO(13), δ CCN(36)	345	336
24	τ NCNN(16), τ NNCN(18), τ CCNN(36), τ NCCN(11)	362	348
25	δ NNC(15), δ OCN(17), δ CCO(13), δ CNN(16)	403	380
26	δ OCO(10), δ CCC(39), δ COC(11)	439	426
27	τ CCCC(47)	460	439
28	τ HNNC(58), τ ONNC(11)	462	451
29	τ HNNC(40), τ HCCC(11), τ CCCN(18)	481	454
30	τ HNNC(17)	488	463
31	δ CCC(21), δ COC(12)	504	492
32	δ CCC(12), δ COC(11), τ HCCC(11), τ OCOC(11), τ OCCC(37)	581	551
33	δ CCC(14), δ COC(19), τ OCCC(14)	583	567
34	δ CCC(10), δ CNN(13)	598	582
35	δ CCC(16), δ CNN(14)	612	592
36	δ OCN(33), δ CNN(11),δ CCN(12), ν NC(13)	621	594
37	τ CCOC(20), τ CCCC(12), δ OCO(10), τ OCCC(11)	628	600
38	ν CC(19), ν NC(13), δ OCN(33), δ CCN(12), δ CCC(14)	664	646

39	τ HNNC(11), τ NNCN(30), τ CNNC(15), τ HCCN(10), τ NCNN(49)	692	658
40	τ HCCC(18), τ CCCC(12), δ CCC(23)	706	683
41	δ CCC(20), τ HCCC(28), τ CCCC(17)	716	685
42	τ HCCC(38), τ CCCC(15), τ CCCN(20)	725	692
43	τ ONNC(80), ν CC(11), δ CCC(10)	779	739
44	τ HCCC(24), τ OCOC(43)	808	753
45	ν NN(10), δ CCC(12), τ CNNC(10), τ ONNC(83)	814	757
46	δ OCO(10), τ HCCC(31)	830	788
47	ν NC(16), ν CC(10), δ CNN(18), τ HCCC(11)	834	799
48	δ CNN(18), ν NC(14), τ HCCC(50), τ OCOC(29)	861	802
49	δ OCO(12), τ HCCC(15)	863	815
50	δ NNC(14), δ NCC(17),δ CCN(12)	887	846
51	ν OC(19), τ HCCC(17)	926	876
52	τ HCCC(42), τ CCCC(10)	966	891
53	ν OC(11), τ HCCC(34)	967	896
54	τ HCCC(40)	982	917
55	ν OC(10), ν CC(11), τ HCCC(37)	984	917
56	ν CC(13), ν OC(11), δ CCC(12), τ HCCC(38)	995	956
57	ν CC(30), δ CCC(23), τ HCCC(55)	1027	961
58	ν CC(19), δ CCC(39), τ HCCC(58)	1035	967
59	δ HCH(13), δ NNC(14), τ HCCN(37)	1043	990
60	ν CC(30), δ CCC(20), τ HCCC(46)	1044	1002
61	τ HCNN(86), τ HCCC(57), τ CCCC(10)	1049	1005
62	ν CC(17), δ CCC(24), τ HCNN(88)	1082	1008
63	ν OC(32), δ HCH(21), τ HCCN(55)	1117	1061
64	ν OC(23), δ NNC(19)	1125	1062
65	δ HCH(25), τ HCCN(56), ν OC(32)	1126	1066
66	ν CC(12), ν OC(11), δ HCC(25)	1130	1085
67	ν CC(15), ν OC(13), δ HCC(16)	1138	1098
68	ν NN(20), ν CC(18), δ HCC(21), τ HCCN(15)	1142	1100
69	ν CC(20), δ HCC(22)	1151	1110
70	δ HCC(32), ν NN(28), δ HNN(14), τ HCCN(15)	1165	1164
71	ν CC(26), δ HCH(25), τ HCOC(28)	1168	1172
72	δ HCC(46)	1211	1180
73	δ HCC(28), δ HCH(25), τ HCOC(26)	1232	1185
74	δ HCH(12), τ HCOC(22), δ HCC(20)	1251	1199
75	ν CC(12), ν NN(18), ν NC(23),δ OCN(11), δ HCC(17)	1261	1205
76	ν CC(11), δ HCC(12)	1268	1223
77	ν NC(26), ν NN(14), δ CNN(14)	1276	1255
78	ν OC(15), ν CC(22)	1313	1282
79	ν OC(43), ν CC(12), ν NN(14), δ NCN(12)	1326	1291
80	δ HCC(17), ν OC(18)	1368	1310
81	δ HCC(26)	1373	1311
82	ν CC(21), δ HCC(68)	1374	1343
83	ν CC(35), δ HCC(16), ν NN(13), δ CNN(28)	1386	1350
84	ν NC(21), δ HCN(35), δ HCH(14)	1443	1373
85	δ HNN(63), δ HCN(14), δ HCH(51)	1475	1396
86	ν OC(11), ν NC(11), δ HCN(17), δ HCH(55), δ HNN(47)	1484	1417
87	δ HCH(10), ν CC(17), δ HNN(11)	1505	1440
88	δ HCN(12), ν CC(17), δ HCC(12)	1524	1459
89	ν CC(12), δ HCC(11), δ HCH(27), δ HCN(10)	1529	1465
90	δ HCH(77), τ HCCN(21)	1530	1475
91	δ HCH(58), δ HCC(10)	1546	1481
92	δ HCH(54), δ HCN(10), τ HCCN(19)	1551	1489
93	δ HCH(74), τ HCOC(14)	1562	1499
94	δ HCH(71), τ HCOC(12)	1570	1509
95	δ HCC(41), δ HCH(18), δ CCC(13)	1574	1511
96	δ HCC(27), δ CCC(14)	1577	1515
97	ν CC(33), δ HCC(10), δ CCC(12)	1691	1609
98	ν CC(33), δ HCC(11), δ CCC(11)	1696	1610
99	ν CC(22), δ HCC(13)	1717	1629
100	ν CC(36), δ HCC(10)	1719	1638
101	ν NC(47)	1779	1640
102	ν NC(58)	1802	1655
103	ν OC, ν NC	1864	1787
104	ν NC(12), ν OC(85)	1903	1793
105	ν CH(91)	3030	2982
106	ν CH(93)	3057	3022
107	ν CH(50)	3086	3040
108	ν CH(100)	3114	3074
109	ν CH(93)	3146	3116

110	ν CH(63)	3149	3116
111	ν CH(52)	3188	3138
112	ν CH(54)	3190	3145
113	ν CH(33)	3199	3146
114	ν CH(42)	3216	3168
115	ν CH(66)	3218	3177
116	ν CH(67)	3220	3180
117	ν CH(40)	3226	3183
118	ν CH(57)	3236	3185
119	ν CH(48)	3239	3195
120	ν NH(100)	3771	3656

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

Table 5. The calculated IR frequencies of compound 3 (3-21G)

	Vibration Frequencies	HF	B3LYP
1	τ CNNC(22), τ NCNC(20), τ COCC(20), τ CCOC(15)	14	16
2	τ CCCC(21), τ COCC(43), τ CCOC(20)	17	22
3	δ NCC(15), δ CCO(14), δ CCC(25), δ COC(27), δ NNC(12), τ CNNC(12), τ CCOC(30)	31	31
4	δ NCC(14), δ COC(27), δ CCC(20), δ NNC(11), τ CNNC(12), τ CCOC(30), τCOCC(41)	31	35
5	τ NCNN(11), τ NNCC(38), τ CCNN(10), τ COCC(15), τ CCCC(14)	62	61
6	δ NCC(13), δ CCC(20), δ COC(25), δ NNC(18), τ COCC(51)	67	77
7	τ CCCC(10), τ COCC(52), δ NCC(14), δ COC(14), δ CCO(17), δ NNC(19)	76	78
8	τ CCCC(19), τ COCC(31)	87	94
9	τ NCNC(20), τ NCNN(18), τ CCCC(12), τ CNNC(14)	124	122
10	δ CCO(12), δ CCC(10), δ COC(15)	128	129
11	τ HCCN(74), τ CCCC(15)	159	150
12	τ CCCC(28)	173	169
13	ν CC(10), δ COC(11), τ NCNC(22), τ CNNC(24), τ CCNN(14)	183	181
14	δ CCC(10), δ COC(16), τ NCNC(25), τ CNNC(23, τ CCNN(10)	185	185
15	τ HCOC(40), τ COCC(14), τ OCCC(17), δ CNN(10), δ COC(17), δ CCC(15)	208	208
16	δ CCC(11), δ COC(24), τ HCOC(45), τ CCCC(13), τ OCCC(10)	210	210
17	ν CC(12), δ CCN(27), δ COC(11)	244	242
18	τ CCCC(23), τ CNNC(14)	263	258
19	τ HCOC(19), τ CCCC(24), δ COC(36)	270	268
20	δ CCO(11), δ CCC(12), δ COC(32), τ HCOC(11), τ CCCC(29)	273	271
21	τ NCNC(12), τ CNNC(32), τ CCCC(17)	281	287
22	δ OCO(14), δ COC(19), δ CCN(20)	327	324
23	τ NCNC(10), τ NCNN(33), τ CNNC(31)	348	330
24	τ NCNN(13), τ NNCC(22), τ CCNN(28), δ OCN(12), δ CNN(13), δ CCN(10), δ COC(10)	363	354
25	δ OCO(10), δ OCN(12), δ CCO(10), τ NCNN(14), τ NNCC(23), τ NNCC(23)	370	356
26	δ OCN(11), δ CCC(15)	422	416
27	δ COC(11), δ CCC(30)	439	435
28	τ CCCC(49)	464	447
29	τ CCOC(14), τ HCCC(20), τ CCCC(42), τ OCCC(10)	485	466
30	δ CCC(19)	492	486
31	τ HNNC(88), δ CCC(16), δ COC(18)	557	536
32	τ HCCC(13), τ CCCC(11), τ OCOC(15), τ OCCCC(39)	572	551
33	δ CCC(16), δ COC(21), ν NC(14), ν CC(13), δ OCN(26), δ CCN(10)	578	553
34	ν NC(12), δ OCN(32), δ CCN(11), τ HNNC(92)	579	565
35	ν CC(14), δ CCC(15), δ CNN(22)	581	572
36	δ COC(18), δ CCC(26), δ CCO(15)	594	584
37	δ CCC(10), ν NC(16), ν CC(15), τ CCOC(35), τ CCCC(16)	637	609
38	ν NC(11), ν CC(18), δ CCC(14), τ OCCC(23), τ CCCC(26)	638	629
39	τ NCNC(23), τ CNNC(14), τ CCNN(15), τ NCNN(11)	674	642
40	ν CC(14), δ OCO(10), δ CCC(28)	694	683
41	τ HCCC(31), τ CCCC(19)	727	702
42	τ CCCC(31), ν NN(12), τ HCCC(42)	735	711
43	ν NN(12), δ CCC(10), τ HCCC(42), τ CCCC(18)	737	723
44	ν OC(10), ν NC(12), ν CC(13), δ NCN(36), δ CNN(14), τ ONNC(76), τ CCNN(12)	776	735
45	τ HCCC(13), τ OCOC(55)	784	744
46	ν NC(11), ν CC(12), δ NCN(34), δ CNN(15), δ OCO(27)	792	761
47	ν OC(11), δ OCO(27), τ ONNC(74), τ CCNN(13)	795	771
48	δ NCC(23), δ NNC(11)	821	801
49	τ HCCC(34), τ CCCC(13)	861	809
50	τ HCCC(62), τ OCOC(10)	865	812
51	ν CC(13), ν OC(19)	876	857
52	ν CC(14), ν OC(10), δ CCC(15), δ NCN(31), δ CNN(22)	932	919
53	δ NCN(28), δ CNN(12), τ HCCC(62)	947	920
54	ν CC(15), ν OC(11), τ HCCC(51)	995	925
55	ν CC(15), ν OC(11), τ HCCC(51)	997	926

56	ν CC(28), δ CCC(10), τ HCCC(38)	1002	945
57	ν CC(12), δ CCC(23),τ HCCC(26)	1011	977
58	ν NC(26), τ HCCC(34)	1017	985
59	ν CC(23), ν NC(34), ν OC(16), δ CNN(15)	1032	986
60	τ HCCC(59), τ CCCC(16), τ HCNN(14)	1041	995
61	ν OC(54), τ HCCC(51)	1050	995
62	ν CC(13), δ CCC(39), τ HCCC(62)	1073	997
63	ν OC(36), δ CCC(21), τ HCCC(47)	1077	1012
64	ν NC(11), δ HCC(13), τ HCNN(83), τ HCCN(36)	1090	1047
65	ν NC(11), δ HCH(15), δ HCC(13), τ HCCN(40)	1090	1060
66	ν CC(18), ν OC(13), δ HCC(17), δ CCC(11)	1099	1070
67	ν CC(18), δ HCC(15), δ HCH(22), τ HCCN(59)	1100	1075
68	ν CC(12), δ HCC(19), δ HCH(19), τ HCNN(12), τ HCCN(49)	1100	1087
69	ν CC(17), δ HCC(20), τ HCNN(61), τ HCCN(14)	1108	1091
70	ν NC(27), ν NN(16), ν CC(14)	1142	1116
71	ν CC(30), δ HCH(24), τ HCOC(26)	1155	1120
72	ν OC(13), ν CC(30), δ HCC(11), δ HCH(24), τ HCOC(26)	1156	1137
73	ν CC(25), δ HCC(12), δ HCH(16), τ HCOC(28)	1158	1149
74	ν OC(12), δ HCC(15)	1172	1173
75	δ HCH(13), δ HCC(31), τ HCOC(24)	1184	1183
76	ν CC(12), δ HCC(26)	1218	1189
77	ν CC(14), δ HCC(41)	1219	1202
78	ν CC(18), ν OC(14), δ HCC(13)	1245	1241
79	ν CC(19), ν OC(12), ν NN(16), δ CNN(14)	1264	1257
80	ν CC(26), ν OC(35)	1279	1279
81	ν CC(15), δ HCC(10), ν OC(23)	1295	1294
82	ν CC(14), δ HCC(41)	1334	1309
83	ν NC(12), δ HNN(57), δ HCN(10), δ HCC(30)	1345	1310
84	δ HCC(67), δ HNN(44)	1353	1323
85	δ HNN(17), δ HCN(32), δ HCC(16)	1367	1341
86	ν NC(12), δ HCN(34)	1418	1390
87	ν CC(15), δ HCC(11), δ HCH(97)	1444	1417
88	δ HCH(87), δ HCN(17), δ HCC(10)	1453	1419
89	ν CC(12), δ HCC(15)	1458	1432
90	δ HCC(10), δ HCH(72)	1483	1452
91	δ HCH(66), τ HCCN(25)	1490	1473
92	δ HCC(22), δ HCH(75), τ HCCN(24)	1498	1482
93	δ HCC(47), δ CCC(10)	1508	1483
94	ν CC(19), δ HCC(25), δ HCH(76), τ HCCN(24)	1513	1490
95	δ HCH(76), τ HCOC(11)	1525	1502
96	δ HCH(74), τ HCOC(10)	1534	1514
97	ν NC(44), ν CC(26), δ HCC(10), δ CCC(10)	1598	1535
98	ν NC(41), δ HCH(16), ν CC(41), δ HCC(17)	1600	1550
99	ν CC(25), δ HCC(20), δCCC(10)	1613	1557
100	ν CC(33), δ HCC(14)	1623	1567
101	ν NC(40), ν CC(32), δ CCC(18)	1638	1572
102	ν CC(22), δ HCC(11), ν NC(45)	1671	1585
103	ν OC(84)	1733	1675
104	ν OC(85)	1745	1710
105	ν CH(91)	2907	2923
106	ν CH(92)	2932	2965
107	ν CH(50)	2956	2976
108	ν CH(100)	2983	3013
109	ν CH(92)	3015	3050
110	ν CH(92)	3016	3056
111	ν CH(51)	3061	3076
112	ν CH(52)	3063	3092
113	ν CH(36)	3080	3094
114	ν CH(68)	3090	3120
115	ν CH(67)	3092	3122
116	ν CH(31)	3097	3126
117	ν CH(55)	3108	3134
118	ν CH(48)	3119	3150
119	ν CH(28)	3138	3167
120	ν NH(100)	3540	3515

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

3.3. ^{13}C and ^{1}H NMR Chemical Shift and Regression Analyses

The ^{1}H and ^{13}C NMR chemical shifts of the title compound in the gas phase and in DMSO solvent have been calculated by using the DFT (B3LYP) and Hartree Fock (HF) methods with 6-311G(d) and 3-21G basis sets (Figure **2**). ^{1}H and ^{13}C-

NMR chemical shift values of this compound given in Table **6** and **7**. The calculated ^{1}H and ^{13}C-NMR resonance signals were compared to the calculated values. The results indicated a good correlation R^2 between experimental and theoretical ^{1}H and ^{13}C-NMR chemical shifts ratios. The calculated R^2 were 0.9935/0.9993, 0.9887/0.9924 for ^{13}C-NMR chemical shifts ratios and 0.7757/0.8851, 0.7449/0.7896 for ^{1}H-NMR chemical shifts ratios. The experimental and theoretical between ^{13}C and ^{1}H NMR chemical shifts ratios of the compound (**3)** were observed a linear correlation whereas the calculated R^2 for ^{1}H-NMR chemical shifts ratios are lower than ^{13}C-NMR chemical shifts ratios because N-H proton of 4,5-dihydro-1*H*-1,2,4-triazole-5-one ring was displayed the acidic character.

Table 6. The calculated ^{1}H and ^{13}C NMR isotropic chemical shifts of compound 3 (with respect to TMS, all values in ppm) (6-311G(d)).

	$\delta_{Exp.}$	$\delta_{cal.}$ HF (Vacum)	$\delta_{cal.}$ HF (DMSO)	Different	Different (DMSO)	$\delta_{cal.}$ B3LYP (Vacum)	$\delta_{cal.}$ B3LYP (DMSO)	Different	Different (DMSO)
C1	144.31	148.18	150.14	-3.87	-5.83	138.83	141.20	5.48	3.11
C2	151.15	152.45	153.50	-1.30	-2.35	141.66	142.64	9.49	8.51
C3	151.01	152.37	152.73	-1.36	-1.72	142.17	142.77	8.84	8.24
C4	135.21	140.01	139.53	-4.80	-4.32	126.65	126.43	8.56	8.78
C5	125.94	130.17	129.44	-4.23	-3.50	117.84	118.28	8.10	7.66
C6	152.40	157.69	157.43	-5.29	-5.03	142.81	141.26	9.59	11.14
C7	124.94	125.83	127.17	-0.89	-2.23	118.66	118.85	6.28	6.09
C8	130.03	131.55	133.08	-1.52	-3.05	120.34	121.10	9.69	8.93
C9	120.22	123.51	123.93	-3.29	-3.71	114.18	114.81	6.04	5.41
C10	164.33	166.45	168.01	-2.12	-3.68	151.05	152.85	13.28	11.48
C11	130.25	134.84	133.83	-4.59	-3.58	122.86	121.81	7.39	8.44
C12	122.13	124.76	122.85	-2.63	-0.72	115.20	113.22	6.93	8.91
C13	159.39	165.16	165.39	-5.77	-6.00	149.51	149.42	9.88	9.97
C14	114.31	114.94	117.77	-0.63	-3.46	103.99	106.58	10.32	7.73
C15	130.16	131.60	133.23	-1.44	-3.07	120.80	122.37	9.36	7.79
C16	120.22	124.19	124.31	-3.97	-4.09	113.43	113.70	6.79	6.52
C17	55.43	53.55	54.11	1.88	1.32	35.28	35.76	20.15	19.67
C18	11.08	12.18	12.15	-1.10	-1.07	0.51	0.57	10.57	10.51
H19	11.87	6.23	6.72	5.64	5.15	5.42	5.86	6.45	6.01
H20	9.79	9.59	9.53	0.20	0.26	8.98	8.96	0.81	0.83
H21	7.61	7.11	7.14	0.50	0.47	6.64	6.85	0.97	0.76
H22	7.47	6.79	7.04	0.68	0.43	6.65	6.84	0.82	0.63
H23	7.77	7.08	7.35	0.69	0.42	6.85	7.11	0.92	0.66
H24	7.78	7.74	7.85	0.04	-0.07	7.56	7.70	0.22	0.08
H25	7.75	7.53	7.35	0.22	0.40	7.44	7.24	0.31	0.51
H26	7.34	6.34	6.73	1.00	0.61	6.05	6.47	1.29	0.87
H27	7.55	7.04	7.30	0.51	0.25	6.79	7.09	0.76	0.46
H28	7.63	7.45	7.55	0.18	0.08	7.19	7.32	0.44	0.31
H29	3.87	3.69	3.77	0.18	0.10	3.07	2.72	0.80	1.15
H30	3.87	3.20	3.38	0.67	0.49	2.51	3.14	1.36	0.73
H31	3.87	3.20	3.38	0.67	0.49	2.51	2.71	1.36	1.16
H32	2.29	1.98	2.10	0.31	0.19	1.50	1.65	0.79	0.64
H33	2.29	1.98	2.09	0.31	0.20	1.50	1.64	0.79	0.65
H34	2.29	1.70	1.76	0.59	0.53	1.30	1.35	0.99	0.94

Table 7. The calculated ^{1}H and ^{13}C NMR isotropic chemical shifts of the compound 3 (with respect to TMS, all values in ppm) (3-21G).

	$\delta_{Exp.}$	$\delta_{cal.}$ HF (Vacum)	$\delta_{cal.}$ HF (DMSO)	Different	Different (DMSO)	$\delta_{cal.}$ B3LYP (Vacum)	$\delta_{cal.}$ B3LYP (DMSO)	Different	Different (DMSO)
C1	144.31	113.63	114.92	30.68	29.39	111.44	113.33	32.87	30.98
C2	151.15	115.48	115.98	35.67	35.17	114.77	115.31	36.38	35.84
C3	151.01	117.40	117.48	33.61	33.53	115.29	115.56	35.72	35.45
C4	135.21	100.74	100.09	34.47	35.12	93.44	92.69	41.77	42.52
C5	125.94	90.32	89.58	35.62	36.36	84.10	83.37	41.84	42.57
C6	152.40	120.82	120.82	31.58	31.58	111.03	110.91	41.37	41.49
C7	124.94	87.72	88.74	37.22	36.20	83.48	84.47	41.46	40.47
C8	130.03	93.45	94.74	36.58	35.29	88.71	90.01	41.32	40.02
C9	120.22	87.29	87.51	32.93	32.71	82.97	83.35	37.25	36.87
C10	164.33	133.14	133.82	31.19	30.51	128.36	129.28	35.97	35.05
C11	130.25	96.56	95.72	33.69	34.53	90.29	89.36	39.96	40.89
C12	122.13	88.41	86.90	33.72	35.23	85.48	83.67	36.65	38.46
C13	159.39	124.15	124.27	35.24	35.12	115.68	115.39	43.71	44.00
C14	114.31	82.57	85.08	31.74	29.23	78.11	80.32	36.20	33.99
C15	130.16	94.30	95.63	35.86	34.53	88.90	90.43	41.26	39.73
C16	120.22	88.14	88.15	32.08	32.07	83.97	84.42	36.25	35.80

C17	55.43	33.37	32.02	22.06	23.41	15.55	16.17	39.88	39.26
C18	11.08	-6.57	-6.80	17.65	17.88	-17.57	-17.70	28.65	28.78
H19	11.87	5.46	5.98	6.41	5.89	4.51	4.95	7.36	6.92
H20	9.79	9.38	9.30	0.41	0.49	8.78	8.69	1.01	1.10
H21	7.61	7.75	7.64	-0.14	-0.03	7.35	7.22	0.26	0.39
H22	7.47	5.73	6.03	1.74	1.44	5.69	6.03	1.78	1.44
H23	7.77	6.05	6.39	1.72	1.38	5.86	6.25	1.91	1.52
H24	7.78	6.87	6.99	0.91	0.79	6.77	6.94	1.01	0.84
H25	7.75	6.69	6.51	1.06	1.24	6.81	6.56	0.94	1.19
H26	7.34	5.22	5.67	2.12	1.67	4.93	5.44	2.41	1.90
H27	7.55	5.99	6.31	1.56	1.24	5.74	6.13	1.81	1.42
H28	7.63	6.64	6.78	0.99	0.85	6.49	6.69	1.14	0.94
H29	3.87	3.37	3.51	0.50	0.36	2.72	2.81	1.15	1.06
H30	3.87	2.72	2.96	1.15	0.91	1.73	2.03	2.14	1.84
H31	3.87	2.72	2.96	1.15	0.91	1.73	2.03	2.14	1.84
H32	2.29	1.50	1.63	0.79	0.66	0.80	0.96	1.49	1.33
H33	2.29	1.50	1.63	0.79	0.66	0.80	0.96	1.49	1.33
H34	2.29	0.97	1.07	1.32	1.22	0.43	0.53	1.86	1.76

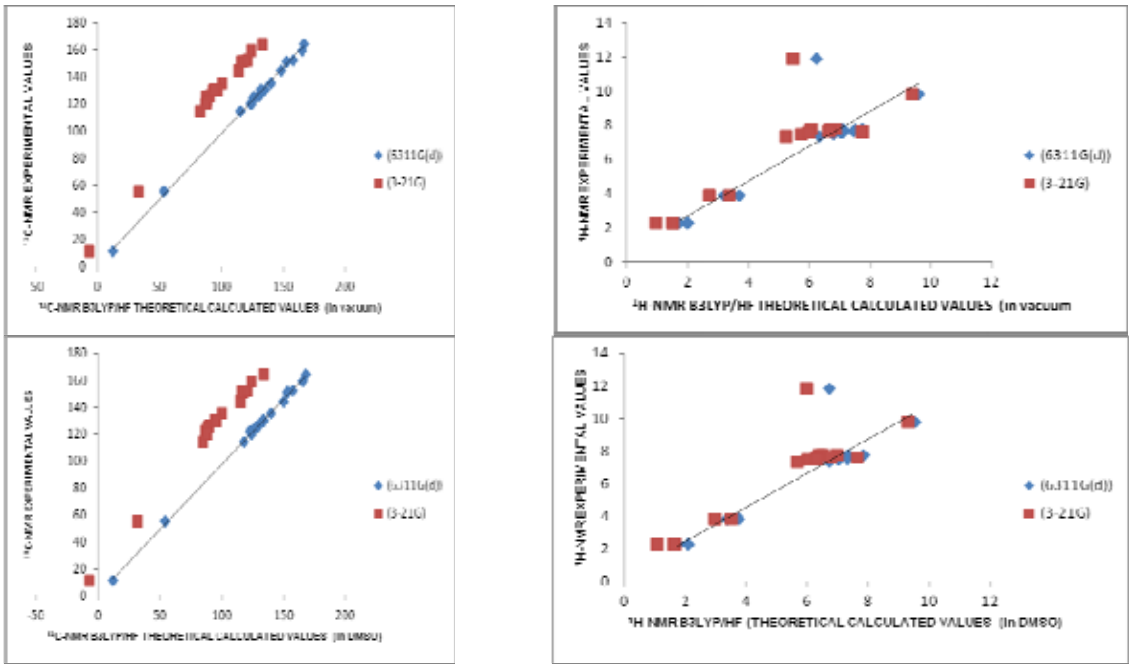
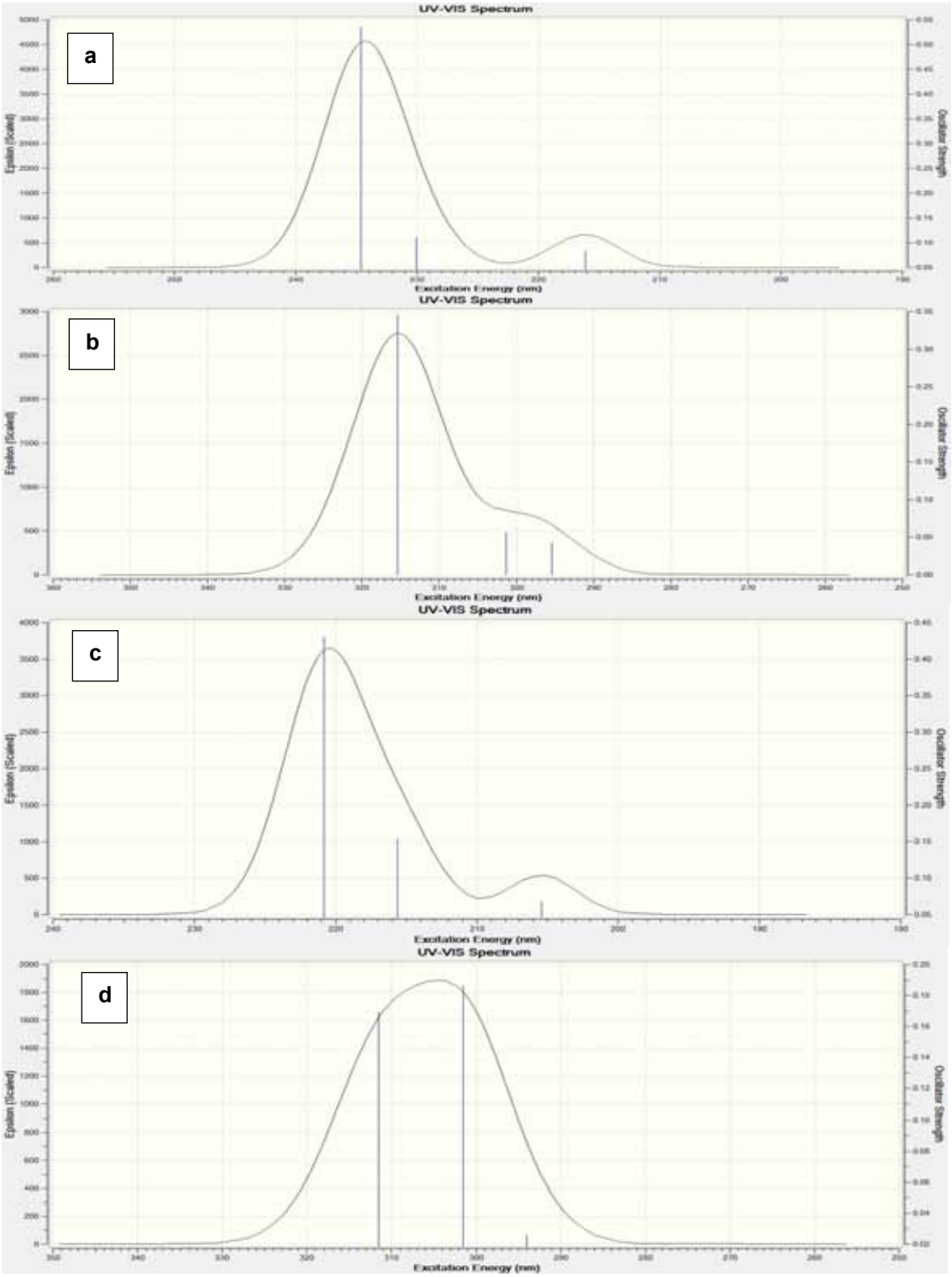


Figure 2. Comparison of experimental and theoretical ^{13}C- and ^{1}H-NMR chemical shifts values of compound 3 with 6-311G(d)(a)/B3LYP, HF, B3LYP(DMSO) ve HF(DMSO) ve 3-21G(b)/B3LYP, HF, B3LYP(DMSO) ve HF(DMSO) methods.

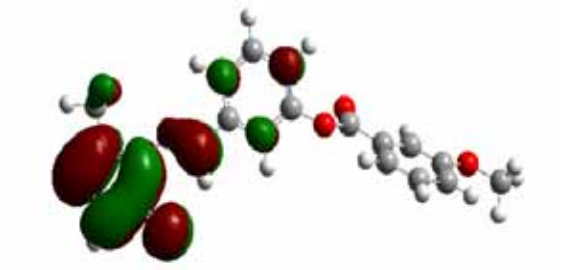
3.4. UV-vis. Spectroscopy, HOMO-LUMO Analyses, Thermodynamic Properties and Dipole Moments

The excitation energies, oscillator strengths (f) and absorption wavelengths (λ) of UV–Vis electron absorption spectroscopy of the title molecule have been calculated in ethanol solvent by using B3LYP/HF methods with 6-311G(d) and 3-21G basis sets and presented in Figure **3** [27]. The absorption wavelengths exhibited at 296, 242 and 220 nm have been assigned to n→π*, π→π* and n→σ* transitions. The UV-vis. wavelengths, excitation energies, oscillator strengths of the compound (**3**) are calculated by using the TD-DFT method in the ethanol solvent. The calculated values (wavelength/excitation energy/oscillator strength) in ethanol of the compound (**3**) are given in Figure **3**. Furthermore, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have been simulated for this compound have been determined. The HOMO and LUMO energies and their 3D plots of this compound are shown in Figure **4**. The molecular electrostatic potential (MEP) of this compound have been performed both two methods (Figure **5**). The quantum molecular descriptors for ionization potential, chemical reactivity, softness, chemical hardness are found by using HOMO-LUMO energy band gap [28].

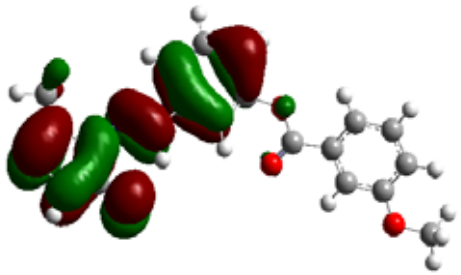


Experimental (nm)	λ (nm) HF/B3LYP 6-311G(d)	λ (nm) HF/B3LYP 3-21G	Excitation Energy (eV) HF/B3LYP 6-311G(d)	Excitation Energy (eV) HF/B3LYP 3-21G	*f* (osillatör strengths) HF/B3LYP 6-311G(d)	*f* (osillatör strengths) HF/B3LYP 3-21G
296.00	234.62/315.39	220.82/311.51	5.2845/3.9311	5.6148/3.9802	0.5356/0.3449	0.4306/0.1692
242.00	230.06/301.32	215.61/301.50	5.3893/4.1147	5.7503/4.1122	0.1096/0.0559	0.1543/0.1862
220.00	216.12/295.38	205.40/294.03	5.7369/4.1975	6.0363/4.2166	0.0836/0.0427	0.0682/0.0260

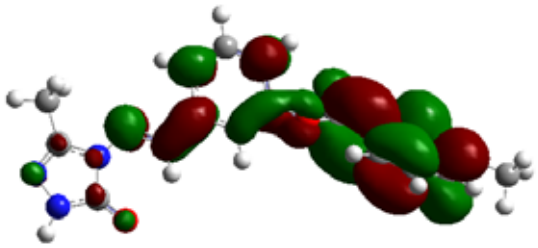
Figure 3. The calculated absorption wavelength (λ), excitation energies and oscillator strengths (*f*) and UV-vis spectrums (B3LYP/HF 6-311G(d), 3-21G) of the compound 3



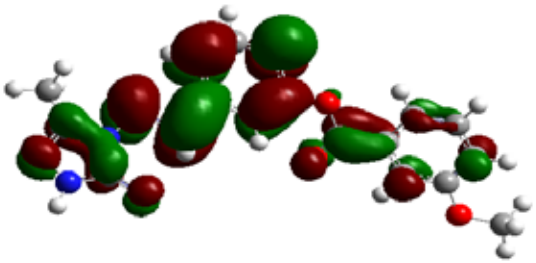
E_{HOMO}(HF (a)) : -8,75539 eV



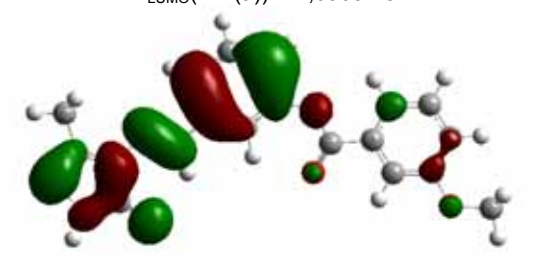
E_{HOMO}(B3LYP (a)) : -6,17698 eV



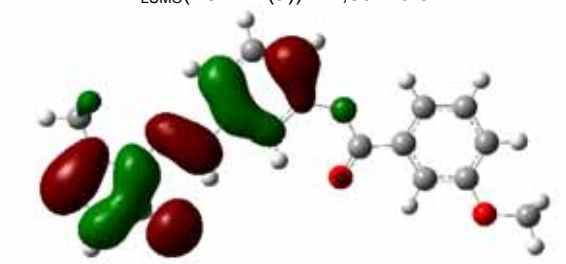
E_{LUMO}(HF (a)) : -2,09092 eV



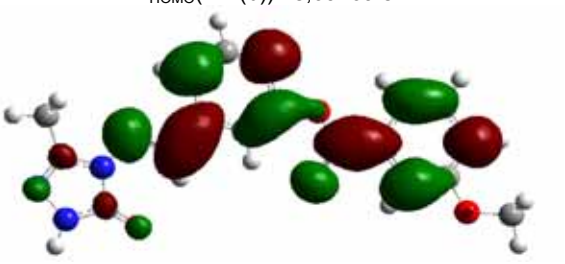
E_{LUMO}(B3LYP (a)) : -1,80710 eV



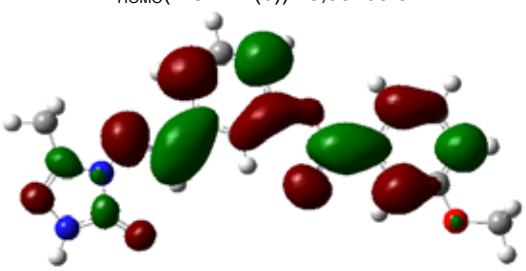
E_{HOMO}(HF (b)) : 8,69169 eV



E_{HOMO}(B3LYP (b)) : 5,93208 eV



E_{LUMO}(HF (b)) : 2,17746 eV



E_{LUMO}(B3LYP (b)) : 1, 57390 eV

Figure 4. 3D plots of HOMO and LUMO energies of compound 3 at the HF/B3LYP 6-311G(d) and 3-21G levels

Total energy values, dipole moments, thermodynamic properties and electronic structure values of the above mentioned compound were calculated by using B3LYP/HF 6-311G(d) and 3-21G methods and given in Table **8, 9** and **10**. The values of heat generation are not known for most organic compounds. The difficulty of studying heat effects increases the importance of quantum chemical calculations. From the thermodynamic point of view, it can be decided whether or not there is a chemical reaction. Thermodynamic quantum chemical parameters are widely used studying the reaction mechanisms of organic compounds. HOMO energy is known as the ability of the molecule to give electrons (π_{donor}), the ability of the LUMO energy molecule to accept electrons ($\pi_{Acceptor}$). Using HOMO and LUMO energy values for title molecule have been calculated the following parameters: Ionization potential (*I*), Electron affinity (*A*), Electronegativity(χ), hardness (η), softness (*S*) are given in Table **11**.

Table 8. The calculated dipole moment of compound 3 (6-311G(d) HF/B3LYP, 3-21G HF/B3LYP)

Dipole Moment	HF 6-311G(d)	HF 3-21G	B3LYP 6-311G(d)	B3LYP 3-21G
μ_x	1.9302	1.5181	1.4471	0.9850
μ_y	5.8613	5.4600	4.0492	3.3631
μ_z	1.7752	1.8080	1.3723	1.2629
μ_{Toplam}	6.4212	5.9486	4.5136	3.7250

Table 9. The calculated total energy of 3-methyl-4-[3-(3-methoxybenzoxy)-benzylidenamino]-4,5-dihydro-1H-1,2,4-triazol-5-one molecule (6-311G(d) HF/B3LYP, 3-21G HF/B3LYP)

Energy	HF 6-311G(d)	HF 3-21G	B3LYP 6-311G(d)	B3LYP 3-21G

(a.u.)	-1208.419	-1201.421	-1208.419	-1215.710

Table 10. The calculated thermodynamic properties of 3-methyl-4-[3-(3-methoxybenzoxy)-benzylidenamino]-4,5-dihydro-1H-1,2,4-triazol-5-one molecule (6-311G(d) HF/B3LYP, 3-21G HF/B3LYP)

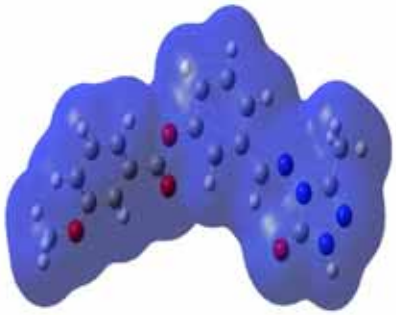
Parameters	Value 6-311G(d)	Value 3-21G
Termal energy, E (cal/mol K)	**Dft/Hf**	**Dft/Hf**
Elektronic	**0.000/0.000**	**0.000/0.000**
Transnational	**0.889/0.889**	**0.889/0.889**
Rotational	**0.889/0.889**	**0.889/0.889**
Vibrational	**214.199/228.881**	**215.431/230.308**
Total	**215.977/230.659**	**217.208/232.085**
Zero-Point Vibrational energy (kcal/mol)	**Dft/Hf** **201.50569/216.99618**	**Dft/Hf** **203.06408/218.81690**
Sum of electronic and zero-point Energy (Hartree/Particle)	**Dft/Hf** **-1215.389135/-1208.073597**	**Dft/Hf** **-1208.404572/-1201.072346**
Sum of electronic and thermal Energies (Hartree/Particle)	**Dft/Hf** **-1215.366074/-1208.051824**	**Dft/Hf** **-1208.382032/-1201.051202**
Sum of electronic and thermal Enthalpies (Hartree/Particle)	**Dft/Hf** **-1215.365130/-1208.050880**	**Dft/Hf** **-1208.381087/-1201.050257**
Sum of electronic and thermal Free Energies (Hartree/Particle)	**Dft/Hf** **-1215.445778/-1208.129698**	**Dft/Hf** **-1208.459254/-1201.126235**
Rotational constants (GHz)		
A	**Dft/Hf**	**Dft/Hf**
B	**0.4977683/0.54730**	**0.4977683/0.4977683**
C	**0.0596771/0.05970**	**0.0596771/0.059677**
	0.0538654/0.05623	**0.0538654/0.0538654**

Table 11. Electronic structure parameters calculated for compound 3

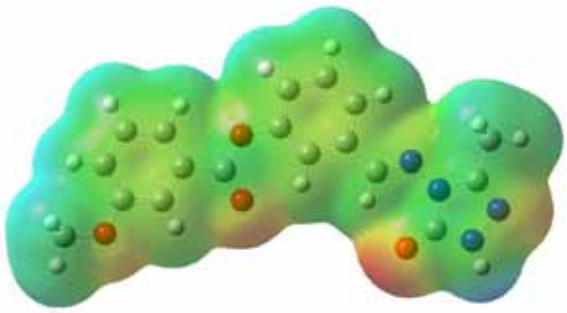
	HF/B3LYP 6-311G(d)	HF/B3LYP 3-21G
E_{HOMO} (eV)	-8,77539/-6,17698	8,69169/5,93208
E_{LUMO} (eV)	-2,09092/-1,80710	2,17746/1,57390
$\Delta E = E_{LUMO}-E_{HOMO}$ (eV)	6,68447/4,36988	-6,51423/-4,35818
I (eV)	8,77539/6,17698	-8,69169/-5,93208
A(eV)	2,09092/1,80710	-2,17746/-1,57390
χ (eV)	5,433155/3,99204	-5,434575/-3,75299
η (eV)	3,342235/2,18494	-3,257115/-2,17909
S (eV^{-1})	0,14960/2,22883	-0,15351/-0,22945

The MEP is related to the electronic density and very useful descriptor for determining sites for nucleophilic and electrophilic reactions**.** The MEP at B3LYP/HF 6-311G(d) and 3-21G methods optimized geometry was calculated and shown in Figure **5**. As seen from Figure **5** the most positive region is located on the H atoms whereas the most negative region is located on O atoms within the molecule which can be considered as possible site electrophilic attack.

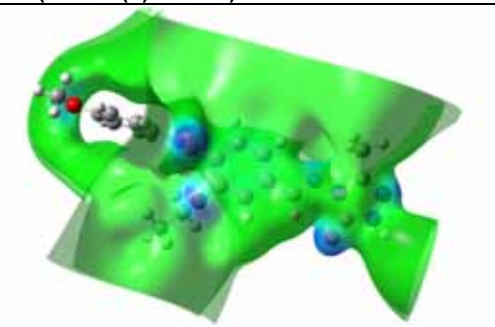
TOTAL DENSITY (6-311G(d)/B3LYP)



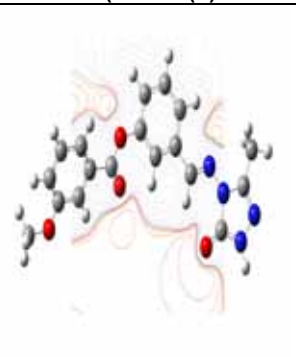
MEP (6-311G(d)/B3LYP)



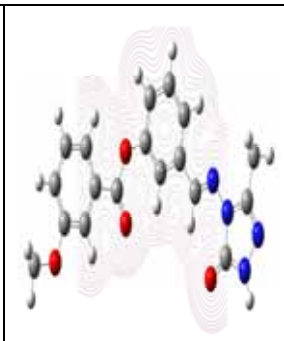
ESP(6-311G(d)/B3LYP)



CONTOUR (6-311G(d)/B3LYP)

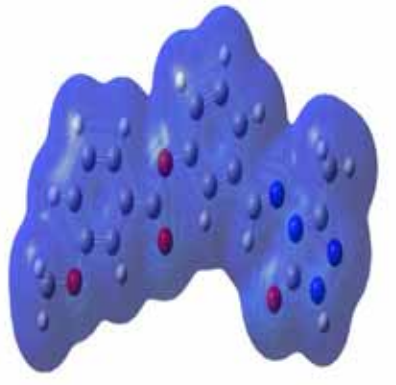


Electrostatic Potential (6-311G(d))

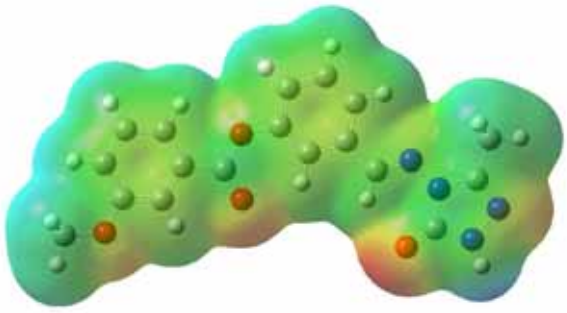


Electron Density (6-311G(d))

TOTAL DENSITY (3-21G/B3LYP)

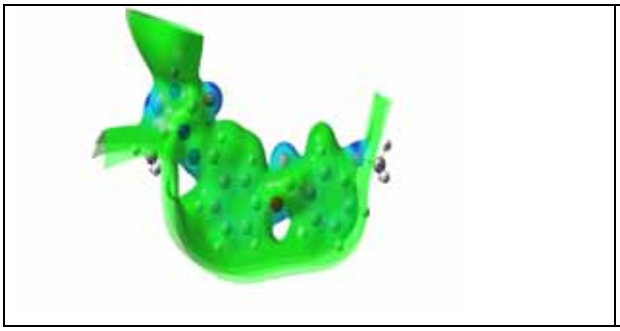


MEP (3-21G/B3LYP)



ESP (3-21G/B3LYP)

CONTOUR (3-21G/B3LYP)



Electrostatic Potential (3-21G/B3LYP)	**Electron Density (3-21G/B3LYP)**

Figure 5. The calculated molecular surfaces of the compound 3

4. CONCLUSION

The calculated geometric parameters (bond lengths (Å) and bond angles (˚) of the molecule suggests a satisfactory agreement. TD-DFT calculations in ethanol solvent lead to a close agreement with experimental absorption spectra. We predicted the most reactive site both nucleophilic and electrophilic attack by means of the MEP map. The maximum negative region is localized over the oxygen and nitrogen atom of triazole ring and the maximum positive region is localized on NH group, indicating a possible site for nucleophilic attack. There is a good agreement between calculated vibrational frequencies and experimental values. The calculated chemical shifts were compared with experimental values in DMSO and gas phase showing a very good agreement. The HOMO-LUMO gap energies are very important in determining the chemical reactivity of the molecule (Table **11**). As a result, the performance of the DFT (B3LYP) methods with 6-311G(d) basis set for the compound (**3**) is quite well.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

AUTHORS' CONTRIBUTIONS

This work was carried out in collaboration together with three authors. Author HY designed the study, managed the literature searches and interpreted all spectroscopic and experimental results. Author HM performed all theoretical studies. Author MB performed wrote the protocol. the first draft of the manuscript and interpreted the theoretical results of the study. Three authors read and approved the final manuscript.

References

[1] Sun N.B., Tong J.Y., Wu H.K. Chin. J. Org. Chem. 2013; 33, 101-105.

[2] Alaraji Y.H., Shneine J.K., Ahmed A.N.A. J. Sci. 2015; 5, 293-299.

[3] Bulcet V.N., Duran C., Bull. Chem. Soc. Ethiop. 2010; 24, 457-460.

[4] Jin R.Y., Sun K.H., Liu Y.F., Long W., Lu W.T., Ma H.X. J. Mol. Struct. 2014;1062, 13-20.

[5] Tanak H., Agar A.A., Büyükgüngör O. Spectrochim. Acta Part A 2014; 118, 672-682.

[6] Gündüzalp A.B., Ozsen I., Alyar H., Alyar S., Ozbek N., J. Mol. Struct. 2016;1120, 259-266.

[7] Harit T., Bellaouchi R., Asehraou A., Rahal M., Bouabdallah I., Malek F. J. Mol. Struct. 2017; 1133, 74-79.

[8] Singh R.K., Singh A.K., Siddiqui S., Arshad M., Jafri A. J. Mol. Struct. 2017;1135 82-97.

[9] Gökce H., Öztürk N., Kazıcı M., Yörür Göreci Ç., Günes S. J. Mol. Struct. 2017;1136, 288-302.

[10] Kanaani A., Ajloo D., Grivani G., Ghavami A., Vakili M. J. Mol. Struct. 2016; 1112 87-96.

[11] Gokce H, Akyildirim O, Bahceli S, Yuksek H, Gursoy Kol O. J. Mol. Struct. 2014; 1056-1057, 273–284.

[12] Yüksek H, Çakmak İ, Sadi S, Alkan M, Baykara H. Int. J. Mol. Sci. 2005; 6 (6-8): 219-229.

[13] Medetalibeyoğlu H, Yüksek H. Bulg. Chem. Com. 2017; 49(1), 78–89.

[14] Manap S, Yüksek H, Medetalibeyoğlu H.. International Journal of Thales Natural Sciences. 2016; 1(3), 37-55.

[15] Yüksek H, Kotan G, Medetalibeyoğlu H, Gürbüz A, Alkan M. Celal Bayar Üniversitesi Fen Bilimleri Dergisi. 2017; 13(1),193-204.

[16] Medetalibeyoğlu H, Yüksek H. International Conference on Research in Education and Science (ACRES). 2016;1505-1513.

[17] Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Mennucci B., Petersson G.A., Nakatsuji H., Caricato M., Li X., Hratchian H.P., Izmaylov A.F., Bloino J., Zheng G., Sonnenberg J.L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J.A., Jr.Vreven T., Peralta J.E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin N., Staroverov V.N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Rega N., Millam J.M., Klene M., Knox J.E., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Martin L.R., Morokuma K., Zakrzewski V.G., Voth G.A., Salvador P., Dannenberg J.J., Dapprich S.,. Daniels A.D., Farkas O., Foresman J.B., Ortiz J.V., Cioslowski J., Fox D.J. 2009; Gaussian Inc. Wallingford, CT.

[18] Frisch A., Nielson A.B., Holder A.J. 2003; Gaussvıew User Manual, Gaussian Inc. Wallingford, CT.

[19] Wolinski K., Hinton J.F., Pulay P. J. Am. Chem. Soc. 1990; 112, 8251-8260.

[20] Jamróz M.H. Vibrational Energy Distribution Analysis: VEDA 4 program. 2004; Warsaw.

[21] Stratmann R.E., Austria S.G.E., M.J. Frisch J. Chem. Phys. 1998; 109, 8218–8224.

[22] Bauernschmitt R., Ahlrichs R. Chem. Phys. Lett. 1996; 256, 454–464

[23] Casida M.E., Jamorski C.,. Casida K.C, Salahub D.R. J. Chem. Phys. 1998; 108, 4439–4449.

[24] Ocak N., Çoruh U., Kahveci B., Şaşmaz S., Agar E., Vazquez-Lopez E.M., Erdönmez A., Acta Cryst. E59. 2003, 750-752.

[25] Ustabas R.¸ , Çoruh U., Sancak K., Ünver Y., Vazquez-Lopez E.M. Acta Cryst. E63. 2007; 2982-2983.

[26] Mulliken R.S. J. Chem Phys. 1955; 23 1833–1840.

[27] Vlcek Jr. A., Zalis S. Coordination Chemistry Reviews. 2007; 251 258–287.

[28] Alpaslan Y.B., Gökce H., Alpaslan G., Macit M., J. Mol. Struct. 2015; 1097, 171-180.

[29] Gümüs H.P., Tamer Ö., Avcı D., Atalay Y., Spectrochim. Acta Part A. 2014; 132 183-190.

[30] Ikizler A.A., Un R. Chim. Acta Turc. 1979, 7, 269, [Chem. Abstr., 94, 15645d]. 1991.