



The Investigation of Novel 3-(*p*-chlorobenzyl)-4-(2-benzyloxy-3-ethoxybenzylideneamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one With Gaussian 09W Program

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Abstract In this study, 3-(*p*-chlorobenzyl)-4-(2-benzyloxy-3-ethoxybenzylideneamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one(**1**) has been optimized using B3LYP/631G(d) and HF/631G(d) basis set. ¹H-NMR and ¹³C-NMR isotropic shift values, IR absorption frequencies, UV-Vis values, bond lengths, dipole moments, Mulliken charges, HOMO-LUMO energies and total energy of the molecule with both methods were calculated theoretically by using the program package Gaussian G09W. In addition, IR, ¹H-NMR, ¹³C-NMR, UV-Vis theoretical spectral data were compared with specific experimental data.

Keywords 1,2,4-Triazol-5-one, B3LYP/631G(d), HF/631G(d), HOMO LUMO energy, Gaussian G09W

Introduction

Quantum chemical calculation methods have widely been used to theoretically predict the structural, spectroscopic, electronic and thermodynamic properties of molecular systems. The quantum chemical calculation methods ensure support for experimental structural and spectroscopic studies [1-6]. Many theoretical methods are available like *ab-initio*, semi-empirical, DFT, HF method etc, to predict such drug activity without synthesis. Amongst these, the DFT method has commonly used to determine molecular effect of halogen group on pharmacological activity [7]. In this study, having a large number of theory and basis set options, including molecular mechanics, semi-empirical and *ab-initio* methods, Gaussian 09W [8] package is used. Hartree-Fock (HF) and Density Functional Theory (DFT/B3LYP) methods are used for the determination of the structure of molecules and the investigation of spectroscopy, electronics, nonlinear optical properties. Experimental data obtained from the literature [9]. The compound was analyzed with IR, ¹H-NMR and ¹³C-NMR, UV-vis spectral data and experimental spectra were drawn. 3-(*p*-chlorobenzyl)-4-(2-benzyloxy-3-ethoxybenzylideneamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**1**) has been optimized using B3LYP/631G(d) and HF/631G(d) basis set [8,10]. ¹H-NMR and ¹³C-NMR isotropic shift values were calculated by the method of Gauge-Including Atomic Orbital (GIAO) using the program package Gaussian G09 [8]. Experimental [9] and theoretical values were inserted into the graphic according to equation of $\delta_{exp} = a + b \cdot \delta_{calc}$. The standard error values were found via SigmaPlot program with regression coefficient of *a* and *b* constants. IR absorption frequencies of analysed molecule were calculated by two methods. The veda4f program, was used in defining IR data, which were calculated theoretically [11]. Furthermore, molecule's experimental [9] and theoretical UV-Vis values, theoretical bond lengths, dipole moments, Mulliken charges, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and total energy of the molecule for both methods were calculated.



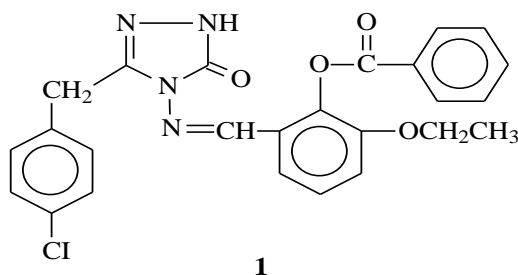


Figure 1: Molecule 1

Materials and Methods

Experimental

Experimental data of 3-(*p*-chlorobenzyl)-4-(2-benzyloxy-3-ethoxybenzylideneamino)-4,5-dihydro-1*H*-1,2,4-triazole-5-one (1) was obtained from the literature [9]. Melting points were checked on WRS-2A Microprocessor Melting-Point Apparatus. The IR spectra were measured on Alpha-P Bruker FT-IR Spectrometer. ¹H- and ¹³C-NMR spectra were recorded in deuterated dimethyl sulfoxide with TMS as internal standard on a Bruker 400 MHz spectrometer, respectively. UV absorption spectra were measured in 10-mm quartz cells between 200 and 400 nm using a PG Instruments Ltd T80 UV-vis Spectrometer. Extinction coefficients (ϵ) are expressed in L·mol⁻¹·cm⁻¹. Yield 89%; m.p: 183 °C; IR (KBr, cm⁻¹): 3170(NH), 1750 and 1707(C=O), 1593(C=N), 1258(COO), 822(1,4-disubstituted benzenoid ring), 776 and 699(monosubstituted benzenoid ring) cm⁻¹. ¹H-NMR (400 MHz, DMSO) δ (ppm): 1.28 (t, 3H, CH₃; $J=6.92$ Hz), 3.75 (s, 1H, CH₃), 3.85 (s, 1H, CH₂), 4.06 (q, 3H, OCH₂; $J=6.96$ Hz), 6.82 (d, 2H, ArH; $J=8.60$ Hz), 7.08 (d, 1H, ArH, $J=8,12$ Hz), 7.18 (d, 2H, ArH, $J=8,56$ Hz), 7.24-7.29 (m, 1H, ArH), 7.45-7.58 (m, 4H, ArH), 8.20-8.23 (m, 2H, ArH), 9.93 (s, 1H, N=CH), 10.13 (s, 1H, N=CH). ¹³C-NMR: δ 64.84(OCH₂CH₃), 55.28(OCH₃), 30.84(CH₂Ph), 14.70(OCH₂CH₃), 158.70; 151.30; 140.52; 133.70; 130.37(2C); 130.16(2C); 129.02; 128.70(2C); 127.69; 126.90; 126.65; 118.59; 116.03; 114.08(2C)(Ar-C), 147.80 (Triazole C₃), 150.23 (N=CH), 151.97(Triazole C₅), 164.57(C=O).

Methods

The quantum chemical calculations were carried out with density functional theory (DFT) and Hartree-Fock (HF) methods using 6-31G (d) basis set at the Gaussian 09W program package on a computing system [8]. Firstly, the compound 1 was optimized by using the B3LYP/6-31G (d) and HF/6-31G (d) basis sets [8,10]. Thus, the most stable geometrical conformer of compound 1 was obtained. Then, ¹H-NMR and ¹³C-NMR isotropic shift values were calculated with method of GIAO [8]. The veda4f program was used in defining IR data [11]. Theoretically calculated IR data are multiplied with appropriate adjustment factors [12]. Scale dft and hf values obtained according to HF and DFT method are formed using theoretical infrared spectrum. Otherwise, bond lengths, the HOMO-LUMO energy, electronegativity and Mulliken charges of compound were calculated theoretically on the computer.

Theoretical Calculations

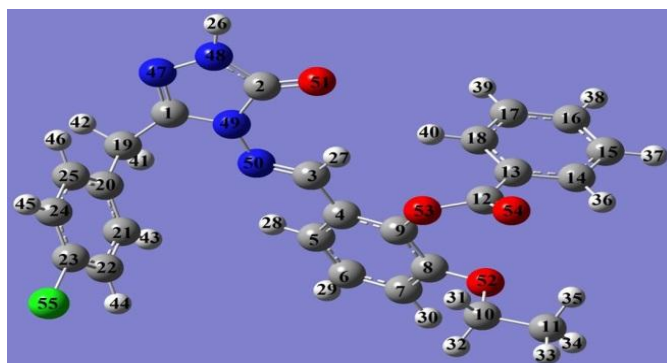


Figure 2: The optimized molecular structure of the molecule (1) with DFT/B3LYP/6-31G(d) level



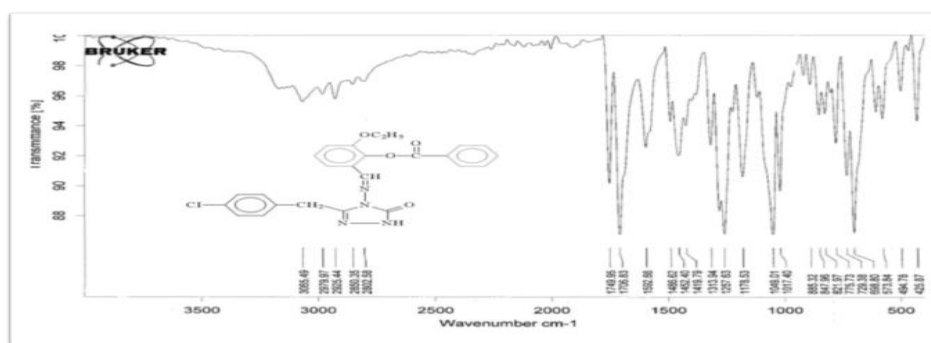
Table 1: Data calculated ^{13}C and ^1H -NMR DMSO(B3LYP/ HF 6-31G(d) isotropic chemical shifts of the molecule (δ/ppm)

No	DFT	HF	No	DFT	HF
C1	152.47	147.26	C24	132.82	125.87
C2	151.91	145.60	C25	134.14	127.40
C3	153.50	146.72	H26	7.53	6.54
C4	130.39	123.34	H27	10.32	9.56
C5	126.40	117.03	H28	8.50	8.21
C6	129.66	123.99	H29	7.61	7.64
C7	132.70	119.89	H30	7.47	7.47
C8	153.49	145.69	H31	4.63	3.92
C9	154.96	137.27	H32	4.13	3.23
C10	79.53	57.72	H33	1.47	1.05
C11	25.65	14.58	H34	1.84	0.72
C12	171.54	157.30	H35	2.01	0.85
C13	134.17	122.09	H36	8.39	8.51
C14	137.06	130.97	H37	7.91	7.62
C15	132.78	123.22	H38	7.94	7.93
C16	137.36	133.75	H39	7.63	7.54
C17	131.75	123.04	H40	7.81	8.39
C18	133.77	129.98	H41	4.41	3.70
C19	42.84	27.55	H42	4.17	3.46
C20	139.64	131.46	H43	7.80	7.64
C21	135.23	127.84	H44	7.43	7.18
C22	132.44	125.49	H45	7.56	7.31
C23	144.39	131.42	H46	7.86	7.61

Theoretically IR values were calculation veda4f programme and scala values were obtain. Theoretically calculated IR data are multiplied with appropriate adjustment factors respectively 0.9613, 0.8929 for DFT/631G(d) and HF/631G(d) basis sets. The negative frequency in the data was not found. This result, structure of compound were shown stable. IR spectrums were drawn with obtained values according to HF and DFT method. Theoretically IR values were compare with experimentally IR values. The result of this compare were found corresponding with each other of values. Experimentally carbonyl peak ($\text{C}=\text{O}$) in $1707, 1750 \text{ cm}^{-1}$ and theoretically ($\text{C}=\text{O}$) peak in 1768 cm^{-1} were observed.

Table 2: The calculated frequencies values of the molecule 1

Vibration Types	Experimental	Skalah dft	Skalah hf
τ HCCC(16)	699	685	718
τ ONNC(12)	776	790	804
τ HCCC(97)	822	807	830
τ HCOC(10)	1258	1261	1257
ν NC(45)	1593	1607	1711
ν OC(47)	1707, 1750	1768	1802
ν NH(100)	3170	3541	3543



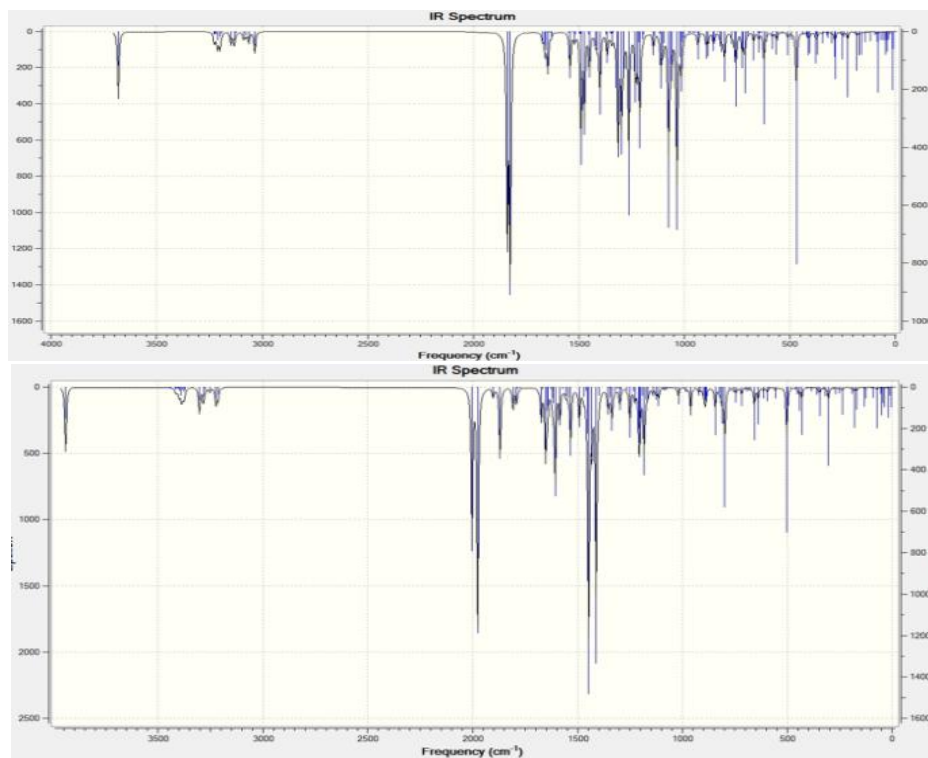


Figure 3: IR spectra experimental and simulated with DFT/B3LYP/6-31G(d) and HF/B3LYP/6-31G(d) levels of the molecule 1

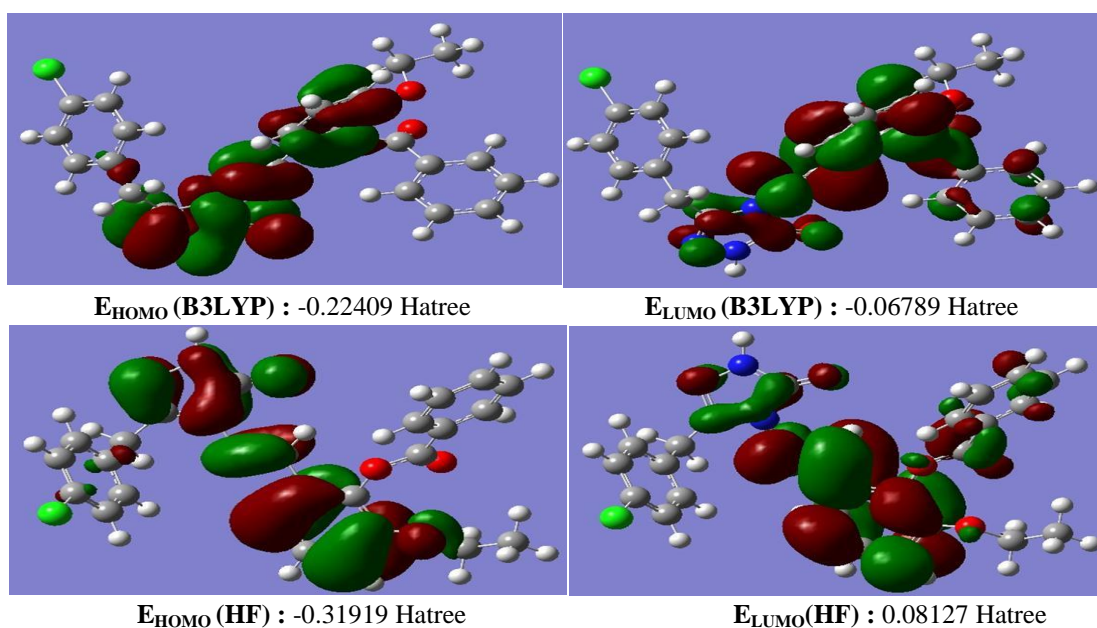


Figure 4: HOMO-LUMO energy calculated with DFT/B3LYP/6-31G(d) and HF/B3LYP/6-31G(d) levels of the molecule 1

Table 3: The calculated total energy values of the molecule 1

Enerji (a.u.)	B3LYP	HF
	-1945.3736	-1935.6520



Table 4. The calculated dipole moments values of the molecule

	μ_x	μ_y	μ_z	μ_{Toplam}
Dft	0.2742	4.1161	1.8357	4.5152
Hf	0.2706	0.6582	5.7821	5.8257

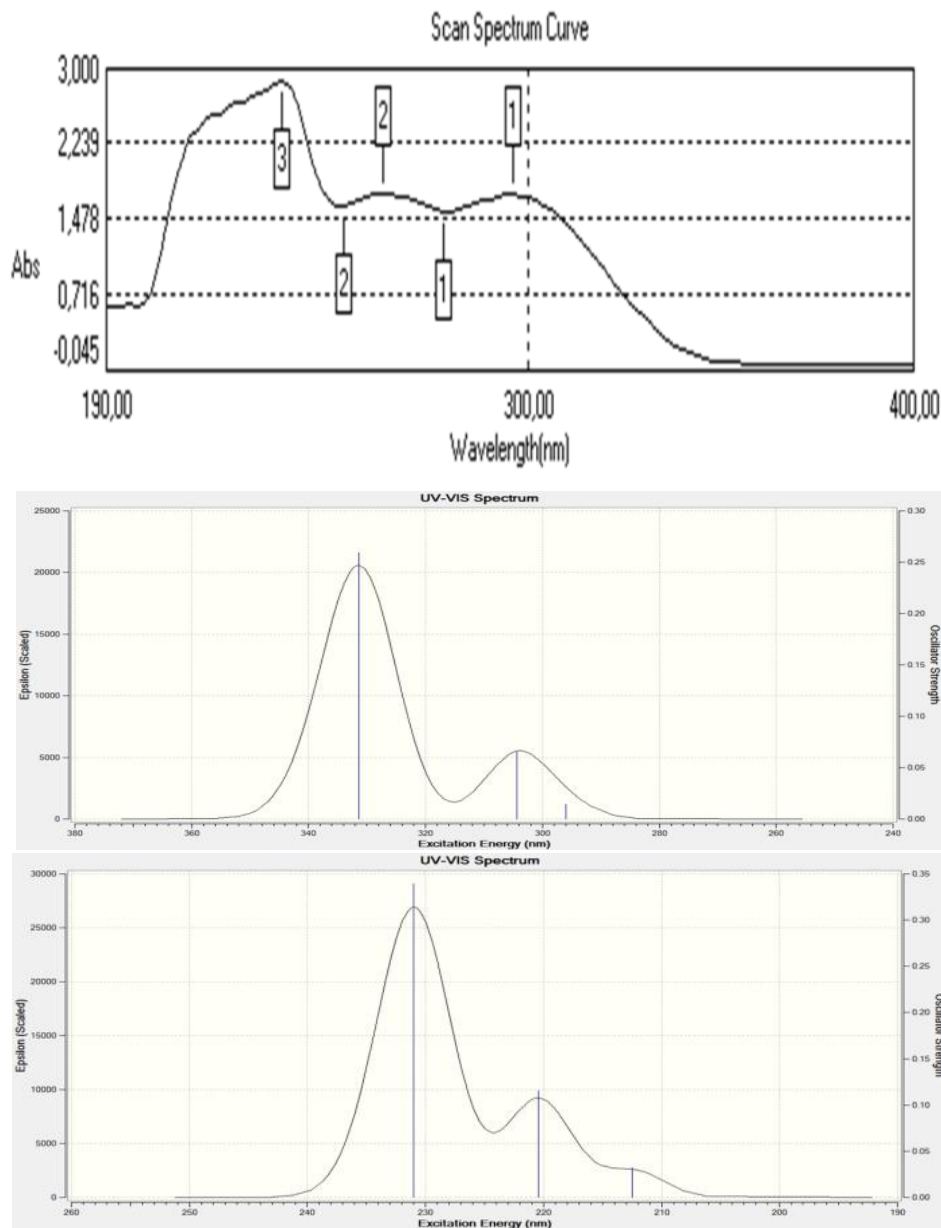


Figure 3: UV-Visible spectra simulated with DFT/B3LYP/6-31G(d) and HF/B3LYP/6-31G(d) levels of the molecule 1

Table 5: The experimental and calculated absorption wavelength (λ) excitation energies of the molecule 1

λ (nm)B3LYP/HF	Uyarma Enerjisi (eV) B3LYP/HF
329.37/230.99	3.7642/5.3675
305.70/220.42	4.0557/5.6248
274.91/212.45	4.5100/5.8359



Table 6: The calculated bond lengths of the molecule 1

No	Bond Lengths	B3LYP	HF		Bond Lengths	B3LYP	HF
1	C(1)-N(47)	1.301	1.269	29	O(53)-C(12)	1.400	1.343
2	C(1)-N(49)	1.386	1.377	30	C(12)-O(54)	1.203	1.186
3	C(1)-H(19)	1.495	1.496	31	C(12)-C(13)	1.487	1.486
4	N(47)-N(48)	1.380	1.369	32	C(13)-C(14)	1.402	1.390
5	N(48)-H(26)	1.008	0.992	33	C(14)-H(36)	1.084	1.073
6	N(48)-C(2)	1.371	1.347	34	C(14)-C(15)	1.391	1.382
7	C(2)-O(51)	1.222	1.200	35	C(15)-H(37)	1.086	1.074
8	C(2)-N(49)	1.419	1.388	36	C(15)-C(16)	1.397	1.387
9	N(49)-N(50)	1.375	1.366	37	C(16)-H(38)	1.086	1.075
10	N(50)-C(3)	1.290	1.260	38	C(16)-C(17)	1.395	1.385
11	C(3)-H(27)	1.085	1.071	39	C(17)-H(39)	1.086	1.074
12	C(3)-C(4)	1.463	1.477	40	C(17)-C(18)	1.394	1.384
13	C(4)-C(5)	1.407	1.395	41	C(18)-H(40)	1.084	1.072
14	C(4)-C(9)	1.406	1.384	42	C(13)-C(18)	1.401	1.389
15	C(5)-H(28)	1.084	1.072	43	C(19)-H(41)	1.094	1.081
16	C(5)-C(6)	1.388	1.375	44	C(19)-H(42)	1.094	1.082
17	C(6)-H(29)	1.085	1.074	45	C(19)-C(20)	1.523	1.520
18	C(6)-C(7)	1.398	1.389	46	C(20)-C(21)	1.397	1.386
19	C(7)-H(30)	1.085	1.073	47	C(21)-H(43)	1.086	1.074
20	C(7)-C(8)	1.392	1.380	48	C(21)-C(22)	1.395	1.386
21	C(8)-O(52)	1.373	1.349	49	C(22)-H(44)	1.084	1.073
22	O(52)-C(10)	1.448	1.418	50	C(22)-C(23)	1.392	1.380
23	C(10)-H(31)	1.096	1.082	51	C(23)-Cl(55)	1.759	1.744
24	C(10)-H(32)	1.098	1.084	52	C(23)-C(24)	1.394	1.384
25	C(10)-C(11)	1.516	1.514	53	C(24)-H(45)	1.084	1.073
26	C(11)-H(33)	1.095	1.084	54	C(24)-C(25)	1.393	1.382
27	C(11)-H(34)	1.094	1.085	55	C(25)-H(46)	1.087	1.075
28	C(11)-H(35)	1.093	1.083	56	C(25)-C(20)	1.400	1.390

Table 7: The calculated mulliken charges of the molecule 1

	DFT	HF		DFT	HF		DFT	HF
C1	0.566	0.641	C20	0.168	0.018	H38	0.139	0.211
C2	0.813	1.053	C21	-0.177	-0.207	H39	0.142	0.211
C3	0.056	0.121	C22	-0.129	-0.180	H40	0.163	0.244
C4	0.076	-0.066	C23	-0.066	-0.137	H41	0.180	0.222
C5	-0.177	-0.206	C24	-0.127	-0.178	H42	0.186	0.229
C6	-0.137	-0.195	C25	-0.172	-0.202	H43	0.144	0.219
C7	-0.169	-0.249	H26	0.358	0.419	H44	0.156	0.232
C8	0.347	0.431	H27	0.219	0.297	H45	0.157	0.232
C9	0.261	0.345	H28	0.153	0.230	H46	0.152	0.228
C10	-0.036	-0.000	H29	0.139	0.212	N47	-0.327	-0.339
C11	-0.463	-0.496	H30	0.147	0.221	N48	-0.514	-0.660
C12	0.558	0.870	H31	0.165	0.186	N49	-0.420	-0.630
C13	0.074	-0.162	H32	0.135	0.148	N50	-0.313	-0.315
C14	-0.136	-0.170	H33	0.151	0.176	O51	-0.536	-0.648
C15	-0.139	-0.214	H34	0.155	0.162	O52	-0.549	-0.687
C16	-0.117	-0.177	H35	0.180	0.185	O53	-0.548	-0.719
C17	-0.138	-0.214	H36	0.159	0.247	O54	-0.442	-0.572
C18	-0.157	-0.164	H37	0.140	0.210	C55	-0.025	-0.005
C19	-0.425	-0.407						

Results and Discussion

In this work, geometric properties such as bond lengths and dihedral angles, electronic properties such as total energy, dipole moment, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular



orbital (LUMO), Mulliken atomic charges and spectroscopic parameters such as IR, UV-vis, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of 3-(*p*-chlorobenzyl)-4-(2-benzyloxy-3-ethoxybenzylideneamino)-4,5-dihydro-1*H*-1,2,4-triazole-5-one (**1**) are calculated by density functional theory (DFT) and Hartree-Fock (HF) methods with the 631G(d) basis set. Obtained spectroscopic parameters are compared with experimental data. The data obtained from density functional theory calculations are more efficient than hartree fock data. The chemical shifts in the calculations $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ 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, linear a correlation were observed. Furthermore, IR vibrational frequencies experimentally carbonyl peak (C=O) in 1707, 1750 cm^{-1} and theoretically (C=O) peak in 1768 cm^{-1} were observed. The negative frequency in the IR data was not found. This result, structure of compound were shown stable.

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