



## A Study on Theoretical and Experimental Spectroscopic Properties of 3-Cyclopropyl-4-(3-acetoxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one

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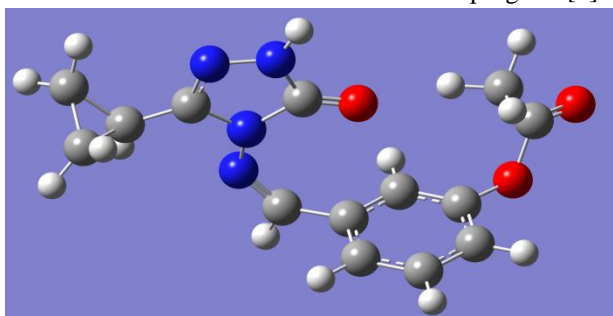
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**Abstract** In this paper, 3-cyclopropyl-4-(3-acetoxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one was synthesized by the reaction of 3-cyclopropyl-4-amino-4,5-dihydro-1H-1,2,4-triazol-5-one with 3-acetoxybenzaldehyde, which were synthesized by the reaction of 3-hydroxybenzaldehyde with acetic anhydride. The molecule was optimized by using the B3LYP/6311G (d) and HF/6311G (d) basis sets. Afterwards,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  isotropic shift values were calculated by the method of GIAO using the program package Gaussian G09W. Experimental and theoretical values were inserted into the graphic according to equation of  $\delta_{\text{exp}}=a+b \cdot \delta_{\text{calc}}$ . The standard error values were found via SigmaPlot program with regression coefficient of a and b constants. IR absorption frequencies of analyzed molecule were calculated by two methods. Then, they were compared with experimental data, which are shown to be accurate. Infrared spectrum was composed by using the data obtained from both methods. The veda4f program, was used in defining IR data, which were calculated theoretically. Furthermore, molecule's theoretical bond lengths, UV-Vis values, dipole moments, formal charges, HOMO-LUMO energies, total energy of the molecule, ionization potential, electron affinity and electronegativity for both methods were calculated.

**Keywords** Theoretical, Experimental, 1,2,4-Triazol-5-one, Gaussian

### 1. Introduction

The optimized molecular structure, vibrational frequencies, UV-Vis spectroscopic parameters, atomic charges and frontier molecule orbitals (HOMO and LUMO) of the titled compound have been calculated by using DFT/B3LYP and HF method with 6-311G(d) basis set. All quantum chemical calculations were carried out by using Gaussian 09W [1, 2] program package and the GaussView molecular visualization program [3].



The molecular structure and vibrational calculations of the molecule was computed by using Becke-3-Lee Yang Parr (B3LYP) [4, 5] density functional method with 6-311G(d) basis set in ground state. IR absorption frequencies of



analyzed molecule were calculated by two methods. Then, they were compared with experimental data, which are shown to be accurate. Infrared spectrum was composed by using the data obtained from both methods [6, 7]. The assignments of fundamental vibrational modes of the title molecule were performed on the basis of total energy distribution (TED) analysis by using VEDA 4f program [8]. In this study, 3-cyclopropyl-4-(3-acetoxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one was synthesized by the reaction of 3-cyclopropyl-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-one with 3-acetoxy-benzaldehyde, which were synthesized by the reaction of 3-hydroxybenzaldehyde with acetic anhydride [9].

## 2. Methods

The molecular structure of the title compound in the ground state (in vacuo) is computed by performing both Hartree-Fock (HF) and the density functional theory (DFT) by a hybrid functional B3LYP functional (Becke's three parameter hybrid functional using the LYP correlation functional) methods [1, 2] at 6-31G(d) level. In all these theoretical calculations, the basic or stimulated state of molecules or atoms can be used [1, 10]. The geometric optimizations of all structures can be generated by the MM2 method and then the semi-empirical PM3 method [11].

## 3. Results and Findings

### Molecular Structure

The optimized molecular geometric parameters (bond lengths) of the molecule by using B3LYP/6-31G(d) and HF/6-31G(d) levels are listed in Table 1.

**Table 1:** The calculated bond lengths of the molecule

Bond lengths		B3LYP	HF	Bond lengths		B3LYP	HF
1	C(1)-N(30)	1.299	1.269	20	C(3)-C(4)	1.466	1.477
2	C(1)-N(31)	1.394	1.384	21	C(4)-C(5)	1.402	1.394
3	C(1)-C(12)	1.471	1.477	22	C(5)-H(17)	1.083	1.072
4	C(12)-H(24)	1.084	1.074	23	C(5)-C(6)	1.385	1.372
5	C(12)-C(13)	1.518	1.505	24	C(6)-O(34)	1.395	1.379
6	C(12)-C(14)	1.518	1.505	25	C(6)-C(7)	1.393	1.385
7	C(13)-H(25)	1.082	1.072	26	C(7)-H(18)	1.081	1.073
8	C(13)-H(26)	1.084	1.075	27	C(7)-C(8)	1.391	1.379
9	C(13)-C(14)	1.501	1.494	28	C(8)-H(19)	1.085	1.074
10	C(14)-H(27)	1.082	1.072	29	C(8)-C(9)	1.392	1.388
11	C(14)-H(28)	1.084	1.075	30	C(9)-H(20)	1.085	1.075
12	N(30)-N(29)	1.378	1.368	31	C(9)-C(4)	1.401	1.385
13	N(29)-H(15)	1.005	0.988	32	O(34)-C(10)	1.373	1.343
14	N(29)-C(2)	1.365	1.343	33	C(10)-O(35)	1.198	1.176
15	C(2)-O(33)	1.216	1.196	34	C(10)-C(11)	1.506	1.501
16	C(2)-N(31)	1.423	1.391	35	C(11)-H(21)	1.088	1.079
17	N(31)-N(32)	1.370	1.364	36	C(11)-H(22)	1.092	1.083
18	N(32)-C(3)	1.285	1.258	37	C(11)-H(23)	1.092	1.083
19	C(3)-H(16)	1.086	1.073				

### Vibrational Frequencies

The 3-cyclopropyl-4-(3-acetoxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule have 33 atoms and the number of the normal vibrations is 99. The observed and calculated vibrational frequencies, the calculated IR intensities and assignments of vibrational frequencies for title compound are summarized in Table 2.



**Table 2:** The calculated frequencies values of the molecule

S/N	Vibration Types	Experi	scaled DFT	scaled Hf
1	$\tau$ NCCC (27), $\tau$ CCOC (11), $\tau$ CNNC (15)		15	14
2	$\tau$ NCCC (10), $\tau$ CCOC (15), $\tau$ COCC (37)		26	15
3	$\tau$ ONCC (66), $\tau$ OCCC (21)		30	33
4	$\tau$ ONCC (25), $\tau$ OCCC (41)		45	51
5	$\delta$ OCC (18), $\delta$ COC (28)		59	58
6	$\tau$ NCCC (11), $\tau$ NCNN (36),		67	60
7	$\delta$ NCC (16), $\tau$ CCOC (18), $\tau$ OCCC (21)		69	75
8	$\tau$ CCOC (14), $\tau$ NCCC (11), $\tau$ CCCC (12)		87	95
9	$\tau$ NCCC (16), $\tau$ CNNC (44)		93	114
10	$\delta$ OCC (13), $\delta$ CCC (19)		142	139
11	$\tau$ CNNC (49), $\tau$ CNNC (10)		165	167
12	$\delta$ CNN (11), $\delta$ CCC (17)		187	173
13	$\tau$ HCCN (51), $\tau$ CNNC (19)		196	180
14	$\tau$ NCNN (10), $\tau$ CCCC (14)		217	221
15	$\delta$ NCC (12), $\tau$ NCNN (13), $\tau$ CCCC (22)		234	229
16	$\nu$ CC (10), $\delta$ CCN (29)		258	240
17	$\tau$ NCCC (22), $\tau$ CCCC (31)		267	267
18	$\tau$ HNNC (25), $\tau$ NNCC (17), $\tau$ CNNC (28)		302	298
19	$\delta$ OCO (16), $\delta$ COC (12), $\delta$ NCC (13)		312	313
20	$\tau$ NCNN (16), $\tau$ CCCC (13), $\tau$ NNCC (21)		318	358
21	$\delta$ CCO (17), $\delta$ CNN (14), $\delta$ OCN (11)		352	394
22	$\delta$ OCC (10), $\delta$ CCC (11)		403	414
23	$\tau$ HCCC (19), $\tau$ CCCC (24)		416	436
24	$\tau$ HNNC (57)		454	460
25	CCO (15), $\tau$ CCCC (10), $\tau$ NCCC (12)		455	473
26	$\tau$ HCCC (13), $\tau$ CCCC (11), $\tau$ CCOC (15)		458	489
27	CCO (21), $\tau$ NCCC (13), $\tau$ CCCC (11)		475	497
28	$\nu$ NC (15), $\delta$ OCO (11), $\delta$ ONC (18)		513	526
29	$\delta$ ONC (41), $\delta$ NCC (12)		541	559
30	$\nu$ CC (10), $\delta$ CCC (11), $\delta$ NCN (13)		561	599
31	$\delta$ CCC (20), $\delta$ CCO (10), $\delta$ OCC (12)		595	609
32	$\delta$ OCN (35), $\delta$ CNN (15), $\delta$ CCN (12)		600	622
33	$\nu$ CC (10), $\delta$ CCC (33)		637	653
34	$\tau$ HCCN (10), $\tau$ NNCC (30), $\tau$ CNNC (15)		648	691
35	$\tau$ CCCC (18), $\tau$ CCOC (22), $\tau$ OCOC (11)		672	704
36	$\tau$ HCCC (30), $\tau$ CCCC (17), $\tau$ CCOC (18)	688	695	727
37	$\delta$ ONO (12), $\delta$ CCC (17)		717	750
38	$\tau$ HCCC (19), $\tau$ OCON (54), $\tau$ OCOC (19)		722	779
39	$\tau$ ONNC (86)		764	814
40	$\nu$ NC (17), $\delta$ CNN (26)		779	833
41	$\tau$ OCON (24), $\tau$ OCOC (41)		796	838
42	$\tau$ HCCC (49),	794	799	843



43	$\nu$ NN (14), $\delta$ NCC (14), $\delta$ NCN (10), $\delta$ NNC (16)	813	862
44	$\delta$ OCO (16), $\delta$ COC (10), $\tau$ HCCC (20)	843	908
45	$\tau$ HCCC (94)	855	909
46	$\nu$ ON (10), $\nu$ CC (18), $\delta$ ONO (46)	871	929
47	$\tau$ HCCC (60)	911	975
48	$\tau$ HCCC (18), $\tau$ CCOC (13)	926	994
49	$\tau$ HCCC (16), $\tau$ CCOC (17)	964	1000
50	$\nu$ CC (22), CCO (28), CCC (10)	966	1033
51	$\delta$ HCH (14), $\tau$ HCCN (40)	989	1037
52	$\tau$ HCCC (42), $\tau$ CCCC (11)	995	1053
53	$\delta$ CCC (38)	997	1054
54	$\tau$ HCCC (80)	1004	1057
55	$\tau$ HCCC (78)	1004	1071
56	$\tau$ HCNN (87)	1022	1083
57	HCH (20), $\tau$ HCCN (55), $\tau$ CNNC (10)	1051	1110
58	$\nu$ CC (20), $\delta$ HCC (36)	1058	1118
59	$\delta$ NNC (10)	1091	1120
60	$\nu$ CC (13), $\nu$ OC (25)	1104	1136
61	$\nu$ NN (23), $\delta$ HNN (11)	1114	1160
62	$\nu$ CC (18), NC (25), $\delta$ HCC (17)	1157	1172
63	$\nu$ OC (15), CC (18), $\delta$ HCC (18)	1182	1209
64	$\nu$ CC (15), $\delta$ HCC (23)	1199	1245
65	$\nu$ CC (39), $\delta$ HCC (30)	1241	1251
66	$\nu$ NC (22), $\nu$ NN (12)	1258	1276
67	$\nu$ CC(11), $\nu$ OC (18)	1275	1308
68	$\nu$ OC (34), $\nu$ CC (13), $\delta$ OCO (12)	1254 1288	1316
69	$\delta$ HCC (86)	1338	1366
70	$\nu$ NN (12), $\delta$ NCN (23), $\delta$ CNN (14)	1346	1386
71	$\nu$ NC (10), $\delta$ HCN (32), $\delta$ HCH (17)	1347	1437
72	$\delta$ HNN (29), $\delta$ HCN (11), $\delta$ HCH (37)	1368	1466
73	$\nu$ CC (19), $\delta$ HCC (29)	1389	1475
74	$\delta$ HNN (35), $\delta$ HCN (11), $\delta$ HCH (22)	1406	1478
75	$\delta$ HCN (11), $\delta$ HCH (42)	1416	1506
76	$\delta$ HCH (78), $\tau$ HCCN (21)	1423	1515
77	$\nu$ NC (12), $\delta$ HCH (29), $\tau$ HCCN(13)	1473	1537
78	$\nu$ ON (76), $\delta$ ONO (10)	1475	1558
79	$\nu$ CC (22), $\delta$ HCC (40)	1501	1566
80	$\nu$ CC (15), $\delta$ HCC (57)	1505	1580
81	$\nu$ ON (18), $\nu$ CC (47)	1585	1678
82	$\nu$ CC (22), $\delta$ HCC (12), $\delta$ CCO (10)	1592	1691
83	$\nu$ CC (12), $\delta$ HCC (15)	1599	1796
84	$\nu$ ON (74), $\nu$ CC (10)	1600	1707
85	$\nu$ NC (48)	1578 1607	1714
86	$\nu$ NC (54)	1585 1654	1718



87	v OC (67), v NC (14)	1712	1746	1801
88	v OC (88)	1763	1803	1854
89	v CH (93)		3005	3039
90	v CH (99)		3060	3099
91	v CH (92)		3098	3132
92	v CH (54)		3105	3170
93	v CH (44)		3177	3202
94	v CH (63)		3179	3214
95	v CH (27)		3188	3216
96	v CH (42)		3197	3221
97	v CH (35)		3196	3203
98	v CH (49)		3252	3265
99	v NH (100)	3182	3593	3604

v, stretching;  $\delta$ , bending;  $\delta_s$ , scissoring;  $\rho$ , rocking;  $\gamma$ , out-of-plane bending;  $\tau$ , 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 [12-14]. In this framework, the optimized molecular geometry of the molecule was obtained by using B3LYP and HF methods with 6-311G(d) basis level in DMSO solvent. By considering the optimized molecular geometry of the title compound the  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shift values were calculated at the same level by using Gauge-Independent Atomic Orbital (GIAO) method. Theoretically and experimentally values [9] were plotted according to  $\delta_{\text{exp}} = a \cdot \delta_{\text{calc}} + b$ , Eq. a and b constants regression coefficients with a standard error values were found using the SigmaPlot program.

**Table 3:** The calculated and experimental  $^{13}\text{C}$  and  $^1\text{H}$  NMR isotropic chemical shifts of the molecule

No	Experim.	DFT/631d/DMSO	Diff./DMSO	HF/631d/DMSO	Diff./DMSO
C1	148.15	152.13	-3.98	143.03	5.12
C2	152.81	153.98	-1.17	143.06	9.75
C3	150.80	152.51	-1.71	142.73	8.07
C4	135.00	140.46	-5.46	126.29	8.71
C5	120.00	118.14	1.86	109.99	10.01
C6	151.18	157.38	-6.20	141.02	10.16
C7	124.81	128.04	-3.23	119.00	5.81
C8	125.65	132.30	-6.65	121.16	4.49
C9	130.05	132.47	-2.42	121.99	8.06
C10	169.06	173.41	-4.35	158.46	10.60
C11	20.73	21.13	-0.40	18.84	1.89
C12	6.49	13.62	-7.13	12.97	-6.48
C13	6.49	6.28	0.21	6.33	0.16
C14	5.37	6.30	-0.93	6.31	-0.94
H15	11.81	6.67	5.14	5.83	5.98
H16	9.72	9.53	0.19	8.96	0.76
H17	7.71	7.31	0.40	7.22	0.49
H18	7.64	7.25	0.39	6.70	0.94
H19	7.52	7.21	0.31	6.99	0.53



H20	7.27	6.99	0.28	6.88	0.39
H21	2.27	1.42	0.85	0.99	1.28
H22	2.27	2.07	0.20	1.54	0.73
H23	2.27	2.09	0.18	1.55	0.72
H24	2.07	1.50	0.57	0.77	1.30
H25	0.88	0.74	0.14	0.08	0.80
H26	0.97	1.26	-0.29	0.61	0.36
H27	0.88	0.75	0.13	0,05	0.83
H28	0.97	1.27	-0.30	0.56	0.41

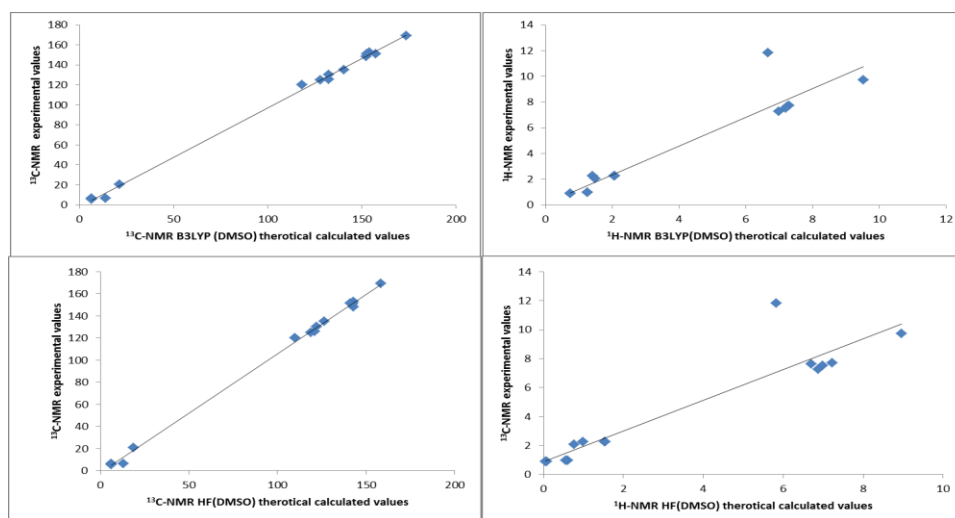
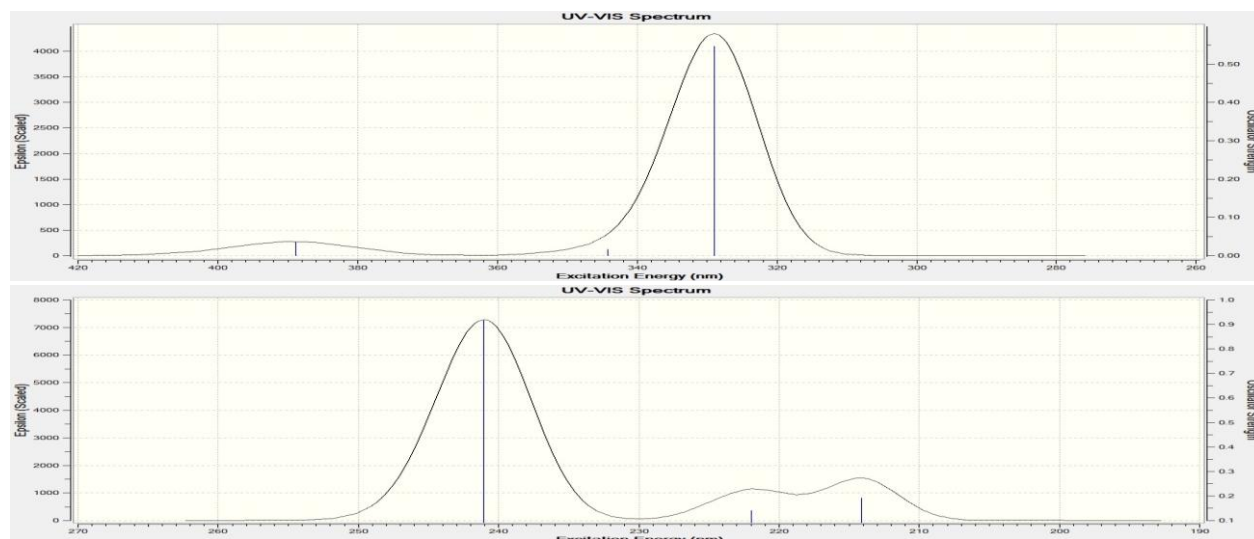


Figure 1: The correlation graphics for  $^{13}\text{C-NMR}$  (DMSO) and  $^1\text{H-NMR}$  (DMSO) chemical shifts of the molecule

Table 4: Mulliken atomic charges of the molecule

	B3LYP	HF		B3LYP	HF
C1	0.459	0.596	H19	0.204	0.229
C2	0.583	0.780	H20	0.208	0.233
C3	-0.067	0.029	H21	0.240	0.244
C4	-0.021	-0.056	H22	0.241	0.245
C5	-0.195	-0.229	H23	0.242	0.251
C6	0.237	0.335	H24	0.228	0.247
C7	-0.183	-0.208	H25	0.222	0.234
C8	-0.205	-0.212	H26	0.238	0.251
C9	-0.202	-0.243	H27	0.222	0.234
C10	0.379	0.534	H28	0.238	0.252
C11	-0.685	-0.695	N29	-0.495	-0.590
C12	-0.285	-0.331	N30	-0.207	-0.271
C13	-0.413	-0.425	N31	-0.395	-0.504
C14	-0.414	-0.424	N32	-0.218	-0.285
H15	0.371	0.405	O33	-0.393	-0.534
H16	0.266	0.313	O34	-0.346	-0.481
H17	0.234	0.267	O35	-0.314	-0.430
H18	0.226	0.238			





$\lambda$ (nm) B3LYP/HF	excitation Energy (eV) B3LYP/HF	f (oscillator values) B3LYP/HF
293.00/388.93/241.05	3.1878/5.1436	0.0352/0.9188
258.00/344.20/222.00	3.6021/5.5848	0.0159/0.1406
217.00/328.97/214.11	3.7689/5.7907	0.5467/0.1920

Figure 2: The experimental and calculated absorption wavelength ( $\lambda$ ), excitation energies and oscillator strengths ( $f$ ) of the molecule

Table 5: Electronic properties of the molecule

	DFT (Hartree)	HF (Hartree)
Ionization Potential	0.28247	0.28889
Electron Affinity	0.18864	-0.18761
Electronegativity	-0.23555	-0.28865
Energy	-1370.029	-1361.671

Table 6: The calculated dipole moment values of the molecule

Dipole Moment	B3LYP (a.u.)	HF (a.u.)
$\mu_x$	0.4985	-0.0184
$\mu_y$	0.8961	2.4874
$\mu_z$	0.2189	1.0634
$\mu_{\text{Toplam}}$	1.0876	2.6868

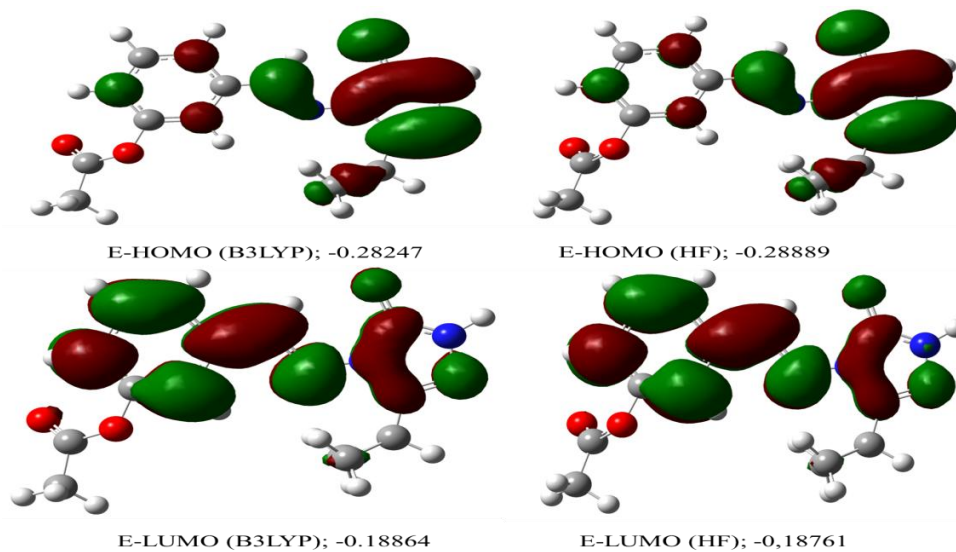


Figure 3: The calculated HOMO-LUMO energies of the molecule according to DFT/B3LYP/6-31G(d) and HF/B3LYP/6-31G(d) levels

## Conclusion

The molecular structures, vibrational frequencies,  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemicals shifts, UV-vis spectroscopies, HOMO and LUMO analyses and atomic charges of 3-ethyl-4-(4-cinnamoyloxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one molecule synthesized for the first time have been calculated by using DFT/B3LYP and HF methods. By considering the results of experimental works, it can be easily stated that the vibrational frequencies,  $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shifts and UV spectroscopic parameters obtained theoretically are in a very good agreement with the experimental data.

## References

1. 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.
2. Wolinski, K., Hilton, J.F., Pulay, P. 1990. *J. Am. Chem. Soc.*, 112, 512.
3. Frisch, A., Nielson, A.B., Holder, A.J. 2003. Gaussview User Manual, Gaussian, Inc., Wallingford, CT.
4. Becke A.D. 1993. Density-functional thermochemistry. III. The role of exact exchange. *The Journal of Chemical Physics*. 98, 5648.
5. Lee, C., Yang, W., Parr. R.G. 1988. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density *Physical Review B*, 37, 785.
6. Gökçe H, Bahçeli S, Akyıldırım O, Yüksek H, Gürsoy Kol Ö, 2013. The Syntheses, Molecular Structures, Spectroscopic Properties (IR, Micro-Raman, NMR and UV-vis) and DFT Calculations of Antioxidant 3-alkyl-4-[3-methoxy-4-(4-methylbenzoxy)benzylidenamino]-4,5-dihydro-1H-1,2,4-triazol-5-one Molecules. *Letters in Organic Chemistry*, 10, 395-441.
7. Gökçe H, Akyıldırım O, Bahçeli S, Yüksek H, Gürsoy Kol O, 2014. The 1-acetyl-3-methyl-4-[3-methoxy-4-(4-methylbenzoxy)benzylidenamino]-4,5-dihydro-1H-1,2,4-triazol-5-one Molecule Investigated by a Joint Spectroscopic and Quantum Chemical Calculations. *Journal of Molecular Structure*, 1056-1057, 273-284.
8. Jamróz M.H. 2004. *Vibrational Energy Distribution Analysis: VEDA 4 program*, Warsaw.
9. Gürsoy Kol, Ö. 2008. Bazı 4,5-dihidro-1H-1,2,4-triazol-5-on türevlerinin sentezi, yapılarının aydınlatılması, antioksidan ve asitlik özelliklerinin incelenmesi, Doktora Tezi, Kafkas Üniversitesi, Fen Bilimleri Enstitüsü, Kars.
10. Gümüş P.H., Tamer Ö., Avcı D., Atalay Y. 2015. 4-(Metoksümetil)-1,6-dimetil-2-okso-1,2-dihidropiridin-3-karbonitril molekülünün teorik olarak incelenmesi. *Sakarya Üniversitesi Fen Bilimleri Dergisi*, 3, 303-311.
11. Turhan Irak Z., Gümüş S. 2017. Heterotricyclic compounds via click reaction: A computational study. *Noble International Journal of Scientific Research*, 1(7), 80-89.
12. Rani, A.U., Sundaraganesan, N., Kurt, M., Çınar, M., Karabacak, M. 2010, *Spectrochim. Acta Part A*, 75, 1523-1529.
13. Subramanian, N., Sundaraganesan, N., Jayabharathi. 2010, *J., Spectrochim Acta Part A*, 76, 259-269.
14. Wade, Jr. L.G. 2006. *Organic Chemistry*, 6nd ed.; Pearson Prentice Hall: New Jersey

