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The Investigation of Molecular and Spectroscopic Properties of 3-Ethyl-4-(4-cinnamoyloxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one Compound Using B3LYP and HF Basis Sets

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Abstract: In this study, we reported a combined experimental and theoretical study on 3-ethyl-4-(4-cinnamoyloxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one compound. The title compound was prepared and characterized by ^{1}H and ^{13}C NMR and FT-IR spectra. The molecular geometry, gauge including atomic orbital (GIAO), Experimental and theoretical values were inserted into the graphic according to equitation of δexp=a+b. δ calc. The standard error values were found via SigmaPlot program with regression coefficient of a and b constants. Also, the calculated IR data of compound were calculated in gas phase by using of 6-31G(d) basis set of B3LYP and HF methods and are multiplied with appropriate scala factors. Theoretical infrared spectrums are formed from the data obtained according to B3LYP method. In the identification of calculated IR data was used the veda4f program. ^{1}H and ^{13}C NMR chemical shift values, vibrational frequencies and HOMO-LUMO analyses properties, Mulliken's atomic charges, dipole moment and total energy of the title compound in the ground state were investigated by using Hartree-Fock (HF) and density functional theory (DFT/B3LYP) methods with 6-31G(d) basic set. Obtained results indicate that there is a good agreement between the experimental and theoretical data.

Keywords: 4.5- Dihydro-1H-1.2.4-triazol-5-on, Gaussian 09W, GIAO, B3LYP, HF, 6-31G(d) basic set.

1. INTRODUCTION

Triazole is an unsymmetrical heterocyclic organic compound having three nitrogen atoms in the five-membered ring. 1,2,4-Triazole and 4,5-dihydro-1H-1,2,4-triazol-5-one derivatives are reported to possess a broad spectrum of biological activities such as antimicrobial, antifungal, antitumor, anti-HIV, antiviral, anticancer, anti-inflammatory, analgesic and antioxidant properties (Alkan et al., 2007; Bayrak et al., 2010; Beytur et al., 2019; Çiftçi et al., 2018; Gürsoy Kol and Yüksek, 2010; Güzeldemirci and Kucukbasmaci, 2010; Hashem et al., 2007; Sancak et al., 2010 Tozkoparan et al., 2007; Turhan Irak and Beytur, 2019). Also, several articles reporting the synthesis of some 1,2,4-triazol-5-one compounds and derivatives have been published (Bahçeci et al., 2002; Beytur et al., 2019;

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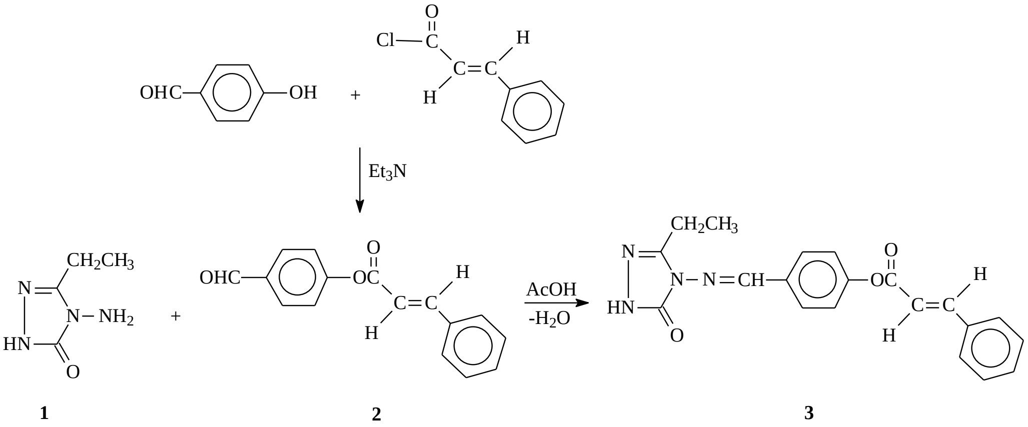
Çiftçi et al., 2018; Yüksek et al., 2005a; Yüksek et al., 2005b; Yüksek et al., 2006; Turhan Irak and Beytur, 2019).

In this paper, 3-ethyl-4-(4-cinnamoyloxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (3) was obtained from the reaction of compound (1) with 4-cinnamoyloxybenzaldehyde (2) (Vasavado and Parekh, 2003) which was synthesized by the reaction of 4-hydroxybenzaldehyde with cinnamoyl chloride by using triethylamine (Scheme 1). The starting compound 3-ethyl-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-one (1) was prepared from the reaction of ethyl acetate ethoxycarbonylhydrazone with an aqueous solution of hydrazine hydrate as described in the literature (İkizler and Yüksek, 1993; İkizler and Un, 1979).



Scheme 1. Synthesis method of titled compound

1. MATERIAL AND METHOD

2.1. Materials and measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER ULTRASHIELD PLUS BIOSPIN GmbH spectrometer using deuterated dimethyl sulfoxide as a solvent and Me_4Si as an internal standard. FT-IR spectrum was taken with ALPHA-P BRUKER FT-IR spectrometer. The electronic spectra were recorded on a PG Instruments Ltd. T80 UV/VIS spectrophotometer. Melting point was taken using an WRS-2A Microprocessor Melting-point Apparatus.

2.2. Synthesis

The compound **1** (10 mmol) was dissolved in acetic acid (20 mL) and treated with 4-cinnamoyloxybenzaldehyde **(2)** (10 mmol). The mixture was refluxed for 2 hour. Several recrystallizations of the residue from ethanol gave pure compound 3-ethyl-4-(4-

cinnamoyloxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**3**) was preparated: m.p. 178 °C; Yield 3.53 g (97 %). IR: (NH) 3168; C=CH 3056; C=O 1729, 1694; C=C 1630; COO 1203; 1,4–disubstituted aromatic ring 843; monosubstituted aromatic ring 764 and 699 cm^{-1}. ^{1}H NMR (400MHz, DMSO-d$_6$): δ; 1.24 (t, 3H, $CH_2C\underline{H}_3$), 2.71 (q, 2H, $C\underline{H}_2CH_3$), 6.92 (d, 1H, =CH; *J*=16.00 Hz), 7.39 (d, 2H, ArH; *J*=8.40 Hz), 7.47-7.50 (m, 3H, ArH), 7.83-7.85 (m, 2H, ArH), 7.91-7.93 (m, 2H, ArH), 7.92 (d, 1H, =CH; *J*=16.00 Hz), 9.77 (s, 1H, N=CH), 11.86 (s, 1H, NH). ^{13}C-NMR (100MHz, DMSO-d$_6$): δ; 10.08 ($CH_2\underline{C}H_3$), 18.53 ($\underline{C}H_2CH_3$), 116.90 and 146.85 (CH=CH), 128.71 (2C); 128.94 (2C); 131.27; 133.80 (monosubstituted Ar-C), 122.57 (2C); 129.01 (2C); 130.97;152.74 (1,4-disubstituted Ar-C), 148.04 (Triazol C$_3$), 151.38 (N=CH), 152.68 (Triazol C$_5$), 164.65 (COO). UV [Ethanol, λ_{max}, nm (ε, L.mol^{-1}.cm^{-1})]: 300 (22563), 262 (20156), 214 (23440).

2.3. Computational Details

The molecular structure of the title compound in the ground state is computed by performing both the Density Functional Theory (DFT) and Hartree-Fock (HF) (Becke, 1993; Lee, 1998) at 6-31G(d) level. Density functionals for all studies reported in this paper have been in the following form

$$E_{XC} = (1-a_0)E_X^{LSDA} + a_0 E_X^{HF} + a_X \Delta E_X^{B88} + a_C E_C^{LYP} + (1-a_C)E_C^{VWN}$$

where the energy terms are the Slater exchange, the Hartree-Fock exchange, Becke’s exchange functional correction, the gradient corrected correlation functional of Lee, Yang and Parr, and the local correlation functional of Vosko, Wilk and Nusair (Vosko et al., 1980). The theoretical geometric structure of the compound is given in Figure 1. Molecular geometry is restricted and the optimized geometrical parameters, of the title compound in this study are carried out by using Gaussian 09W program package (Frisch et al., 2009) and the visualization parts were done with GaussView program (Dennington et al., 2009) on personal computer employing 6-31G(d) basis set. Additionally, harmonic vibrational frequencies for the title compound are calculated with these selected methods and then scaled by 0.9516 and 0.9905, respectively (Avcı and Atalay, 2008) and these results were compared with the experimental data.

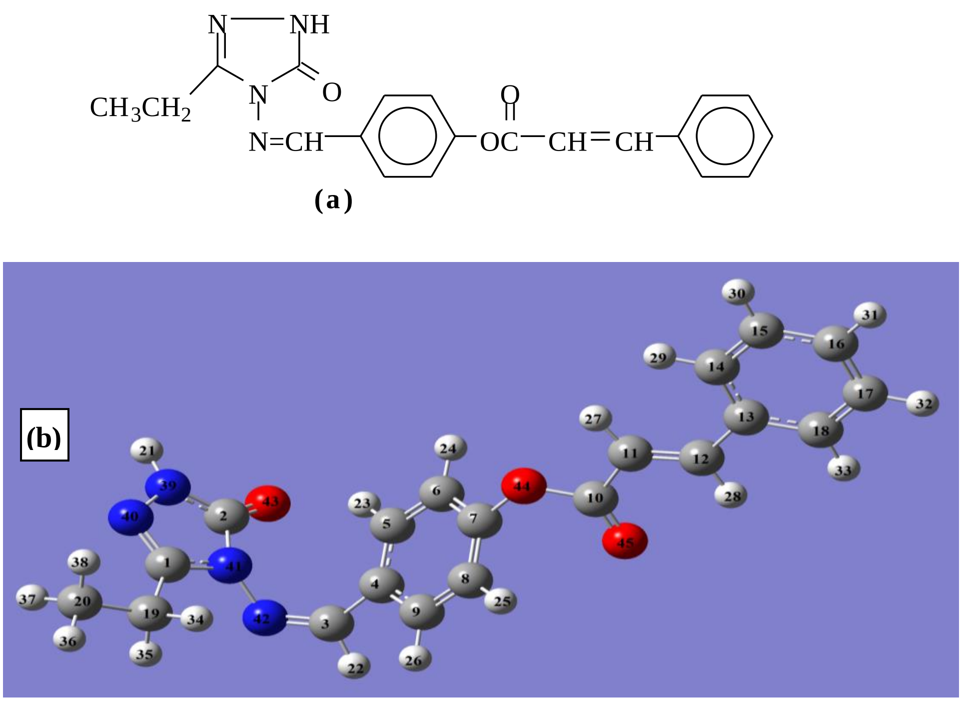


Figure 1. The chemical structure (a) and optimized molecular structure (b) of titled compound (**3**) with DFT/B3LYP/6-31G(d) level.

3. RESULTS

3.1. Molecular Structure

The optimized molecular structures and chemical structure of the compound 3 was given in Figure 1. Similarly, the optimized molecular geometric parameters (bond angles and bond lenghts) of the titled compound by using B3LYP/6-31G(d) and HF/6–31G(d) levels are listed in Tables 1 and 2, respectively.

Table 1. The calculated bond angles of the titled compound (A°).

Bond Angles	B3LYP	HF	Bond Angles	B3LYP	HF
C(1)-N(40)-N(39)	104.47	104.87	N(42)-C(3)-H(22)	110.80	112.37
C(1)-N(41)-N(42)	121.20	122.12	N(42)-C(3)-C(4)	135.56	132.56
C(1)-N(41)-C(2)	108.12	113.31	C(6)-C(7)-O(44)	123.66	116.98
C(1)-C(19)-H(34)	108.66	10797	O(44)-C(7)-C(8)	115.51	121.88
C(1)-C(19)-H(35)	107.96	108.14	C(7)-O(44)-C(10)	121.99	121.38
N(40)-C(1)- N(41)	111.51	111.32	O(44)-C(10)-O(45)	124.10	123.60
N(40)-N(39)- H(21)	119.90	120.54	O(44)-C(10)-C(11)	109.16	110.12
N(40)-N(39)- C(2)	114.40	113.38	O(45)-C(10)-C(11)	126.74	126.29
N(40)-C(1)-C(19)	125.80	126.17	C(10)-C(11)-H(27)	116.78	116.54
H(21)-N(39)-C(2)	124.61	125.33	C(10)-C(11)-C(12)	119.89	119.65
N(39)-C(2)-N(41)	100.99	102.11	H(27)-C(11)-C(12)	123.34	123.81
N(39)-C(2)-O(43)	130.43	129.67	C(11)-C(12)-H(28)	116.31	116.76
O(43)-C(2)-N(41)	128.58	128.19	C(11)-C(12)-C(13)	127.81	127.70
C(2)-N(41)-N(42)	125.89	123.68	H(28)-C(12)-C(13)	115.88	115.54
N(41)-C(1)-C(19)	122.66	122.49	C(12)-C(13)-C(14)	123.21	123.13
N(41)-N(42)-C(3)	119.35	117.29	C(12)-C(13)-C(18)	118.53	118.37

Table 2. The calculated bond lengths of the titled compound (°).

Bond Lengths	B3LYP	HF	Bond Lengths	B3LYP	HF
C(1)-N(40)	1.301	1.269	C(7)-C(8)	1.395	1.384
C(1)-N(41)	1.390	1.381	C(8)-H(25)	1.085	1.072
C(1)-C(19)	1.494	1.495	C(8)-C(9)	1.389	1.380
N(39)-N(40)	1.383	1.371	C(9)-H(26)	1.087	1.076
N(39)-H(21)	1.008	0.992	O(44)-C(10)	1.380	1.345
N(39)-C(2)	1.375	1.349	C(10)-O(45)	1.212	1.187
C(2)-O(43)	1.218	1.201	C(10)-C(11)	1.471	1.475
N(41)-C(2)	1.421	1.382	C(11)-H(27)	1.085	1.072
N(41)-N(42)	1.391	1.398	C(11)-C(12)	1.347	1.328
N(42)-C(3)	1.290	1.260	C(12)-H(28)	1.089	1.076
C(7)-O(44)	1.386	1.374	C(12)-C(13)	1.461	1.472

3.2. Analysis of Vibrational Modes

In spectroscopic field, the vibrational spectra of substituted benzene derivatives have been greatly investigated by various spectroscopic, since the single substitution can have a tendency to put greater changes in vibrational wavenumbers of benzene (Pir et al., 2013; Tereci et al., 2012; Turhan Irak and Gümüş, 2017; Taşdemir et al., 2016; Özbek et al., 2017). In other words, molecular system of benzene is greatly affected by the nature of substituents. The number of potentially active fundamentals of non-linear molecule which have N atoms is equal to (3N-6) apart from three translational and three rotational degrees of freedom. The molecule contains 45 atoms and 129 normal vibration modes have C1 symmetry (Table 3).

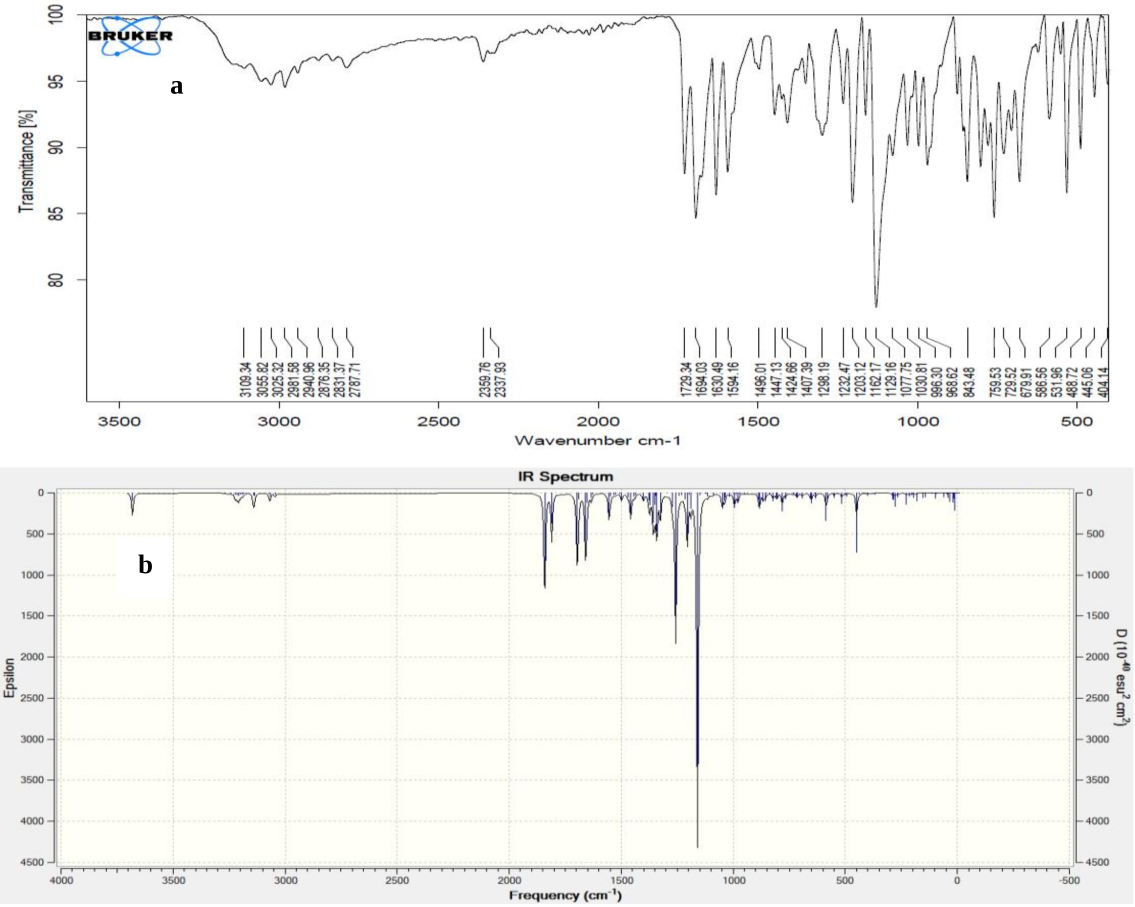
Table 3. The calculated frequencies values of the titled compound (3).

Selected Vibrational Types	Scaled B3LYP	Scaled HF
τ NNCC, τ OCCC	474	434
δ CCO, τ OCCC	510	484
τ HNNC	527	496
τ HNNC, τ OCCC	528	527
ν NN, τ NNCC	557	557
ν CC, δ OCO, δ CCC	578	565
τ NCNC	627	622
ν NC, ν CC, ν OC, NN, δ CCC	665	672
τ HCCC, τ OCOC	698	707
τ ONNC	714	714
ν OC, δ OCO, δ OCC	724	751
ν OC, ν NC, δ NCN, δ CNN	760	770
τ CCCC, τ OCOC	767	781
ν OC	779	784
NCC, τ HCCC	834	836
τ HCCC, τ OCCC	888	885
δ NCN, τ HCNN	944	971
ν CC, τ HCNN	948	973
ν NC, ν CC, ν OC, τ HCNN	1009	1007
ν NC, ν NN	1092	1091
ν CC, ν OC, δ OCO	1098	1093
τ HCCN, τ HCCC	1109	1095
ν NC, ν CC	1158	1155
ν CC, ν OC, δ HCC	1224	1209
ν NC, δ HCC	1257	1228
δ HCC, τ HCCN	1283	1293

δ HNN	1315	1317
ν CC, τ HCCN	1366	1388
ν NC, δ HCH	1528	1588
ν NC	1561	1620
ν NC, ν CC	1578	1670
ν OC	1669	1763
ν OC	1698	1786
ν NH	3503	3519

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

Experimentally, the investigated titled compound (**3**), as expected the IR spectra data, the N-H stretching vibration at 3172 cm^{-1} and two C=O peak at 1729 cm^{-1} and 1694 cm^{-1} range was observed. In addition, C=C stretching vibrations at 1630 cm^{-1}, C=N stretching vibration at 1594 cm^{-1} and COO stretching vibrations at 1232 cm^{-1} are occurred. Theoretically, the calculated vibrational frequencies for the compound **3** are summarized in Table 2. Furthermore the experimental IR and simulated spectra by using B3LYP/6-31G(d) and HF/6-31G(d) levels of the compound **3** under investigation are given in Figure 2.



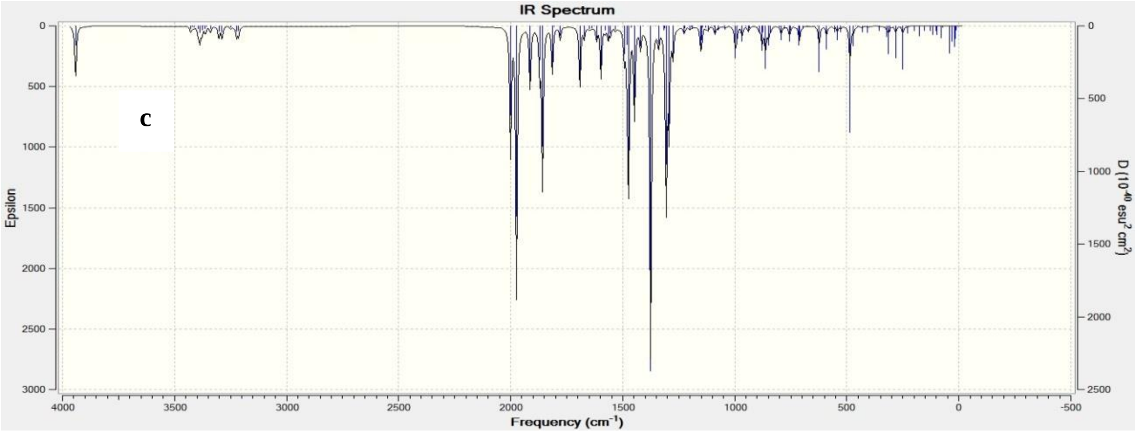


Figure 2. IR spectra (a) experimental and (b and c) simulated with DFT/B3LYP/6–31G(d) and HF/6–31G(d) levels of the titled compound.

3.3. NMR spectral analysis

The isotropic chemical shift analysis allows us to identify relative ionic species and to calculate reliable magnetic properties in nuclear magnetic resonance (NMR) spectroscopy which provide the accurate predictions of molecular geometries, (Rani, et al., 2010; Subramanian et al., 2010; Wade, 2006). For this purpose, the optimized molecular geometry of the compound **3** was obtained by using B3LYP and HF methods with 6-31G(d) basis level in DMSO solvent. By considering the optimized molecular geometry of the compound **3** the ^{1}H and ^{13}C NMR chemical shift values were calculated at the same level by using Gauge-Independent Atomic Orbital method (Table 4). Theoretically and experimentally 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. The correlation graphics are given Figure 3 and the linear correlation data of the compound **3** by considering the results are given in Table 5.

Table 4. The calculated and experimental ^{13}C and ^{1}H NMR isotropic chemical shifts of the titled compound (with respect to TMS, all values in ppm).

Nucleus	Experi-mental	B3LYP	B3LYP/ DMSO	Different	Different/ DMSO	HF	HF/ DMSO	Different	Different/ DMSO
C1	148.04	153.08	154.64	-5.04	-6.60	145.79	148.11	2.25	-0.07
C2	152.68	148.60	149.65	4.08	3.03	147.57	148.63	5.11	4.05
C3	151.38	160.23	161.54	-8.85	-10.16	169.27	171.80	-17.89	-20.42
C4	130.97	134.32	133.98	-3.35	-3.01	122.02	122.35	8.95	8.62
C5	129.01	134.00	133.85	-4.99	-4.84	129.84	128.83	-0.83	0.18
C6	122.57	125.86	125.09	-3.29	-2.52	117.28	116.79	5.29	5.78
C7	152.74	157.18	157.54	-4.44	-4.80	147.79	147.62	4.95	5.12
C8	122.57	123.19	124.06	-0.62	-1.49	118.50	118.59	4.07	3.98
C9	129.01	138.16	139.70	-9.15	-10.69	127.26	129.11	1.75	-0.10
C10	164.65	166.01	167.28	-1.36	-2.63	156.23	157.88	8.42	6.77
C11	116.90	119.96	119.17	-3.06	-2.27	107.98	107.26	8.92	9.64

C12	146.85	152.85	154.37	-6.00	-7.52	148.18	149.53	-1.33	-2.68
C13	133.80	137.51	136.74	-3.71	-2.94	127.92	126.96	5.88	6.84
C14	128.94	129.36	129.95	-0.42	-1.01	123.10	123.66	5.84	5.28
C15	128.71	132.33	132.77	-3.62	-4.06	124.34	124.41	4.37	4.30
C16	131.27	134.74	136.11	-3.47	-4.84	128.29	129.45	2.98	1.82
C17	128.71	132.51	132.87	-3.80	-4.16	124.54	124.54	4.17	4.17
C18	128.94	137.95	138.53	-9.01	-9.59	130.22	130.84	-1.28	-1.90
C19	18.53	31.52	31.38	-12.99	-12.85	16.96	16.84	1.57	1.69
C20	10.18	20.09	19.88	-9.91	-9.70	7.65	7.52	2.53	2.66
H21	11.86	6.84	7.32	5.02	4.54	6.16	6.60	5.70	5.26
H22	9.77	8.01	8.22	1.76	1.55	8.48	8.73	1.29	1.04
H23	7.92	7.97	8.07	-0.05	-0.15	8.51	8.32	-0.59	-0.40
H24	7.39	7.95	7.97	-0.56	-0.58	7.03	7.17	0.36	0.22
H25	7.39	7.22	7.46	0.17	-0.07	7.31	7.46	0.08	-0.07
H26	7.92	7.52	7.84	0.40	0.08	7.25	7.66	0.67	0.26
H27	6.92	6.71	6.86	0.21	0.06	6.14	6.32	0.78	0.60
H28	7.92	8.02	8.08	-0.10	-0.16	7.98	8.04	-0.06	-0.12
H29	7.84	7.57	7.74	0.27	0.10	7.93	8.14	-0.09	-0.30
H30	7.49	7.71	7.88	-0.22	-0.39	7.40	7.58	0.09	-0.09
H31	7.48	7.72	7.93	-0.24	-0.45	7.43	7.66	0.05	-0.18
H32	7.49	7.74	7.92	-0.25	-0.43	7.36	7.53	0.13	-0.04
H33	7.84	8.17	8.35	-0.33	-0.51	7.36	7.57	0.48	0.27
H34	2.71	2.86	3.04	-0.15	-0.33	1.36	1.63	1.35	1.08
H35	2.71	3.27	3.28	-0.56	-0.57	1.94	2.04	0.77	0.67
H36	1.24	1.41	1.60	-0.17	-0.36	0.63	0.86	0.61	0.38
H37	1.24	1.83	1.76	-0.59	-0.52	1.09	0.98	0.15	0.26
H38	1.24	1.92	1.84	-0.68	-0.60	0.98	0.89	0.26	0.35

Therefore the (R^2) values (DFT/HF) for ^{1}H NMR, ^{13}C NMR, ^{1}H NMR (DMSO) and ^{13}C NMR (DMSO) chemical shifts in different solvents has been found as 0.8140/0.8150, 0.9833/0.9795, 0.8505/0.8387 and 0.9821/0.9761 for the compound **3** (Table 5 and Figure 4). In our study, the ^{1}H-NMR spectrum of compound 3 was observed belong to H21 proton peak at 11.86 ppm because acidic show feature (Beytur et al., 2019; Çiftçi et al., 2018; Yüksek et al., 2006a; Yüksek, 1992). H22 protons were observed at 9.77 ppm. Since the values of coupling constants 6.92 and 7.92 ppm in about (*J*) 16.00 Hz alkenic concluded that the trans position of protons H27 and H28 (Balcı, 2011). Therotically, in vacum and DMSO solvents these values for the mentioned proton atoms were found as 6.71/6.14, 8.02/7.98 and 6.86/6.32, 8.08/8.04 ppm, respectively. In Table 4, the biggest ^{13}C chemical shift value of the compound **3** are observed at 164.65 ppm for the C10 carbon atom double bounded to the oxygen in carbonyl group (Anderson et al., 2004). In vacum and DMSO solvents the calculated ppm values (DFT/HF) for C10 carbon atom were theoretically found as 166.01/156.23 and 167.28/157.88 ppm, respectively. Similarly, the NMR chemical shift values (DFT/HF) for C11 and C12 carbon atoms of trans alkenic H28 (Balcı, 2011) bounded to other oxygen atoms in the compound **3** are observed at 116.90 and 146.85 ppm, while in vacum and DMSO solvents these values for the mentioned carbon atoms were found as 119.96/107.98, 152.85/148.18 and 119.17/107.26, 154.37/149.153 ppm, respectively. Additionaly, due to the electronegative property of nitrogen atoms in molecule, the experimental NMR chemical shift values for C1 and C2 carbon atom the bounded to nitrogen atoms in 1,2,4–triazol ring and C3 carbon atom with sp^2 hybride are observed at 148.04 and 152.68 ppm and 151.38 ppm, respectively . The ^{1}H-NMR and ^{13}C NMR spectrum of the title compound are given in Figure 3.

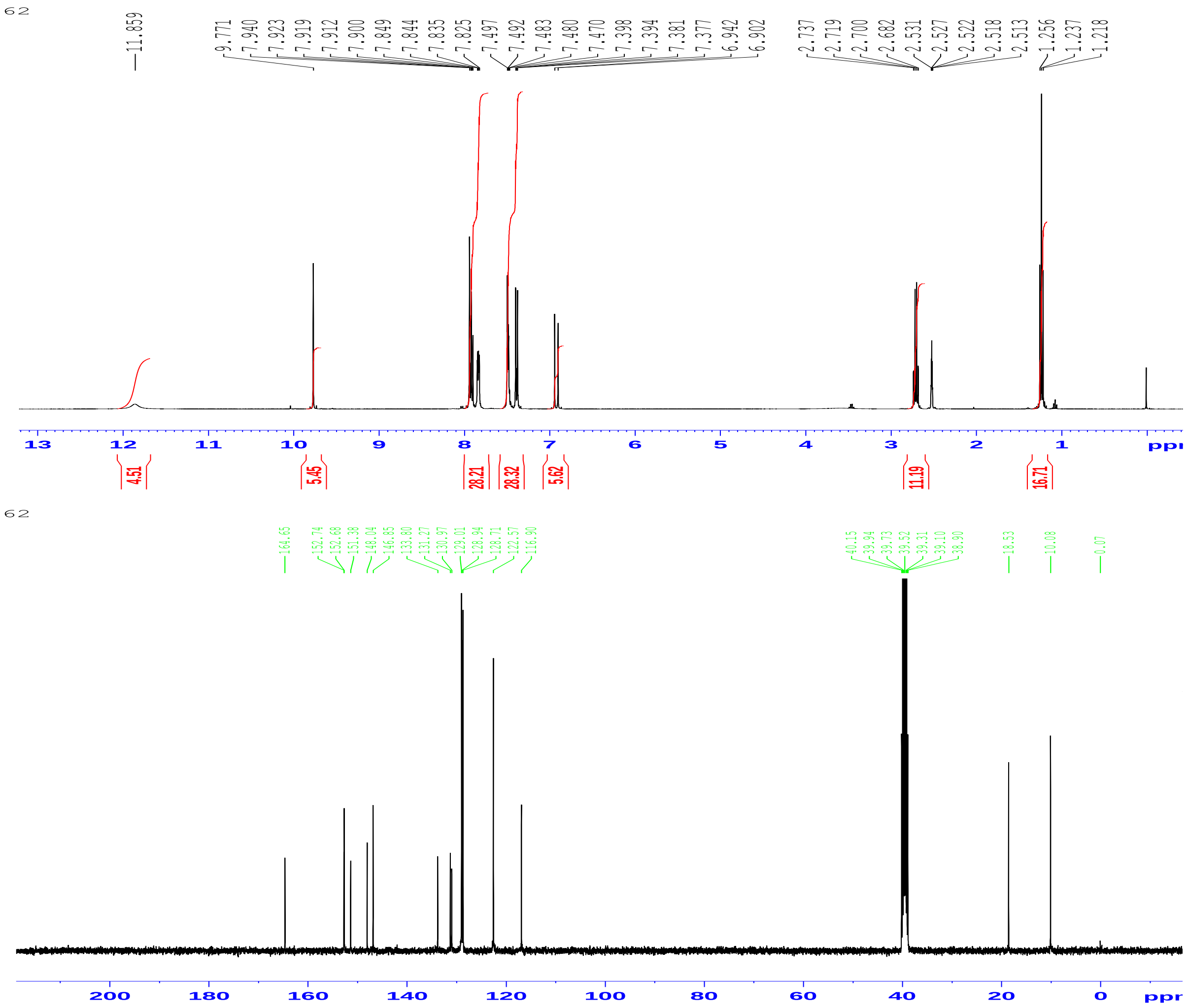
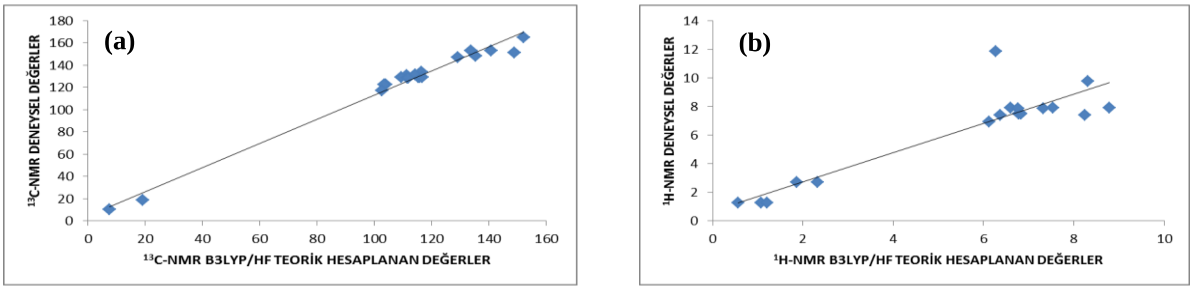


Figure 3. ^{1}H and ^{13}C-NMR (DMSO-d$_6$) spectra of the titled compound (3).



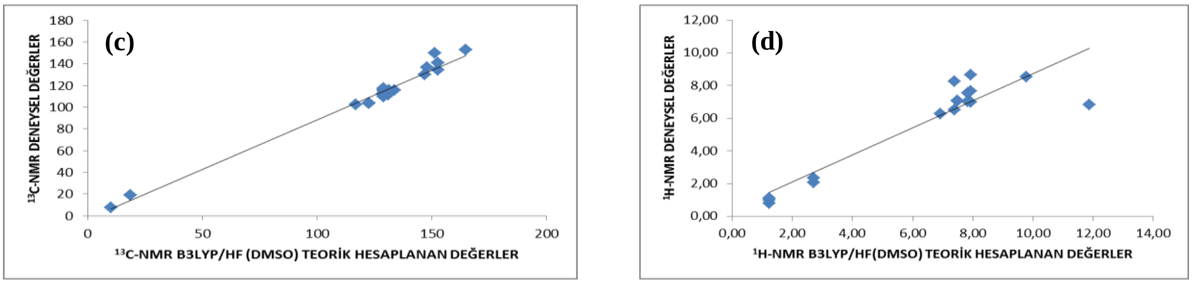


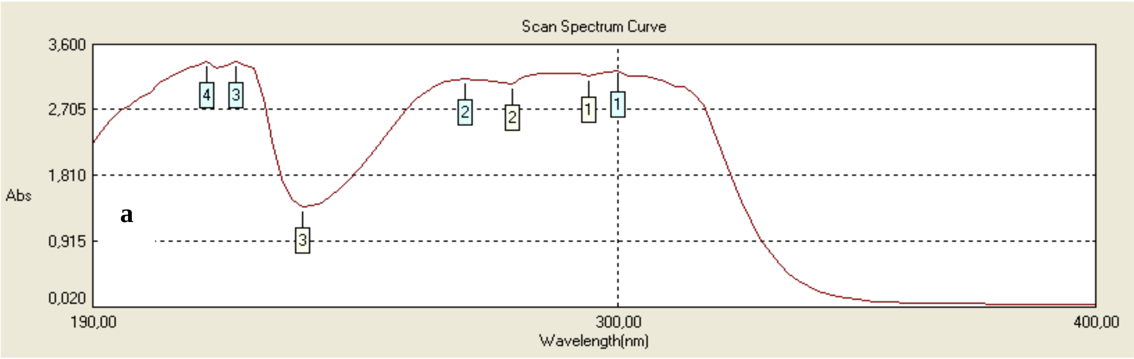
Figure 4. The correlation graphics according to ^{13}C-NMR (a), ^{1}H-NMR (b), ^{13}C-NMR (DMSO) (c) and ^{1}H-NMR (DMSO) (d) chemical shifts of the titled compound (3).

Table 5. The correlation data for chemical shifts of the titled compound (3).

	^{13}C NMR					^{1}H NMR			
	Methods	**R**	**S. error**	**a**	**b**	**R**	**S. error**	**a**	**b**
3	**DFT**	0,9916	5,2627	1,0840	4,6544	0,9022	1,3855	1,0197	0,6998
	HF	0,9897	5,8031	0,9747	5,8456	0,9028	1,3817	0,9581	0,9064
3	**DFT(DMSO)**	0,9910	5,4444	1,0756	5,2136	0,9222	1,2423	1,0258	0,4975
	HF(DMSO)	0,9880	6,2646	0,9618	6,9266	0,9158	1,2899	0,9595	0,7475

3.4. UV–visible Spectroscopy

The title molecule allow strong $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions in UV–vis region with high extinction coefficients (Silverstein, et al., 1991). The experimental absorption wavelengths of the compound **3** in ethanol solvent have been observed at 300, 262 and 216 nm. The absorption wavelengths (λ) excitation energies, and oscillator strengths (*f*) of UV–vis absorption spectroscopy of the compound **3** has been calculated in ethanol solvents by using TD–DFT/B3LYP and TD–HF method. The calculated absorption wavelengths for the compound **3** were found as 372.61/241.21, 324.69/218.93 and 317.07/215.07 nm in ethanol solvent. The experimental and calculated UV parameters of the compound **3** are given in Table 3. The calculated and experimental UV spectrums of the compound 3 are given in Figure 5.



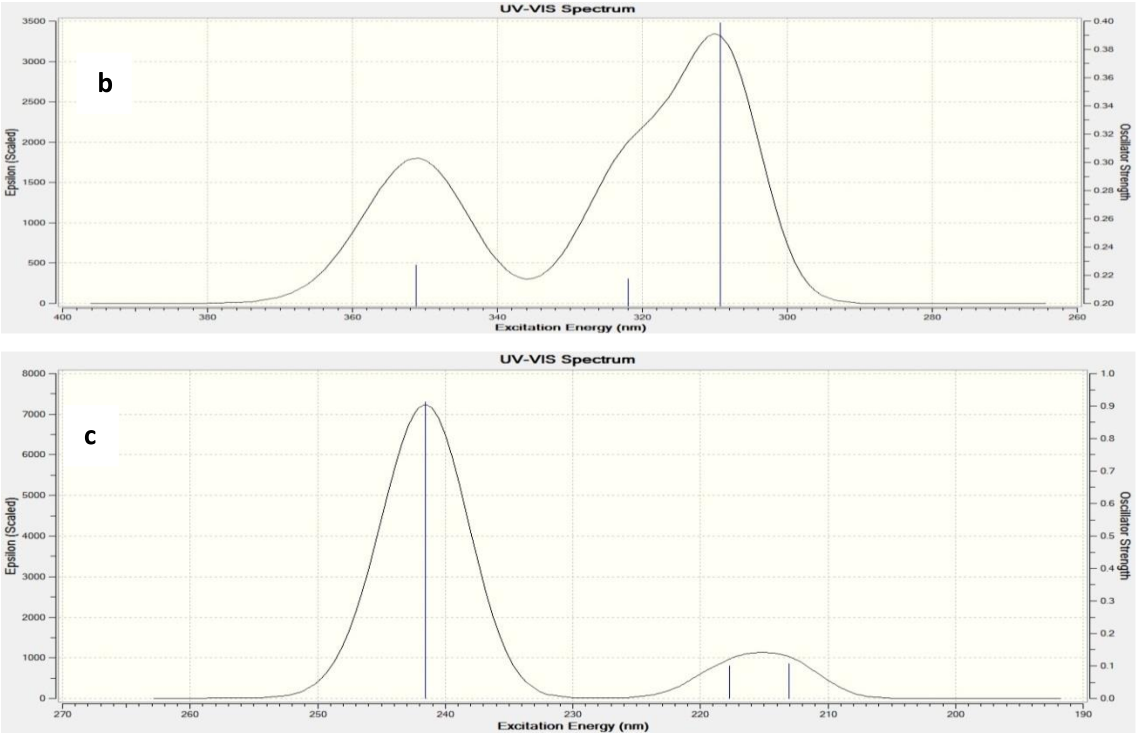


Figure 5. UV-Visible spectra (a) experimental and (b and c) simulated with DFT/B3LYP/6-31G(d) and HF/6-31G(d) levels of the titled compound (3).

Table 6. The experimental and calculated absorption wavelength (λ), excitation energies and oscillator strengths (*f*) the titled compound (3).

Exp. (in ethanol)	**The calculated with B3LYP/6–31G(d) level in vacum / ethanol solvents**		
λ (nm)/ε (L.mol^{-1}.cm^{-1})	**λ (nm)**	**Excitation energy (eV)**	***f*** **(oscillator strength)**
300 / 22563	372.61/241.21	3.3274/5.1402	0.0601/0.8828
262/ 20156	324.69/218.93	3.8185/5.6632	0.0073/0.0569
214 / 11869	317.07/215.07	3.9104/5.7648	0.6969/0.0107

3.5. Mulliken's Atomic Charges

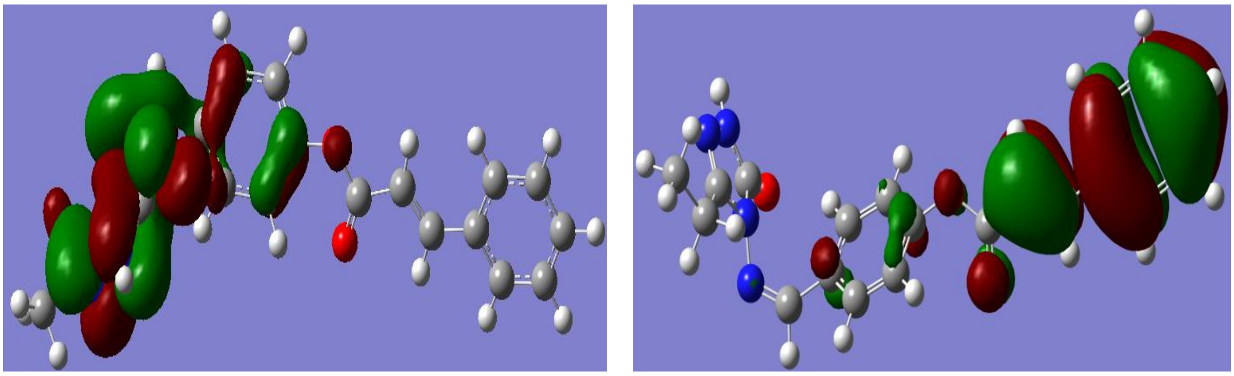
The Mulliken atomic charges at the HF/6-31 G(d) and B3LYP/6-31 G(d) level of compound 3 in gas phase are given in Table 7 (Mulliken, 1955). The electronegative N39, N40, N41, N42, O43, O44 and O45 atoms of compound **3** have negative atomic charge values. The Mulliken atomic charges (DFT/HF) of the mentioned atoms were calculated as -0.498/-0.638, -0.341/-0.349, -0.443/-0.644, -0.258/-0.253, -0.526/-0.657, -0.542/-0.701 and -0.479/-0.571 a.u., respectively. The C1, C2, C3, C7, and C10 carbon atoms bounded to the mentioned electronegative atoms in the molecule under study have positive atomic charge values. The values of the positive charges of the mentioned carbon atoms were found as 0.552/0.619, 0.771/1.026, 0.003/0.121, 0.359/0.410 and 0.619/0.815 a.u., respectively. Therefore the C1 atom surrounded with two electronegative N40 and N41 atoms, the C2 atom surrounded with the electronegative N39, N41 and O43 atoms and the C10 atom surrounded with two electronegative O44 and O45 atoms have the highest positive charge values. In the compound **3** the atomic charges of all hydrogen atoms have positive values.

Table 7. Mulliken atomic charges of the titled compound (3).

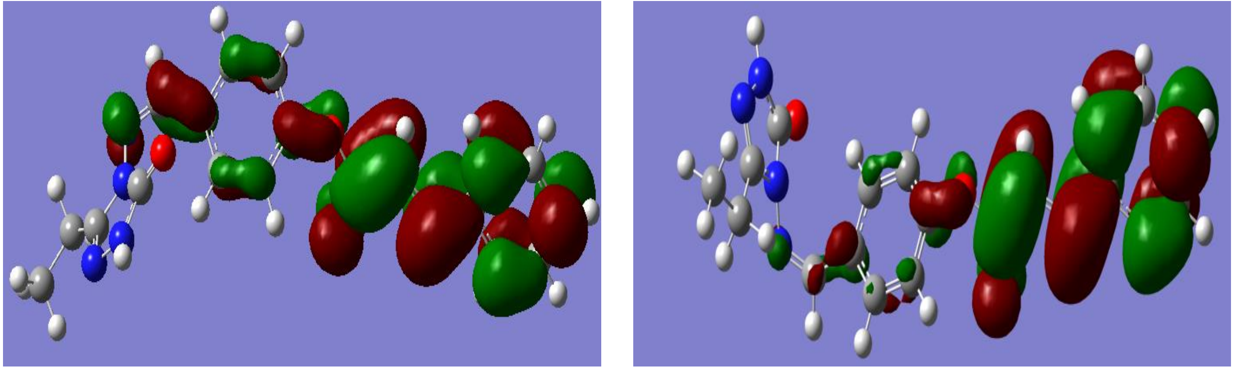
	DFT	HF		DFT	HF		DFT	HF
Atoms	**Charges (a.u.)**		**Atoms**	**Charges (a.u.)**		**Atoms**	**Charges (a.u.)**	
C1	0.552	0.619	**C16**	-0.122	-0.192	**H31**	0.140	0.211
C2	0.771	1.026	**C17**	-0.131	-0.203	**H32**	0.140	0.211
C3	0.003	0.121	**C18**	-0.185	-0.215	**H33**	0.143	0.216
C4	0.200	-0.062	**C19**	-0.331	-0.369	**H34**	0.165	0.192
C5	-0.171	-0.212	**C20**	-0.441	-0.484	**H35**	0.181	0.208
C6	-0.143	-0.246	**H21**	0.353	0.416	**H36**	0.145	0.168
C7	0.359	0.410	**H22**	0.157	0.221	**H37**	0.163	0.184
C8	-0.169	-0.211	**H23**	0.156	0.298	**H38**	0.164	0.184
C9	-0.196	-0.213	**H24**	0.168	0.231	**N39**	-0.498	-0.638
C10	0.619	0.815	**H25**	0.147	0.237	**N40**	-0.341	-0.349
C11	-0.215	-0.349	**H26**	0.142	0.218	**N41**	-0.443	-0.644
C12	-0.146	-0.119	**H27**	0.155	0.223	**N42**	-0.258	-0.253
C13	0.166	0.016	**H28**	0.170	0.246	**O43**	-0.526	-0.657
C14	-0.169	-0.202	**H29**	0.138	0.213	**O44**	-0.542	-0.701
C15	-0.131	-0.204	**H30**	0.140	0.210	**O45**	-0.479	-0.571

3.6. Frontier molecular orbital analysis

The energies of two important molecular orbitals of the molecule; the second highest and highest occupied MO’s (HOMO), the lowest and the second lowest unoccupied MO’s (LUMO) were calculated by using DFT/B3LYP and HF methods with 6-31G(d) level and are presented in Figure 6. The energy gap of the title molecule was calculated at DFT/B3LYP and HF level, which reveals the chemical reactivity and proves the occurrence of eventual charge transfer. The HOMO is located almost over the carbon atoms, oxygen atoms and also slightly delocalized in hydrogen atom and the LUMO is mainly delocalized in carbon atoms of benzene ring. The energy gap (energy difference between HOMO and LUMO orbital) is a critical parameter in determining molecular electrical transport properties (Fukui, 1982). The HOMO-LUMO energy gap of the title molecule is found to 0.1652/0.4443 a.u. obtained at DFT/HF method with 6-31G(d) levels.



E_{HOMO} (B3LYP) :-0,23984 Hatree E_{HOMO} (HF) : -0,36644 Hatree



E_{LUMO} (B3LYP) : -0,07464 Hatree E_{LUMO} (HF) : 0,07788 Hatree

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

3.7. Dipole moment and total energy

The energetic behavior of title molecule was investigated in vacum. Dipol moments and total energy values of title molecule were calculated by using B3LYP/6-31G(d), HF/6-31G(d) level. The calculated dipole moments and total energy values are given in Table 8.

Table 8. The calculated dipole moment values and total energy of the titled compound (3).

Dipole Moment	B3LYP	HF
μ_x	1.0680	0.2597
μ_y	0.6420	1.8129
μ_z	0.2154	1.1321
μ_{Toplam}	1.2646	2.1531
Energy	-1217.608	-1210.197

4. CONCLUSION

In this paper, 3-ethyl-4-(4-cinnamoyloxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one (3) was synthesized from the reaction of compound (1) with 4-cinnamoyloxybenzaldehyde. The structure of the titled compound is characterized by using ^{1}H, ^{13}C NMR, FT-IR and UV spectroscopic methods. The molecular structures, vibrational frequencies, ^{1}H and ^{13}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 (3) 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 ^{1}H and ^{13}C NMR chemical shifts, vibrational frequencies, and UV spectroscopic parameters obtained theoretically are in a very good agreement with the experimental data.

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