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Theoretical and Experimentical Properties of 3-Ethyl-4-(3-Acetoxy-4-Methoxy-Benzylidenamino)-4,5-Dihydro-1*H*-1,2,4-Triazol-5-One

Songul ULUFER BULUT
Kafkas University

Murat BEYTUR
Kafkas University

Haydar YUKSEK
Kafkas University

Abstract: In the theoretical study, the 3-ethyl-4-(3-acetoxy-4-methoxy-benzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one has been optimized using B3LYP/6-311G(d) basis set. ^{1}H-NMR and ^{13}C-NMR isotropic shift values were calculated by the method of GIAO using the program package Gaussian G09. Experimental and theoretical values were inserted into the graphic according to equitation of δ exp=a+b. δ calc. The standard error values were found via SigmaPlot program with regression coefficient of a and b constants. IR absorption frequencies of this compound were calculated with same method. Theoretically calculated IR data are multiplied with appropriate adjustment factors and the data obtained according to DFT method are formed using theoretical infrared spectrum. The veda4f program was used in defining IR data which were calculated theoretically. The thermodynamic parameters, HOMO and LUMO energies, electronic properties, Mulliken atomic charges of titled compound has been investigated by using Gaussian 09W program. The spectroscopic data of this compound has been calculated by using 6-311G(d) basis set with density functional method (DFT/B3LYP) and compared with experimental values.

Keywords: Schiff base, B3LYP, Spectroscopic, Thermodynamic, Mulliken

Introduction

Heterocyclic compounds are defined as cyclic compounds consisting of carbon and heteroatom within a ring. They exhibit a variety of chemical and biological applications as a result of their structural diversity (Bahçeci et al., 2016; Koç et al., 2019; Bahçeci et al., 2017; Beytur et al., 2019; Çiftçi et al., 2018; Beytur et. al., 2021; Beytur, 2020; Turhan Irak et. al., 2019; Uğurlu et. al.,, 2020; Boy et al, 2021). 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 method with 6-311G(d) basis set. All quantum chemical calculations were carried out by using Gaussian 09W (Frisch et al., 2009; Wolinski et. al., 1990) program package and the GaussView molecular visualization program (Frisch et. al., 2003). The molecular structure and vibrational calculations of the molecule were computed by using Becke-3-Lee Yang Parr (B3LYP) (Becke, 1993; Lee et. al., 1988) density functional method with 6-311G(d) basis set in ground state. IR absorption frequencies of analyzed molecule were calculated. 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 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 (Jamróz, 2004).

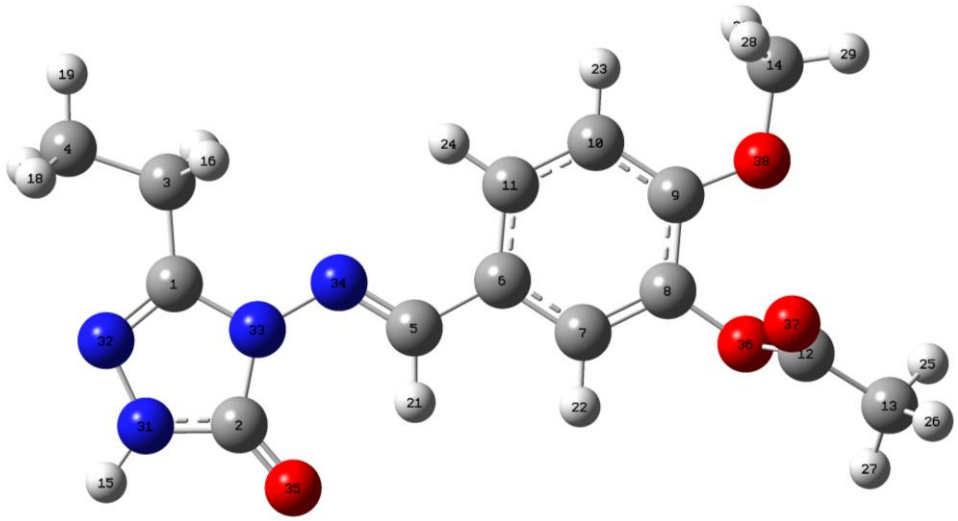


Figure 1. The optimized molecular structure of titled molecule with DFT 6–311G(d,p) level.

Table 1. The calculated and experimental ^{13}C and ^{1}H NMR isotropic chemical shifts of the molecule.

No	Experim.	DFT/6311(d)/DMSO	Diff./DMSO
1C		153,83	-153,83
2C		153,81	-153,81
3C		21,96	-21,96
4C		7,67	-7,67
5C		151,70	-151,70
6C		130,76	-130,76
7C		129,84	-129,84
8C		145,67	-145,67
9C		159,97	-159,97
10C		113,83	-113,83
11C		126,30	-126,30
12C		174,08	-174,08
13C		20,30	-20,30
14C		54,33	-54,33
15H	11,74	6,74	5,00
16H	2,55	2,49	0,06
17H	2,60	2,50	0,10
18H	1,20	0,98	0,22
19H	1,20	0,92	0,28
20H	1,20	0,99	0,21
21H	9,49	9,42	0,07
22H	7,10	6,75	0,35
23H	6,98	6,62	0,36
24H	7,51	7,83	-0,32
25H	2,45	2,10	0,35
26H	2,30	1,36	0,94
27H	2,4	2,01	0,39
28H	3,86	3,34	0,52
29H	3,86	3,76	0,10
30H	3,86	3,47	0,39

Method

The molecular structure of the title compound in the ground state (in vacuo) is computed by performing the density functional theory (DFT) by a hydrid functional B3LYP functional (Becke's three parameter hybrid functional using the LYP correlation functional) methods (Becke, 1993; Lee et. al., 1988) at 6-311G(d) level.

Results and Discussion

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 (Rani et al., 2010; Subramanian et. al., 2010; Wade, 2006). In this framework, the optimized molecular geometry of the molecule was obtained by using B3LYP method with 6-311G(d) basis level in DMSO solvent. By considering the optimized molecular geometry of the title compound the ^{1}H and ^{13}C NMR chemical shift values were calculated at the same level by using Gauge-Independent Atomic Orbital (GIAO) method (Table 1). Theoretical and experimental (Bahçeci et al., 2017) 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.

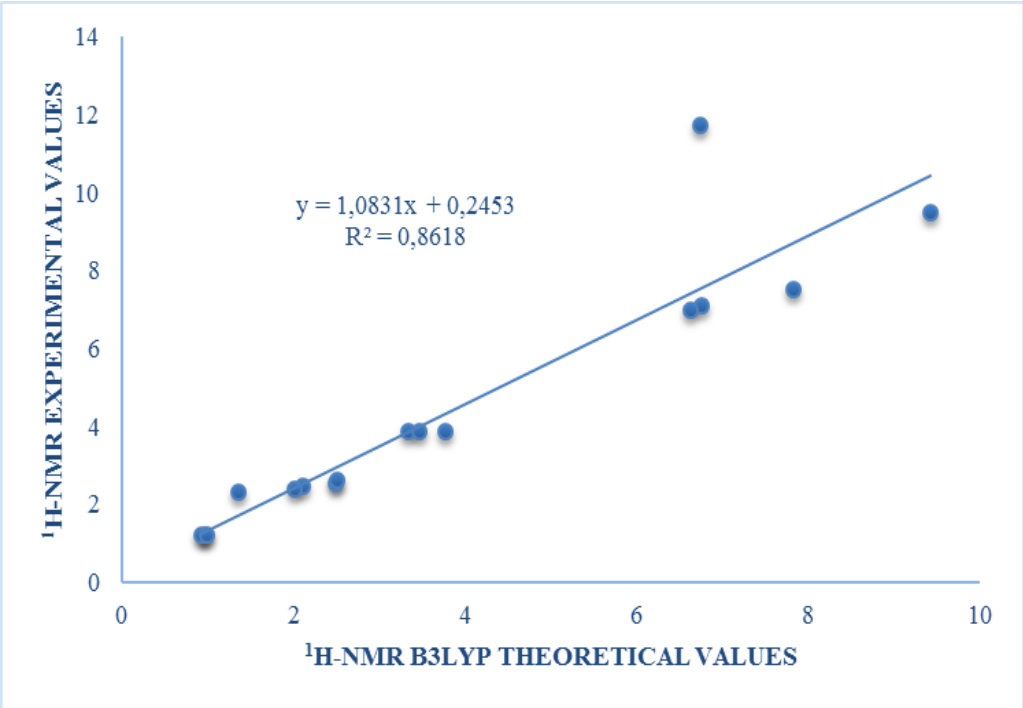


Figure 2**.** The correlation graphics for ^{1}H-NMR (DMSO) chemical shifts of the molecule

Vibrational frequencies

The 3-ethyl-4-(3-acetoxy-4-methoxy-benzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one has 38 atoms and the number of the normal vibrations are 108. The observed and calculated vibrational frequencies, the calculated IR intensities and assignments of selected vibrational frequencies for title compound are summarized in Table **2**.

Table 2. The calculated frequencies values of the molecule.

Selected Vibrational Types	Experimental	scaled DFT
ν $O_{36}C_8$, $O_{36}C_{12}$ (10)	1270	1208
ν $O_{36}C_8$, $O_{36}C_{12}$ (22)	1270	1308
ν $N_{32}C_1$, $N_{34}C_5$ (48)	1605	1644
ν $N_{32}C_1$, $N_{34}C_5$ (31)	1605	1649
ν $N_{32}C_1$, $N_{34}C_5$ (37)	1605	1671
ν $O_{35}C_2$ (73)	1710	1806
ν $O_{37}C_{12}$ (88)	1760	1850
ν $N_{31}H_{15}$ (100)	3190	3691

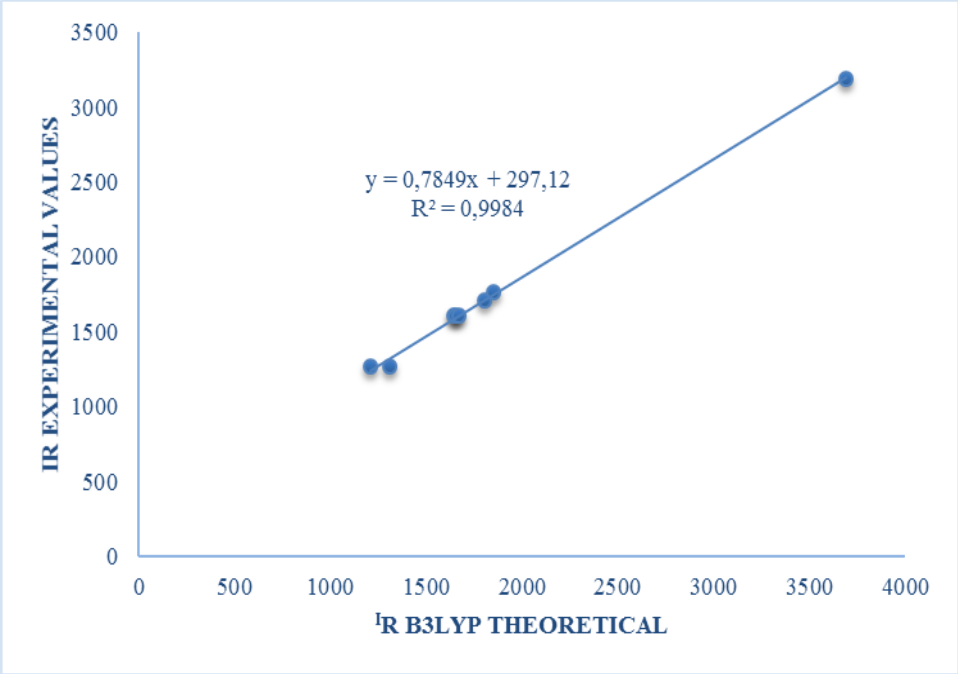
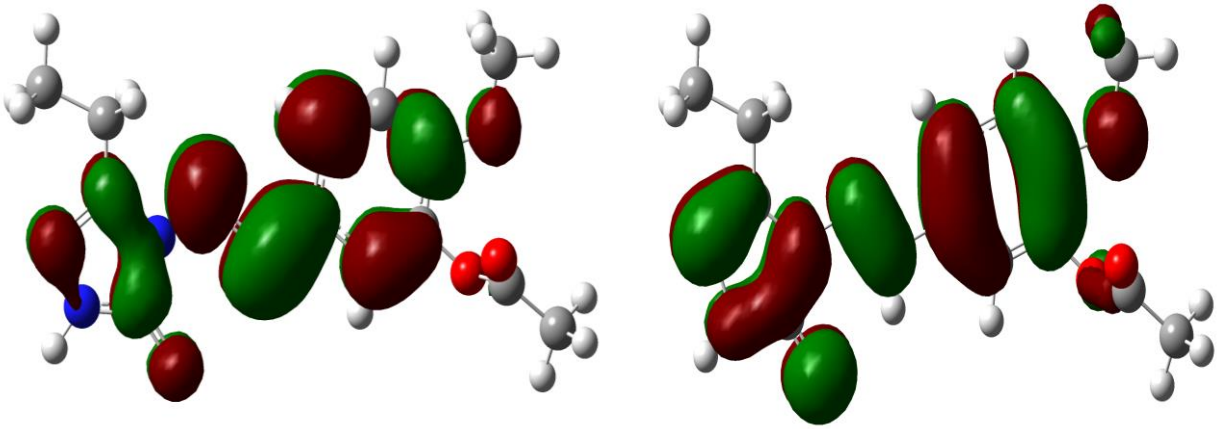


Figure 3. The correlation graphic for vibrational frequencies of the titled compound.

Electronic Properties



E_{LUMO} (B3LYP): -37.234 Kcal/mol E_{LUMO} (B3LYP): -136.82 Kcal/mol

Figure 3. The calculated HOMO-LUMO energies of the molecule according to DFT/B3LYP/6-31G(d) level

Table 3. Electronic properties of the molecule

	DFT (kcal/mol)
Ionization Potential	136.82
Electron Affinity	37.27
Electronegativity	87.05
Chemical hardness	99.55

Table 4. The calculated dipole moment values of the molecule

Dipole Moment	B3LYP (a.u.)
μ_x	1.6480
μ_y	3.0189
μ_z	-1.1653
μ_{Toplam}	3.6315

Table 5. Mulliken atomic charges of the molecule

Atoms	DFT	Atoms	DFT	Atoms	DFT
1C	0.4347	14C	-0.4626	27H	0.2375
2C	0.5819	15H	0.3700	28H	0.2210
3C	-0.4685	16H	0.2321	29H	0.2337
4C	-0.6179	17H	0.2312	30H	0.2128
5C	-0.0602	18H	0.2200	31N	-0.4961
6C	-0.0146	19H	0.2083	32N	-0.2064
7C	-0.2260	20H	0.2198	33N	-0.3734
8C	0.2083	21H	0.2580	34N	-0.2106
9C	0.2731	22H	0.2099	35O	-0.3945
10C	-0.2712	23H	0.2182	36O	-0.3552
11C	-0.1566	24H	0.2104	37O	-0.3158
12C	0.3912	25H	0.2409	38O	-0.3334
13C	-0.6885	26H	0.2387		

Table 6. The thermodynamic properties of the titled compound

Rotational temperatures (Kelvin)	B3LYP
A	0.0290
B	0.0052
C	0.0046
Rotational constants (GHZ)	
A	0.6041
B	0.1092
C	0.0948
Zero-point vibrational energy (Kcal/Mol)	186.0992
Thermal correction to Energy	0.3182
Thermal correction to Enthalpy	0.3191
Thermal correction to Gibbs Free Energy	0.2432
Sum of electronic and zero-point Energies	-1062.9562
Sum of electronic and thermal Energies	-1062.9346
Sum of electronic and thermal Enthalpies	-1062.9336
Sum of electronic and thermal Free Energies	-1063.0095
Thermal Energies E(Kcal/mol)	
Translational	0.889
Rotational	0.889
Vibrational	197.886
Total	199,663
Thermal Capacity CV(Cal/Mol-Kelvin	
Translational	2.981
Rotational	2.981
Vibrational	72.515
Total	78.477
Entropy S (Cal/Mol-Kelvin)	
Translational	43.033
Rotational	35.196
Vibrational	81.502
Total	159.732

Conclusion

The ^{1}H and ^{13}C NMR chemicals shifts, vibrational frequencies, HOMO and LUMO analyses and atomic charges of 3-ethyl-4-(3-acetoxy-4-methoxy-benzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one have been calculated by using DFT/B3LYP method. ^{1}H NMR chemical shifts parameters were obtained theoretically are in a very good agreement with the experimental data. Mulliken atomic charges of the titled compound have been investigated by the same basis set. Thermodynamic properties of analyzed molecule were calculated.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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Author Information

Songul ULUFER- BULUT
Kafkas University
Kars, Turkey
Contact e-mail: *sngulufer@gmail.com*

Murat BEYTUR
Kafkas University
Kars, Turkey

Haydar YUKSEK
Kafkas University
Kars, Turkey

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