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Investigation of Spectroscopic, Electronic and Geometric Properties of 2-(3-Methyl-4,5-Dihydro-1*h*-1,2,4-Triazol-5-On-4-Yl)-Azomethine)-Benzoic Acid using B3lyp and Hf Basis Sets

Gül Kotan^{1*}, Gül Özdemir², Haydar Yüksek²

¹Kafkas University, Kars Vocational School, Kars, Turkey

²Kafkas University, Department of Chemistry, Kars, Turkey

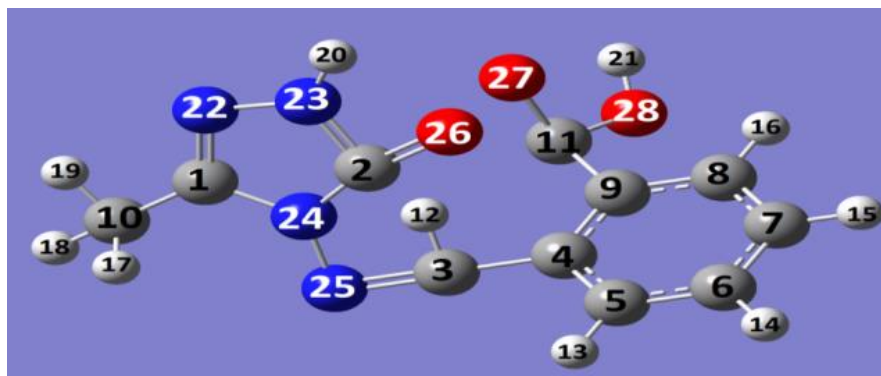
ABSTRACT

2-(3-Methyl-4,5-dihydro-1*h*-1,2,4-triazol-5-on-4-yl)-azomethine)-benzoic acid has been optimized using B3LYP/6-31G(d) and HF/6-31G(d) basis sets. Thus, the most stable geometrical conformer of compound was obtained. Proton Nuclear Magnetic Resonance (¹H-NMR) and Carbon-13 Nuclear magnetic Resonance (¹³C-NMR) spectral values according to GIAO method was calculated using Gaussian G09W program package in gas phase and in DMSO solvent. Theoretical and experimental values were plotted according to $\delta_{exp} = a + b \cdot d$ calc. Theoretical spectral values of molecule were calculated and compared with experimental values. The veda4f program was used in defining Infrared (IR) data. The standard error values were found via the Sigma plot with regression coefficient of a and b constants. The vibrational frequency values of this molecule have been calculated by using 6-31G (d) basis set with DFT and HF methods. Then, these values are multiplied with appropriate adjustment factors. In addition, the, thermodynamics properties (heat capacity CV^0 , entropy S^0 and enthalpy H^0), electronic properties (electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), $E_{LUMO} - E_{HOMO}$ energy gap (ΔE_g) and ionization potential (I), HOMO-LUMO energy), geometric properties (bond angles, bond lengths), dipole moments, mulliken atomic charges, total energy of the molecule were calculated with Gaussian 09W program on the computer.

Keywords: B3LYP, HF, GIAO, Mulliken charge, Veda4f.

INTRODUCTION

Schiff bases have an azomethine group (-CH=N-) which is synthesis by the condensation of a primary amine with a carbonyl compound. Schiff base compounds indicate a sort of biological properties [1,2] and have been used as bacteriocides, insecticides, pesticides, and fungicides [3,4]. Besides, the compounds including 1*h*-1,2,4-triazol group and their derivatives have very imported biological activities such as antioxidant [5-7] antibacterial [8-12], antifungal [13], anti-inflammatory [14], anti-HIV [15], antitumor [16], anticonvulsant [17], pharmacological activity [18], antiviral [12], antihypertensive [19], antitubercular [20] and analgesic [21,22] properties. In this study, we then investigated theoretically the structural, molecular, electronic, thermodynamics and vibrational properties of the synthesized compound. Experimental data obtained from the literature [23]. All quantum chemical calculations were conducted with the GaussView and Gaussian 09 packet programs [24,25]. For this, firstly, 2-(3-Methyl-4,5-dihydro-1*h*-1,2,4-triazol-5-on-4-yl)-azomethine)-benzoic acid molecule was optimized by using 631G (d,p) basis set of Density Functional Theory (DFT/B3LYP) and Hatree Fock (HF) methods. The subsequent theoretical calculations were made by targeting this optimized geometry which from this the most stable structure of the molecule. The optimized structure along with the atom numbering is given in Figure 1. Furthermore, the ¹H and ¹³C-NMR chemical shifts (Table 1) calculations were performed using the Gauge-Independent Atomic Orbital (GIAO) [26] with B3LYP/631G(d,p) and HF/631G(d,p) levels in ethanol. Theoretical and experimental values were inserted into the graphic according to equation of $\delta_{exp} = a + b \cdot \delta$ calc. The standard error values were found via Sigma Plot program with regression coefficient of a and b constants. The veda4f program [27] was used in defining of IR data theoretically and the theoretical vibrational (Table 2) spectra were calculated at the B3LYP/6-31G (d) in the gas phase, then scaled by 0.9617 and 0.8992 [28], while an identical scaling factors of 0.9617 and 0.8992 were applied for all B3LYP/DFT/HF6-31G (d) frequencies [29]. The data obtained according to calculate theoretically are formed using theoretical infrared spectrum. The experimental and theoretical IR spectra are given in Figure 2. The experimental and the calculated theoretical spectral values were compared and they were recorded to be compatible with each other. In addition to, geometric properties (bond angles, bond lengths and dihedral angles) (Tables 3 and 4), electronic properties ($E_{LUMO} - E_{HOMO}$) energy gap (ΔE_g), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), total energy of the molecule, dipole moment) (Figures 3-7 and Tables 5-8), thermodynamics properties, the highest occupied molecular orbital (HOMO) (Figure 8) and the lowest unoccupied molecular orbital (LUMO) (Figure 8), mulliken atomic charges have been examined by using Gaussian 09W program.

Method*Computational details***Figure 1: The Gauss view structure of the molecule****The IR data of the compound**

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), HF/631G(d) basis sets. All values are found positive. IR spectrums were drawn with obtained values according to HF and DFT method (Figure 2). Experimentally IR values were compared with theoretically IR values. In this compared were estimated corresponding with each other of values.

Table 1: The calculated and experimental ^{13}C and ^1H -NMR DMSO (B3LYP/HF 631G (d) isotropic chemical shifts

No.	Exp.	DFT/dms0	Differ/DFT	HF/dms0	Differ/HF
C1	144.34	150.39	-6.05	145.27	-0.93
C2	151.02	152.01	-0.99	145.61	5.41
C3	152.48	156.71	-4.23	153.80	-1.32
C4	133.61	142.23	-8.62	135.24	-1.63
C5	126.79	132.07	-5.28	125.35	1.44
C6	132.01	137.56	-5.55	132.65	-0.64
C7	130.71	134.78	-4.07	126.25	4.46
C8	131.52	137.02	-5.50	130.80	0.72
C9	130.17	132.37	-2.20	123.14	7.03
C10	11.06	22.90	-11.84	11.80	-0.74
C11	167.75	168.64	-0.89	158.67	9.08
H12	10.39	10.83	-0.44	9.96	0.43
H13	7.91	8.56	-0.65	8.00	-0.09
H14	7.65	8.13	-0.48	7.97	-0.32
H15	7.62	8.00	-0.38	7.76	-0.14
H16	8.01	8.63	-0.62	8.45	-0.44
H17	2.26	2.71	-0.45	2.00	0.26
H18	2.26	2.86	-0.60	2.22	0.04
H19	2.26	2.42	-0.16	1.83	0.43
H20	11.82	7.41	4.41	6.56	5.26
H21	11.82	6.67	5.15	5.83	5.99

Table 2: Significant vibrational frequencies (cm^{-1}) of the molecule

Vibration	Experimental	Theoretical DFT/HF
v (OH)	3528	3553/3622
v (NH)	3302	3541/3520
v (C=N)	1614	1610/1696
v (C=O)	1695-1652	1741/1792

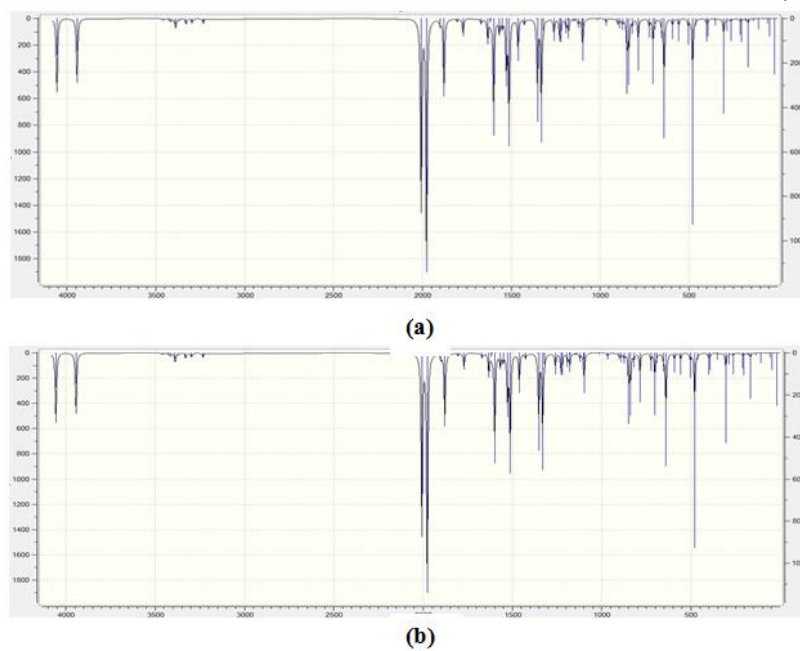


Figure 2: Theoretical IR spectrums and simulated with DFT/B3LYP/631G (d)(a) and HF/B3LYP/631G (d)(b) levels of the molecule

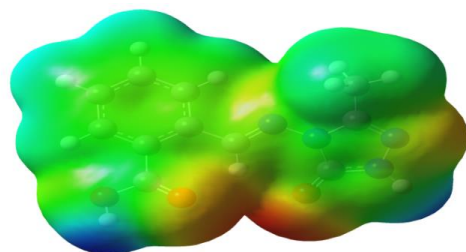


Figure 3: The MEP of the molecule

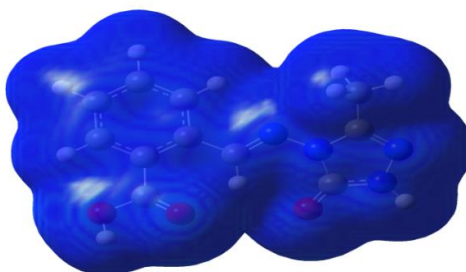


Figure 4: The Total density of the molecule

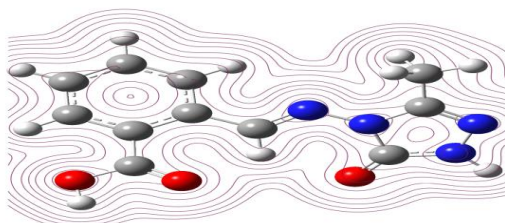


Figure 5: The Electron Density

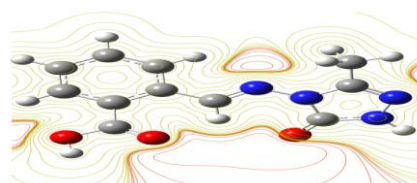


Figure 6: The Electrostatic Potential

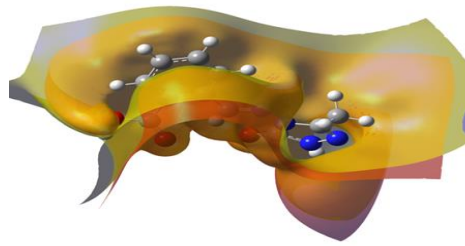


Figure 7: The ESP of the molecule

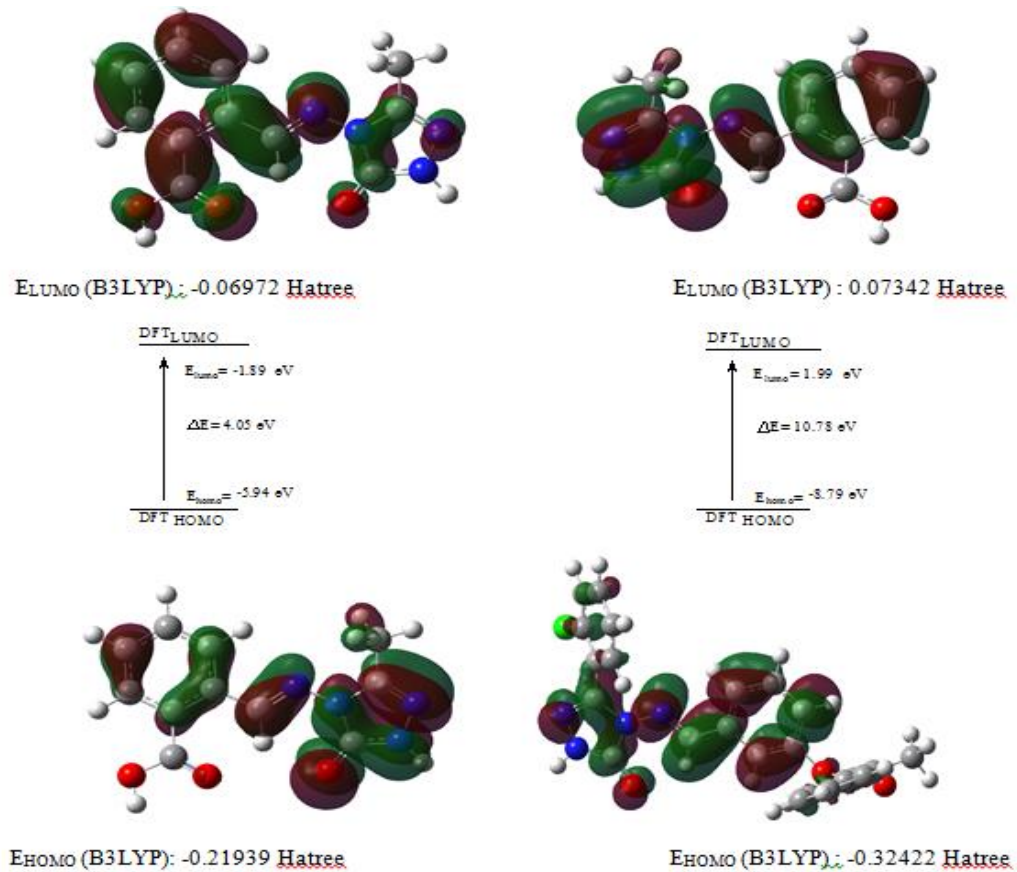


Figure 8: HOMO-LUMO energy gap

Table 3: The calculated bond angles of the molecule

Bond angles	B3LYP	HF	Bond angles	B3LYP	HF
N(22)-C(1)-N(24)	111.44	111.32	C(3)-C(4)-C(5)	121.42	118.63
N(22)-N(23)-H(20)	120.24	120.75	C(3)-C(4)-C(9)	122.57	122.68
C(22)-N(23)-C(2)	114.64	113.81	C(4)-C(5)-H(13)	118.04	118.77
N(23)-C(2)-O(26)	130.11	129.63	C(4)-C(5)-C(6)	121.42	121.03
O(26)-C(2)-N(24)	128.91	128.61	C(5)-C(6)-H(14)	119.74	119.63
N(23)-C(2)-N(24)	100.97	101.75	C(5)-C(6)-C(7)	120.05	120.18
N(22)-C(1)-C(10)	125.12	125.46	H(14)-C(6)-C(7)	120.20	120.17
C(1)-C(10)-H(17)	111.09	110.58	C(6)-C(7)-H(15)	120.47	120.48
C(1)-C(10)-H(18)	111.02	110.57	H(15)-C(7)-C(8)	119.96	119.97
C(1)-C(10)-H(19)	108.67	108.66	C(7)-C(8)-H(16)	120.16	119.95
C(1)-N(24)-C(2)	108.41	108.32	C(7)-C(8)-C(9)	120.97	120.72
C(24)-N(25)-C(3)	118.41	118.64	C(9)-C(11)-O(27)	126.08	125.13
N(25)-C(3)-H(12)	122.60	122.87	C(9)-C(11)-O(28)	112.63	113.25
H(12)-C(3)-C(4)	119.44	119.08	C(11)-O(28)-H(21)	105.31	107.66

Table 4: The calculated bond lengths of the molecule

bond lengths	DFT	HF	bond lengths	DFT	HF
C(1)-N(22)	1.300	1.269	C(3)-C(4)	1.475	1.486
C(1)-N(24)	1.388	1.377	C(4)-C(5)	1.405	1.389
C(1)-C(10)	1.487	1.488	C(4)-H(13)	1.084	1.072
N(22)-N(23)	1.381	1.371	C(5)-C(6)	1.390	1.383
N(23)-H(20)	1.007	0.992	C(6)-H(14)	1.086	1.075
N(23)-C(2)	1.371	1.347	C(6)-C(7)	1.396	1.383
C(2)-N(24)	1.421	1.387	C(7)-H(15)	1.086	1.074
C(2)-O(26)	1.220	1.200	C(7)-C(8)	1.391	1.382
N(24)-N(25)	1.371	1.368	C(8)-H(16)	1.083	1.071
C(10)-H(17)	1.095	1.083	C(8)-C(9)	1.403	1.390
C(10)-H(18)	1.095	1.083	C(8)-C(11)	1.489	1.490
C(10)-H(19)	1.091	1.080	C(11)-O(27)	1.215	1.190
N(25)-C(3)	1.290	1.259	C(11)-O(28)	1.359	1.329
C(3)-H(12)	1.083	1.069	O(28)-H(21)	0.975	0.952

Table 5: The calculated total energy datas B3LYP/HF of the molecule

Enerji (a.u.)	DFT	HF
	-869.8542	-864.7481

Table 6: The calculated dipole moments datas of the molecule

	μ_x	μ_y	μ_z	μ_{Toplam}
Dft	-1.5832	2.8439	1.1798	3.4622
Hf	2.4571	-1.6573	-2.496	3.8748

Table 7: The calculated mulliken charges datas B3LYP/HF 631G (d,p) of the molecule

	DFT	HF		DFT	HF
C1	0.544	0.607	H15	0.143	0.217
C2	0.189	1.048	H16	0.168	0.251
C3	0.046	0.117	H17	0.183	0.203
C4	0.078	-0.018	H18	0.180	0.201
C5	-0.166	-0.200	H19	0.184	0.210
C6	-0.120	-0.183	H20	0.356	0.417
C7	-0.126	-0.204	H21	0.415	0.474
C8	-0.170	-0.182	N22	-0.321	-0.340
C9	0.032	-0.144	N23	-0.519	-0.659
C10	-0.507	-0.522	N24	-0.411	-0.622
C11	0.534	0.790	N25	-0.303	-0.290
H12	0.237	0.299	O26	-0.531	-0.651
H13	0.159	0.238	O27	-0.469	-0.568
H14	0.143	0.218	O28	-0.579	-0.708

The relation between R values

B3LYP/631G (d,p) (DMSO): ^{13}C : 0.997, ^1H : 0.651; HF/631G (d,p) (DMSO): ^{13}C : 0.992, ^1H : 0.598. There is such a relationship between R-values of the compound. Found standard error rate R and a, b constants regression values were calculated according to formule $\exp = a + b \cdot \delta$ calc Eq. These values for compound were summarized in the Table 9. Theoretical and experimental ^1H and ^{13}C chemical shifts ratios between according to R and a, b values, linear correlations (Figure 9) were observed.

Table 8: The calculated electronic structure parameters with DFT/B3LYP/631G (d) of the molecule

	Hatree	ev	kcal/mol	KJ/mol
LUMO	-0.06972	-189.713	-437.495	-183.05
HOMO	-0.21939	-596.976	-137.668	-576.008
A=electron affinity	0.06972	189.713	437.495	183.05
I=ionization potential	0.21939	596.976	137.668	576.008
ΔE =energy gap	0.14967	407.263	939.184	392.959
χ =electronegativity	0.144555	393.344	907.087	379.529

Pi=chemical potential	-0.144555	-393.344	-907.087	-379.529
ω =electrophilic index	0.000781882	0.02128	0.49063	205.283
IP=Nucleophilic index	-0.01081777	-0.29436	-678.819	-284.021
S=molecular softness	133.627	363.609	8385.15	35083.9
η =molecular hardness	0.074835	203.631	469.592	196.479

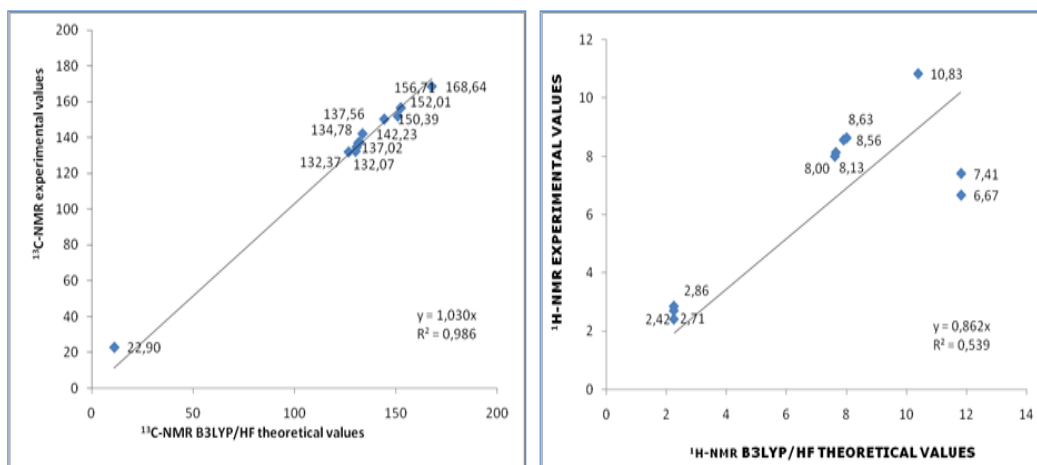


Figure 9: The correlation graphs for B3LYP/HF 631G (d) chemical shifts

Table 9: The correlation data for chemical shifts

	¹³ C				¹ H			
	R	S. hata	a	b	R	S. hata	a	b
DFT	0.997	2.215	1.063	-13.5	0.651	2.358	0.337	1.036
HF	0.992	3.837	1.024	-1.047	0.598	2.53	1.303	0.973

Investigation of thermodynamics properties of compound

Thermodynamics parameters of molecule calculated with B3LYP/DFT631G (d) and B3LYP/HF631G (d) basis sets and shown in the Table 10. Thermodynamic parameters of molecule (Table 10) (such as thermal energy, zero-point vibrational energies (ZPVE), heat capacity, entropy, rotational temperatures and rotational constants) were calculated 298.150 K and 1 atm of pressure. In addition to, the standard thermodynamic functions of heat capacity CV^0 , entropy S^0 and enthalpy H^0 were obtained at the B3LYP/DFT/HF 631G (d,p) level.

Table 10: The calculated thermodynamics parameters of the molecule

Rotational temperatures (Kelvin)	DFT	HF
A	0.03712	0.03764
(B	0.01158	0.0115
C	0.00922	0.00966
Rotational constants (GHZ)	DFT	HF
A	0.77344	0.78431
B	0.24128	0.23969
C	0.19214	0.20137
Thermal Energies E(kcal/mol)	DFT	HF
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	139.66	149.712
Total	141.437	151.489
Thermal Capacity CV(cal/mol-K)	DFT	HF
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	52.793	48.68

Total	58.755	54.641
Entropy S(cal/mol-K)	DFT	HF
Translational	42.402	42.402
Rotational	33.46	33.407
Vibrational	53.711	49.924
Total	129.574	125.733
Zero-point correction (Hartree/Particle)	0.209677	0.226634
Thermal correction to Energy	0.225394	0.241414
Thermal correction to Enthalpy	0.226339	0.242358
Thermal correction to Gibbs Free Energy	0.164774	0.182618
Sum of electronic and zero-point Energies	-869.644549	-864.521565
Sum of electronic and thermal Energies	-869.628832	-864.506786
Sum of electronic and thermal Enthalpies	-869.627888	-864.505841
Sum of electronic and thermal Free Energies	-869.689453	-864.565581
Zero-point vibrational energy (Kcal/mol)	131.57455	142.21514

CONCLUSION

In this work, geometrical parameters and spectroscopic parameters such as IR, ¹H-NMR and ¹³C-NMR spectra of molecule are calculated by Density Functional Theory (DFT) and Hartree-Fock (HF) methods with the 631G (d) basis sets of the program package Gaussian G09W. Obtained spectroscopic parameters are compared with experimental data. Otherwise, calculated theoretical properties of the compound according to two different basis sets were compared. In the result, the obtained data with B3LYP/HF631G (d) basis sets were found to be closer to the experimental data. The chemical shifts in the calculations ¹H-NMR and ¹³C-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 R² and a, b values, linear correlation were observed. The positive frequency in the IR data was found. This result, structures of compound were shown stable. In addition, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), bond lengths, bond angles, mulliken charges, E_{LUMO}-E_{HOMO} energy gap (ΔE_g), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), total energy of the molecule, thermodynamics properties (thermal energies (E), entropy (S), thermal capacity (CV), dipole moments were calculated B3LYP/HF 631G (d) basis sets.

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