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# Experimental and Theoretical Properties of 3-Methyl/*n*-Propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-ones

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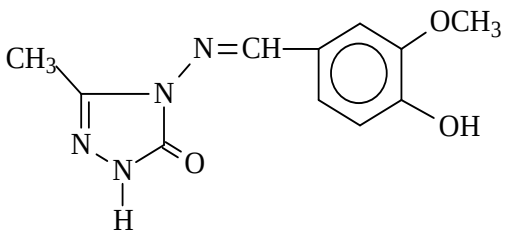
**ABSTRACT:**

In this study, theoretically spectral values of 3-methyl/*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-oneswere calculated and these values were compared with experimental valuesand obtained conclusions were evaluated. For this purpose, firstly, these compounds have been optimized using B3LYP/6-311G(d,p) and HF/6-311G(d,p) basis set. $^{1}$H-NMR and $^{13}$C-NMR spectral values according to GIAO method was calculated using Gaussian G09W programpackagein gas phase and in DMSO solvent. Theoretically and experimentally valueswere 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 Sigma plot program. Theoretically calculated IR values of these compounds were calculated in gas phaseby using of 6-311G(d,p) basis sets of B3LYP and HF methods and are multiplied with appropriate scale factors and the values obtained according to B3LYP and HF methods are formed using theoretical infrared spectrum. The identification of calculated IR value was used veda4f program. UV-vis values in ethanol were calculated. In addition, bond angles, bond lengths, dipole moments, the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy, mulliken charges and total energy of the molecule were calculated with both methods.The calculated and experimental results were exhibited a very good agreement.

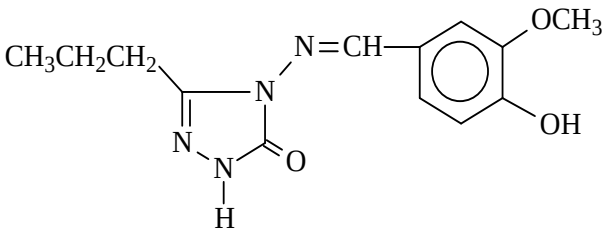
**Key words:** 4,5-dihydro-1*H*-1,2,4-triazol-5-on, Gaussian 09W, GIAO, B3LYP, HF, 6-311G(d,p) basic set.

## 1 INTRODUCTION

The geometry of 3-methyl/*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-ones(**1** and **2)** were optimized by using the B3LYP/6-311G(d,p) and HF/6-311G(d,p) basis sets [1]. Nuclear shielding consants were also calculated by using with the same basic sets. $^{1}$H-NMR and $^{13}$C-NMR spectrums of these compounds were studied experimentally [2] and theoretically. Afterwards, the shift values of $^{1}$H NMR ve $^{13}$C NMR were calculated by using the Gaussian G09W program package in gas phase and in DMSO solventaccording to method of GIAO [3]. The standard error rate was calculated according to δ calc=a δexp + b formula. In addition, theoretically UV-vis values in ethanol were calculated and compared with experimental values [2]. The identification of calculated IR values were used veda4f program [4]. Furthermore, the bond angles, bond lengths, dipole moments, mulliken charges, the HOMO-LUMO energy and total energy of the molecules **1** and **2** for both methods were calculated.




**1**




**2**

## 2 THEORETICAL

Geometry of compound **1** and **2**were optimized using B3LYP/HF methods 6-311G(d,p) basis set.The vibrational frequencies and their relative intensities were calculated by B3LYP and HF methods. The most widely used technique for calculating NMR shielding values is the GIAO (Gauge Including Atomic Orbital) method[3].This method was used for calculating $^{1}H$ NMR and $^{13}C$ NMR chemical shifts at the HF and B3LYP with the 6-311G(d,p) basis set.Time–dependent density functional theory (TD-DFT) was used to compute excitation energies and oscillator strengths for electronic transitions from ground to excited states [5-7].Some quantum chemical descriptors (bond lengths, bond angles, UV-Vis values, dipole moments, mulliken charges, HOMO-LUMO energies and total energy) are calculated at the HF/6-311G(d,p) and DFT/6-311G(d,p) level.All the calculations were carried out with the GAUSSIAN09W software [1].

## 3 RESULTS AND DISCUSSION:

### 3.1 Molecular geometry

The optimized molecular and chemical structures of 3-methyl/*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one are shown in (Figure1 and 2) respectively. The calculated molecular geometric parameters by using the Hartree Fock (HF) and DFT (B3LYP) methods with 6-311G(d,p) basis setare given in Table 1-4. The calculated double N25=C1, N27=C3 and N31=C1, N33=C8 bond lengths according to DFT/HF methods with 6-311G(d,p) basis set of compounds **1** and **2** were found as 1.296 /1.267, 1.286 /1.258 $A^0$ and 1.297/1.267, 1.286/1.258 $A^0$while the single N26-C2, N26-C1, N24-C2 and N30-C2, N32-C1, N32-C2 bond lengths in 1,2,4-triazole ring are calculated as 1.419/1.387, 1.388/1.378, 1.369/1.346 $A^0$ and 1.368/1.346, 1.392/1.380, 1.420/1.387 $A^0$, respectively. The calculated double C=O bond lenghts were found as 1.217/1.196 and 1.217/1.197 $A^0$ for compounds**1**and **2** respectively. Also the single bond lenghts of C6-O29, O7-O30 and C6-O35, O7-O36 were found as 1.369/1.354 1.364/1.347 and 1.369/1.354 1.364/1.347 $A^0$ for **1**and **2** respectively. The dihedral angles of 3-methyl/*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecules is given in Table1 and3. The N27-C3-C4-C5 and N33-C3-C4-C5 dihedral angles are calculated as -179.930/-179.948 and -179.402/-178.113 $A^0$ for compound **1**and **2** respectively. The C6-O29-C11, C7-O30-H23 and C6-O35-C11, C7-O36-H29 bond angles are calculated as 116.468/116.175, 109.109/110.634 and 116.423/116.175, 109.098/110.637 $A^0$ for compounds**1**and **2** respectively.

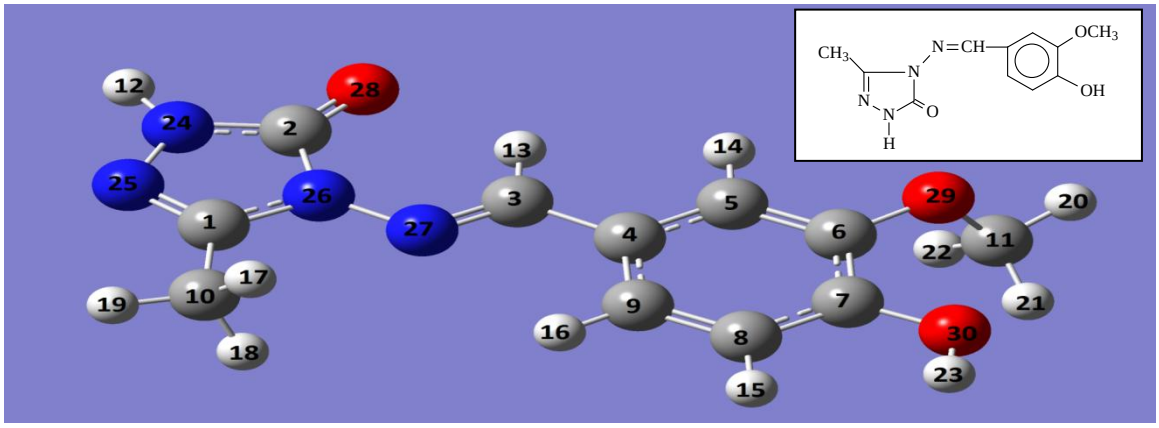


**Fig.1.** The optimized molecular structure of 3-methyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**1**) with DFT/HF 6–311G(d,p) level.

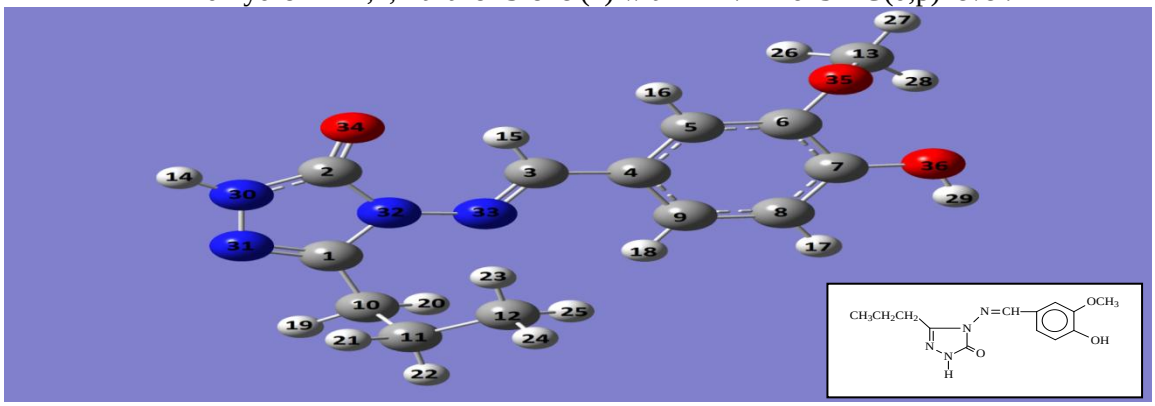


**Fig.2.** The optimized molecular structure of 3-*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**2**) with DFT/HF 6–311G(d,p) level.

**Table 1.** The calculated bond angles and selected dihedral angles ($A^0$) of 3-methyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**1**)

| **Bond Angles ($A^0$)** | **B3LYP** | **HF** | **Selected Dihedral Angles ($A^0$)** | **B3LYP** | **HF** |
|---|---|---|---|---|---|
| C1-N25-N24 | 104.680 | 104.976 | C1-N25-N24-C2 | -0.042 | 0.009 |
| C1-N26-N27 | 121.239 | 121.028 | N25-N24-C2-N26 | 0.015 | -0.097 |
| C1-N26-C2 | 108.254 | 108.060 | H12-N24-C2-O28 | -0.191 | -0.127 |
| C1-C10-H17 | 110.925 | 110.454 | O28-C2-N26-N27 | -0.165 | -0.553 |
| C1-C10-H18 | 110.936 | 110.447 | N26-C1-C10-H17 | 59.457 | 59.543 |
| C1-C10-H19 | 108.553 | 108.439 | N26-C1-C10-H18 | -59.797 | -59.814 |
| H17-C10-H18 | 107.380 | 107.958 | N26-C1-C10-H19 | 179.846 | 179.866 |
| H17-C10-H19 | 109.531 | 109.769 | C1-N26-N27-C3 | -179.408 | -178.746 |
| N25-N24-H12 | 120.467 | 121.003 | N26-N27-C3-H13 | 0.003 | -0.010 |
| N25-N24-C2 | 114.413 | 113.703 | N27-C3-C4-C5 | -179.930 | -179.948 |
| N24-C2-O28 | 129.980 | 129.461 | H14-C3-C4-C5 | -0.078 | 0.122 |
| H12-N24-C2 | 125.120 | 125.294 | C3-C4-C5-C6 | 179.524 | 179.661 |
| O28-C2-N26 | 128.834 | 128.641 | C3-C4-C5-O29 | -176.499 | -177.690 |
| C2-N26-N27 | 130.507 | 130.908 | H14-C5-C6-O29 | 2.634 | 1.390 |
| N26-N27-C3 | 118.930 | 119.783 | C6-O29-C11-H20 | 176.151 | 178.509 |
| N27-C3-H13 | 121.898 | 122.231 | C6-O29-C11-H21 | -64.697 | -62.391 |
| N27-C3-C4 | 120.490 | 120.652 | C6-O29-C11-H22 | 57.843 | 59.740 |
| H13-C3-C4 | 117.612 | 117.117 | O29-C6-C7-O30 | -2.266 | -2.086 |

| Bond Angles ($A^0$) | B3LYP | HF | Selected Dihedral Angles ($A^0$) | B3LYP | HF |
|---|---|---|---|---|---|
| C3-C4-C5 | 118.571 | 118.510 | O29-C6-C7-C8 | 177.124 | 177.921 |
| C3-C4-C9 | 122.870 | 122.833 | C6-C7-C8-H15 | 179.910 | -179.950 |
| C4-C5-H14 | 120.665 | 120.649 | C6-C7-C8-C9 | -0.822 | -0.245 |
| C4-C5-C6 | 121.813 | 121.629 | C7-C8-C9-H16 | -179.529 | -179.775 |
| H14-C5-C6 | 117.516 | 117.716 | C7-C8-C9-C4 | 0.179 | 0.057 |
| C5-C6-C7 | 118.962 | 119.194 | H15-C8-C9-C4 | 179.739 | 179.760 |
| C5-C6-O29 | 118.836 | 119.767 | C8-C9-C4-C5 | 0.559 | 0.198 |
| C6-O29-C11 | 116.468 | 116.175 | H16-C9-C4-C5 | -179.730 | -179.970 |
| O29-C11-H20 | 105.847 | 106.557 | C9-C4-C5-C6 | -0.670 | -0271 |
| O29-C11-H21 | 111.458 | 111.153 | | | |
| O29-C11-H22 | 110.612 | 110.687 | | | |
| H20-C11-H21 | 109.648 | 109.386 | | | |
| H20-C11-H22 | 109.321 | 109.324 | | | |
| H21-C11-H22 | 109.864 | 109.668 | | | |
| O29-C6-C7 | 122.108 | 121.001 | | | |
| C6-C7-O30 | 117.910 | 117.912 | | | |
| C7-O30-H23 | 109.109 | 110.634 | | | |
| O30-C7-C8 | 122.564 | 122.537 | | | |
| C7-C8-H15 | 119.001 | 119.296 | | | |
| C6-C7-C8 | 119.524 | 119.551 | | | |
| C7-C8-C9 | 120.979 | 120.782 | | | |
| H15-C8-C9 | 120.015 | 119.921 | | | |
| C8-C9-H16 | 120.448 | 120.060 | | | |
| C8-C9-C4 | 120.156 | 120.187 | | | |
| H16-C9-C4 | 119.396 | 119.753 | | | |

**Table 2.** The calculated bond lenghts ($A^0$) of 3-methyl/*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**1** and **2**)

| Bond Lenghts ($A^0$) Compound 1 | B3LYP | HF | Bond Lenghts ($A^0$)Compound 2 | B3LYP | HF |
|---|---|---|---|---|---|
| C1-N26 | 1.388 | 1.378 | C1-N32 | 1.392 | 1.380 |
| C1-N25 | 1.296 | 1.267 | C1-N31 | 1.297 | 1.267 |
| C1-C10 | 1.485 | 1.487 | C1-C10 | 1.495 | 1.493 |
| C10-H17 | 1.093 | 1.084 | C10-H19 | 1.093 | 1.084 |
| C10-H18 | 1.093 | 1.084 | C10-H20 | 1.092 | 1.085 |
| C10-H19 | 1.089 | 1.081 | C10-C11 | 1.544 | 1.535 |
| N25-N24 | 1.380 | 1.369 | C11-H21 | 1.094 | 1.087 |
| N24-H12 | 1.006 | 0.990 | C11-H22 | 1.095 | 1.085 |
| N24-C2 | 1.369 | 1.346 | C11-C12 | 1.530 | 1.527 |
| C2-O28 | 1.217 | 1.196 | C12-H23 | 1.093 | 1.085 |
| C2-N26 | 1.419 | 1.387 | C12-H24 | 1.093 | 1.089 |
| N26-N27 | 1.372 | 1.365 | C12-H25 | 1.093 | 1.087 |
| N27-C3 | 1.286 | 1.258 | N31-N30 | 1.379 | 1.369 |
| C3-H13 | 1.087 | 1.075 | N30-H14 | 1.006 | 0.990 |
| C3-C4 | 1.462 | 1.472 | N30-C2 | 1.368 | 1.346 |
| C4-C5 | 1.402 | 1.390 | C2-O34 | 1.217 | 1.197 |
| C5-H14 | 1.084 | 1.075 | C2-N32 | 1.420 | 1.387 |
| C5-C6 | 1.389 | 1.379 | N32-N33 | 1.372 | 1.366 |
| C6-O29 | 1.369 | 1.354 | N33-C3 | 1.286 | 1.258 |
| O29-C11 | 1.433 | 1.409 | C3-H15 | 1.087 | 1.075 |
| C11-H20 | 1.089 | 1.083 | C3-C4 | 1.462 | 1.473 |

| Bond Lenghts ($A^0$) Compound 1 | B3LYP | HF | Bond Lenghts ($A^0$) Compound 2 | B3LYP | HF |
|---|---|---|---|---|---|
| C11-H21 | 1.092 | 1.087 | C4-C5 | 1.402 | 1.391 |
| C11-H22 | 1.096 | 1.083 | C5-H16 | 1.084 | 1.076 |
| C6-C7 | 1.407 | 1.391 | C5-C6 | 1.389 | 1.380 |
| C7-O30 | 1.364 | 1.347 | C6-O35 | 1.369 | 1.354 |
| C7-C8 | 1.398 | 1.387 | O35-C13 | 1.433 | 1.409 |
| O30-H23 | 0.963 | 0.941 | C13-H26 | 1.092 | 1.087 |
| C8-C9 | 1.386 | 1.380 | C13-H27 | 1.096 | 1.081 |
| C8-H15 | 1.087 | 1.077 | C13-H28 | 1.089 | 1.083 |
| C9-H16 | 1.082 | 1.073 | C6-C7 | 1.407 | 1.392 |
| | | | C7-O36 | 1.364 | 1.347 |
| | | | C7-C8 | 1.398 | 1.387 |
| | | | O36-H29 | 0.963 | 0.941 |
| | | | C8-C9 | 1.386 | 1.387 |
| | | | C8-H17 | 1.087 | 1.077 |
| | | | C9-H18 | 1.082 | 1.073 |

**Table 3.** The calculated bond angles ($A^0$) of 3-*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**2**)

| Bond Angles ($A^0$) | B3LYP | HF | Selected Dihedral Angles ($A^0$) | B3LYP | HF |
|---|---|---|---|---|---|
| C1-N30-N31 | 104.896 | 105.109 | C1-N30-N31-C2 | 0.497 | 0.539 |
| C1-N32-N33 | 121.801 | 121.273 | N31-N30-C2-N32 | -0.617 | -0.799 |
| C1-N32-C2 | 108.232 | 108.076 | H14-N30-C2-O34 | 0.921 | 0.943 |
| C1-C10-H19 | 107.111 | 106.475 | O34-C2-N32-H14 | -2.145 | -2.994 |
| C1-C10-H20 | 108.560 | 108.867 | N31-C1-C10-H19 | 40.662 | 17.125 |
| C1-C10-C11 | 113.803 | 113.130 | N32-C1-C10-H19 | -140.486 | -164.035 |
| H20-C10-C11 | 110.175 | 109.974 | N32-C1-C10-H20 | -24.093 | -47.672 |
| H19-C10-H20 | 108.994 | 108.133 | C1-C10-C11-C12 | -63.777 | 179.163 |
| H20-C10-C11 | 110.175 | 109.974 | C1-C10-C11-H21 | 59.276 | 57.712 |
| H19-C10-C11 | 108.994 | 110.091 | C1-C10-C11-H22 | 174.168 | 178.683 |
| C10-C11-C12 | 114.500 | 111.999 | H21-C11-C12-H23 | -60.256 | -61.144 |
| H21-C11-C12 | 109.881 | 109.703 | H22-C11-C12-H24 | 62.862 | 58.738 |
| H22-C11-C12 | 109.556 | 109.710 | H22-C11-C12-H25 | -57.302 | -58.585 |
| H21-C11-H22 | 106.565 | 107.044 | C1-N32-N33-C3 | -178.303 | -178.113 |
| C11-C12-H23 | 111.616 | 111.172 | N32-N33-C3-H15 | 0.169 | 0.008 |
| C11-C12-H24 | 110.669 | 111.246 | N33-C3-C4-C5 | -179.402 | -178.941 |
| H23-C12-H24 | 107.521 | 110.879 | H15-C3-C4-C5 | 0.727 | 1.195 |
| H23-C12-H25 | 107.456 | 107.780 | C3-C4-C5-C6 | 179.493 | 179.583 |
| H24-C12-H25 | 107.991 | 107.790 | C4-C5-C6-O35 | -176.543 | -177.664 |
| N31-N30-H14 | 120.506 | 121.028 | H16-C5-C6-O29 | 2.605 | 1.411 |
| N31-N30-C2 | 114.401 | 113.681 | C6-O35-C13-H26 | 58.248 | 59.691 |
| N30-C2-O34 | 129.891 | 129.407 | C6-O35-C13-H27 | 176.562 | 178.460 |
| H14-N30-C2 | 125.073 | 125.265 | C6-O35-C13-H28 | -64.286 | -62.440 |
| O34-C2-N32 | 128.847 | 128.649 | O35-C6-C7-O36 | -2.243 | -2.082 |
| C2-N32-N33 | 129.912 | 130.542 | O35-C6-C7-C8 | 177.215 | 177.955 |
| N32-N33-C3 | 119.046 | 119.788 | C6-C7-C8-H17 | 179.827 | 179.977 |
| N33-C3-H15 | 121.945 | 122.243 | C6-C7-C8-C9 | -0.835 | -0.271 |
| N33-C3-C4 | 120.492 | 120.673 | C7-C8-C9-H18 | -179.720 | -179.888 |
| H15-C3-C4 | 117.562 | 117.083 | C7-C8-C9-C4 | 0.132 | 0.035 |
| C3-C4-C5 | 118.547 | 118.474 | H17-C8-C9-C4 | 179.463 | 179.787 |
| C3-C4-C9 | 122.922 | 122.888 | C8-C9-C4-C5 | 0.646 | 0.277 |
| C4-C5-H16 | 120.650 | 120.639 | H18-C9-C4-C5 | -179.500 | -179.799 |

| Bond Angles ($A^0$) | B3LYP | HF | Selected Dihedral Angles ($A^0$) | B3LYP | HF |
|---|---|---|---|---|---|
| C4-C5-C6 | 121.824 | 121.640 | C9-C4-C5-C6 | -0.740 | -0.364 |
| H16-C5-C6 | 117.521 | 117.715 | | | |
| C5-C6-C7 | 118.967 | 119.195 | | | |
| C5-C6-O35 | 118.867 | 119.769 | | | |
| C6-O35-C11 | 116.423 | 116.175 | | | |
| O35-C13-H26 | 110.610 | 110.686 | | | |
| O35-C13-H27 | 105.854 | 106.557 | | | |
| O35-C13-H28 | 111.447 | 111.150 | | | |
| H26-C13-H27 | 109.323 | 109.325 | | | |
| H26-C13-H28 | 109.649 | 109.387 | | | |
| H27-C13-H28 | 109.866 | 109.670 | | | |
| O35-C6-C7 | 122.074 | 120.998 | | | |
| C6-C7-O36 | 117.918 | 117.912 | | | |
| C7-O30-H29 | 109.098 | 110.637 | | | |
| O36-C7-C8 | 122.563 | 122.544 | | | |
| C7-C8-H17 | 119.000 | 119.297 | | | |
| C6-C7-C8 | 119.516 | 120.783 | | | |
| C7-C8-C9 | 120.975 | 120.783 | | | |
| H17-C8-C9 | 120.021 | 119.920 | | | |
| C8-C9-H18 | 120.386 | 119.920 | | | |
| C8-C9-C4 | 120.179 | 120.198 | | | |

### 3.2 Vibrational frequencies

3-alkyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (Me, *n*-Pr) molecules have 30, 36 atoms and the normal vibrational numbers are 84 and 102 respectively. The observed and calculated vibrational frequencies for compunds**1**and**2**are summarized in Table**4**and**5.** The stretching OH bands for compounds**1**and**2**were found as 3682/3763 and 3711/3763 $cm^{-1}$ (Fig**.** 3-6)at B3LYP/HF(6-311G(d,p)) level, respectively.The NH stretching bands for compounds**1**and**2**are observed at 3540/3534 and 3576/3534 $cm^{-1}$, respectively. The C=O stretching vibrations of 1,2,4-triazol ring were observed at 1736/1759 and 1563/1757 $cm^{-1}$ for compounds **1**and **2** The C=N stretching vibrations were found as 1588/1678 and 1505/1671 $cm^{-1}$.

**Table 4.** The calculated IR frequencies of 3-methyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**1**).

| Vibration Frequencies | | Scaled DFT | Scaled HF |
|---|---|---|---|
| **1** | τ NCCC(51), τ CNNC(42),τ CCCN(18), τ NCCN(10) | **21** | **16** |
| **2** | δ NCNN(21), τ NNCN(16), τ COCC(13), τ CCCC(19) | **45** | **43** |
| **3** | τ NCC(27), δ CCC(23), τ COCC(13) | **59** | **58** |
| **4** | τ COCC(53), τ HCOC(15) | **73** | **79** |
| **5** | τ CNNC(30), τ NCNN(17), τ CNNC(12) | **104** | **100** |
| **6** | δ COC(13), τ HCOC(14), τ CCCC(23), τ OCCC(11) | **131** | **134** |
| **7** | τ HCOC(39) | **149** | **145** |
| **8** | τ HCCN(60) | **155** | **155** |
| **9** | τ CNNC(32),τ HCCN(54) | **163** | **170** |
| **10** | δ CCC(19), δ CNN(18) | **181** | **182** |
| **11** | ν CC(13), δ CCN(16) | **196** | **187** |

| Vibration Frequencies | | Scaled DFT | Scaled HF |
|---|---|---|---|
| **12** | τ NCCC(16), δ COC(12), τ OCCC(21) | **214** | **198** |
| **13** | δ NCNN(19), τ CCCC(15), δ OCC(15) | **266** | **256** |
| **14** | τ CNNC(33), τ HNNC(20) | **284** | **271** |
| **15** | δ OCC(39),δ CCC(10) | **292** | **279** |
| **16** | δ CCN(31), τ HOCC(15) | **322** | **305** |
| **17** | τ HOCC(74), δ COC(22), τ CCCC(27) | **330** | **325** |
| **18** | δ COC(22), τ CCCC(27) | **349** | **353** |
| **19** | δ CNN(15), δ NNC(14), δ OCN(16), δ OCC(12) | **375** | **383** |
| **20** | τ CCCC(11), τ NNCN(17) | **394** | **405** |
| **21** | τ HNNC(58), τ ONNC(11) | **442** | **435** |
| **22** | δ CCC(39) | **446** | **453** |
| **23** | τ OCCC(30), τ CCCC(19), τ HCCC(19) | **475** | **496** |
| **24** | δ NCN(13), δ OCC(15), ν NN(12) | **547** | **549** |
| **25** | δ OCN(12), δ OCC(12), δ CCC(10) | **565** | **569** |
| **26** | δ OCN(21), δ OCC(14), δ CNN(11) | **586** | **591** |
| **27** | ν CC(23), δ CCC(11) | **615** | **616** |
| **28** | τ CCCC(28) | **624** | **632** |
| **29** | τ HNNC(12), τ NNCN(32), τ CNNC(14) | **639** | **655** |
| **30** | τ CCCC(10), τ OCCC(25) | **709** | **721** |
| **31** | τ ONNC(80) | **716** | **748** |
| **32** | τ OCCC(14), ν CC(10), δ CCC(23) | **723** | **768** |
| **33** | δ CCC(13), ν OC(17) | **762** | **769** |
| **34** | δ CNN(25), ν NC(20) | **778** | **788** |
| **35** | τ HCCC(67), τ OCCC(13) | **783** | **823** |
| **36** | δ NCC(19), δ NNC(17), ν NN(13), δ CCC(10) | **820** | **834** |
| **37** | τ CCCC(13), τ HCCC(48) | **871** | **914** |
| **38** | ν CC(15), ν OC(16) | **910** | **923** |
| **39** | τ HCCC(54), τ CCCC(13) | **915** | **966** |
| **40** | δ NNC(13), τ HCCN(40), δ HCH(14) | **957** | **981** |
| **41** | δ HCNN(89) | **979** | **1027** |
| **42** | ν OC(59), δ CCC(17) | **1004** | **1036** |
| **43** | τ HCCN(13), δ HCH(20), τ HCCN(58) | **1028** | **1049** |
| **44** | δ NNC(26), ν NC(14), ν NN(13) | **1030** | **1061** |
| **45** | ν NN(26), δ HNN(11), τ HCCN(16) | **1062** | **1084** |
| **46** | δ CCC(10), ν OC(10), δ HOC(20), δ HCC(25) | **1077** | **1094** |
| **47** | τ HCOC(29), δ HCH(24) | **1127** | **1097** |
| **48** | δ HCC(33) | **1138** | **1151** |
| **49** | δ HCC(15), δ HOC(25) | **1144** | **1157** |
| **50** | τ HCOC(23), δ HCH(14) | **1162** | **1174** |
| **51** | ν NC(15), ν NN(10) | **1176** | **1203** |
| **52** | ν OC(32) | **1220** | **1208** |

| Vibration Frequencies | Scaled DFT | Scaled HF | |
|---|---|---|---|
| **53** | ν NN(21), δ NCN(21), δ CNN(10) | **1241** | **1248** |
| **54** | δ HCC(42), ν CC(16) | **1261** | **1285** |
| **55** | ν CC(22), ν OC(33) | **1270** | **1303** |
| **56** | δ HOC(26), δ HCC(11), ν CC(38) | **1315** | **1306** |
| **57** | ν NC(19), δ HCN(36), δ HCH(14) | **1328** | **1357** |
| **58** | δ HNN(61), δ HCH(47) | **1343** | **1380** |
| **59** | ν CC(10), δ HCN(13), δ HCH(52) | **1364** | **1390** |
| **60** | ν CC(24), δ HCH(18) | **1384** | **1407** |
| **61** | δ HCN(16), δ HCH(40) | **1404** | **1428** |
| **62** | δ HCH(78),τ HCCN(21) | **1416** | **1431** |
| **63** | δ HCH(42) | **1426** | **1446** |
| **64** | δ HCH(45), τ HCOC(17) | **1430** | **1451** |
| **65** | τ HCCN(13), δ HCH(34) | **1436** | **1461** |
| **66** | δ HCH(51),τ HCOC(21) | **1454** | **1465** |
| **67** | ν OC(15), δ HCC(39), δ CCC(12), ν CC(11) | **1488** | **1516** |
| **68** | ν CC(13), δ CCC(19) | **1559** | **1604** |
| **69** | ν CC(42) | **1579** | **1617** |
| **70** | ν NC(53) | **1588** | **1678** |
| **71** | ν NC(58), ν CC(11) | **1602** | **1697** |
| **72** | ν OC(73), ν NC(13) | **1736** | **1759** |
| **73** | ν CH(91) | **2899** | **2849** |
| **74** | ν CH(93) | **2929** | **2872** |
| **75** | ν CH(70) | **2974** | **2916** |
| **76** | ν CH(100) | **2980** | **2928** |
| **77** | ν CH(71) | **3013** | **2951** |
| **78** | ν CH(93) | **3021** | **2959** |
| **79** | ν CH(34) | **3024** | **2977** |
| **80** | ν CH(42) | **3031** | **3003** |
| **81** | ν CH(40) | **3062** | **3014** |
| **82** | ν CH(33) | **3083** | **3031** |
| **83** | ν NH(100) | **3540** | **3534** |
| **84** | ν OH(100) | **3682** | **3763** |

**Table 5.** The calculated IR frequencies of 3-*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**2**)

| Vibration Frequencies | | Scaled DFT | Scaled HF |
|---|---|---|---|
| **1** | τ CNNC (39), τ CCCN(17), τ NCCN(11) | **13** | **13** |
| **2** | τ CCCN(14), τ CCNN(13), τ NCCN(13) | **33** | **34** |
| **3** | δ NCC(18), τ NNCN(11), δ CCC(19) | **50** | **48** |
| **4** | τ COCC(27) | **64** | **61** |
| **5** | δ CCC(11), τ CNNC(15), τ CCCN(20) | **77** | **76** |
| **6** | τ COCC(34), τ CCCN(12) | **85** | **83** |
| **7** | τ COCC(12), τ CCCN(27), τ HCCN(10) | **91** | **89** |
| **8** | τ CNNC(29), τ CCCN(11), τ NCCN(10) | **115** | **113** |
| **9** | τ CCCN(24), τ OCCC(10), δ COC(14) | **116** | **135** |
| **10** | τ HCOC(39) | **117** | **146** |
| **11** | τ HOCC(43), τ CNNC(17), τ CCCN(21), δ CCC(11) | **118** | **182** |
| **12** | τ CCCN(19), τ OCCC(18), δ COC(10) | **119** | **185** |
| **13** | τ HOCC(49), τ CCCN(17), τ NCNN(18), δ CCN(11) | **143** | **191** |
| **14** | τ NNCN(15), τ COCC(30), δ CCN(24),τ CCCC(13) | **178** | **202** |
| **15** | ν CC(21), τ HCCC(71) | **213** | **238** |
| **16** | τ CCCC(14), δ CNN(18), δ CCC(11) | **231** | **256** |
| **17** | δ CCC(10), τ HOCC(88) | **284** | **271** |
| **18** | δ CCN(11), δ OCC(11) | **294** | **292** |
| **19** | δ OCC(12), δ COC(16) | **308** | **302** |
| **20** | τ CCCC(22),τ NNCN(10) | **346** | **322** |
| **21** | τ HCOC(57), τ COCC(20), δ OCC(12) | **380** | **339** |
| **22** | δ CCC(23) | **395** | **361** |
| **23** | τ CCCC(16), τ NNCN(11) | **417** | **384** |
| **24** | δ CNN(11), δ CCC(17), ν NC(11) | **432** | **410** |
| **25** | τ CCCC(13), τ OCCC(31), τ HCCC(18) | **454** | **451** |
| **26** | δ CCC(34) | **472** | **454** |
| **27** | ν CC(25), δ NNC(10), τ HCCN(11) | **509** | **497** |
| **28** | δ OCC(24), δ CCC(11) | **532** | **554** |
| **29** | δ CCC(13), ν OC(11), δ OCN(10) | **547** | **571** |
| **30** | δ NCC(15), δ OCN(25) | **595** | **593** |
| **31** | τ CCCC(22), τ HCCC(19), τ OCCC(20) | **611** | **630** |
| **32** | ν NC(16) | **660** | **638** |
| **33** | δ OCC(10), δ COC(15),τ CCCC(20), τ HCCC(11) | **678** | **706** |
| **34** | δ CCC(10) | **690** | **718** |
| **35** | τ OCCC(14), τ HCCC(14) | **692** | **734** |
| **36** | τ HCCN(11) | **702** | **749** |
| **37** | δ COC(14), ν OC(18), δ CCC(18), ν CC(12) | **711** | **768** |
| **38** | τ OCCC(20), τ HCCC(31) | **736** | **773** |
| **39** | ν CC(10), δ NNC(12), δ CNN(16), ν NC(13) | **749** | **803** |
| **40** | ν OC(15) | **771** | **823** |

| Vibration Frequencies | Scaled DFT | Scaled HF | |
|---|---|---|---|
| **41** | τ HCCC(32),τ CCCC(11) | **804** | **834** |
| **42** | δ OCN(14), τ ONNC(23) | **822** | **855** |
| **43** | τ HCCN(18), ν CC(49) | **836** | **868** |
| **44** | ν CC(12), ν NC(10) | **849** | **914** |
| **45** | τ HCCC(68) | **871** | **923** |
| **46** | ν CC(35), τ HCCC(81) | **887** | **965** |
| **47** | ν NC(14) | **904** | **993** |
| **48** | τ HCNN(79) | **928** | **1025** |
| **49** | ν NN(37) | **963** | **1029** |
| **50** | ν OC(57), δ HCC(10) | **1008** | **1036** |
| **51** | ν OC(23), ν CC(13) | **1012** | **1068** |
| **52** | ν OC(37) | **1016** | **1083** |
| **53** | ν CC(32), τ HCCC(15) | **1019** | **1085** |
| **54** | ν NN(45) | **1043** | **1094** |
| **55** | ν CC(28), τ HCCC(22), τ HCCN(23) | **1059** | **1117** |
| **56** | δ HOC(21), δ HCC(16) | **1068** | **1151** |
| **57** | δ HCC(21), τ HCOC(15), δ HCH(11) | **1091** | **1157** |
| **58** | δ HCC(30) | **1093** | **1174** |
| **59** | ν NN(16), δ CNN(12) | **1108** | **1203** |
| **60** | δ CCC(11), δ HOC(21) | **1115** | **1209** |
| **61** | δ HCC(42) | **1126** | **1227** |
| **62** | τ HCOC(19) | **1130** | **1248** |
| **63** | ν CC(28), ν OC(27) | **1145** | **1272** |
| **64** | δ HNN(19), δ HCC(34), τ HCCN(11) | **1174** | **1285** |
| **65** | δ HNN(33), δ HCC(51), τ HCCN(15) | **1182** | **1289** |
| **66** | δ CNN(13), τ HCCN(17) | **1209** | **1305** |
| **67** | δ HCC(45) | **1221** | **1314** |
| **68** | δ HCC(33), τ HCCN(22) | **1241** | **1359** |
| **69** | τ HCCN(41) | **1267** | **1370** |
| **70** | ν CC(24) | **1269** | **1384** |
| **71** | δ HCH(38) | **1314** | **1391** |
| **72** | δ HCN(62) | **1323** | **1404** |
| **73** | δ CCC(10), δ OCC(10), ν CC(16) | **1361** | **1435** |
| **74** | δ HCH(28) | **1388** | **1441** |
| **75** | δ HCH(43), τ HCOC(10) | **1402** | **1450** |
| **76** | δ HCH(37), τ HCCC(12) | **1408** | **1451** |
| **77** | δ HCH(43), τ HCOC(11) | **1418** | **1452** |
| **78** | δ HCH(52) | **1422** | **1456** |
| **79** | δ HCC(14), ν CC(16) | **1428** | **1463** |
| **80** | δ HCH(43), τ HCCC(18) | **1442** | **1465** |

| Vibration Frequencies | Scaled DFT | Scaled HF | |
|---|---|---|---|
| **81** | ν OC(44), ν NC(19) | **1458** | **1516** |
| **82** | ν OC(23), ν NC(45) | **1467** | **1604** |
| **83** | ν NC(32) | **1505** | **1617** |
| **84** | ν NC(38), ν CC(23), δ HCH(14) | **1519** | **1671** |
| **85** | ν CC(26), δ HCH(16) | **1544** | **1696** |
| **86** | ν OC(17) | **1563** | **1757** |
| **87** | ν CH(94) | **3091** | **2838** |
| **88** | ν CH(98) | **3093** | **2849** |
| **89** | ν CH(56) | **3116** | **2855** |
| **90** | ν CH(56) | **3128** | **2879** |
| **91** | ν CH(58) | **3168** | **2880** |
| **92** | ν CH(53) | **3178** | **2898** |
| **93** | ν CH(88) | **3179** | **2901** |
| **94** | ν CH(88) | **3179** | **2917** |
| **95** | ν CH(81) | **3182** | **2927** |
| **96** | ν CH(89) | **3186** | **2951** |
| **97** | ν CH(66) | **3190** | **2977** |
| **98** | ν CH(41) | **3190** | **3004** |
| **99** | ν CH(67) | **3194** | **3014** |
| **100** | ν CH(35) | **3207** | **3031** |
| **101** | ν NH(100) | **3576** | **3534** |
| **102** | ν OH(100) | **3711** | **3763** |

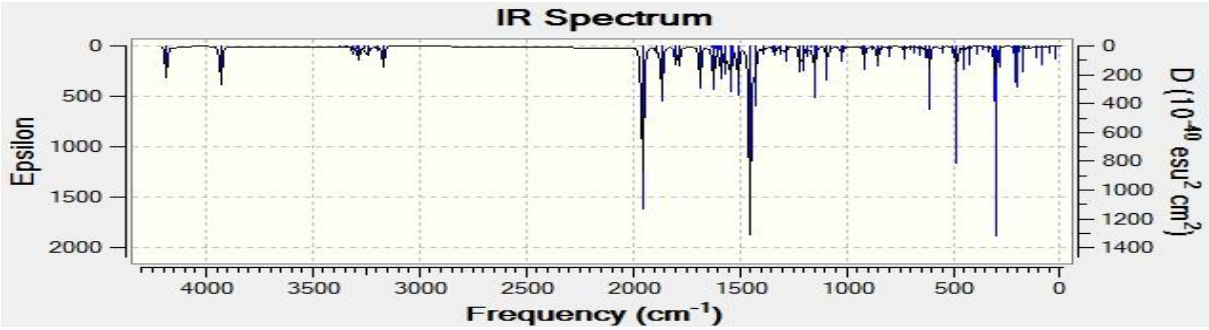



**Fig.3.** IR spectrum simulated DFT/6-311G(d) level of 3-methyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**1**)

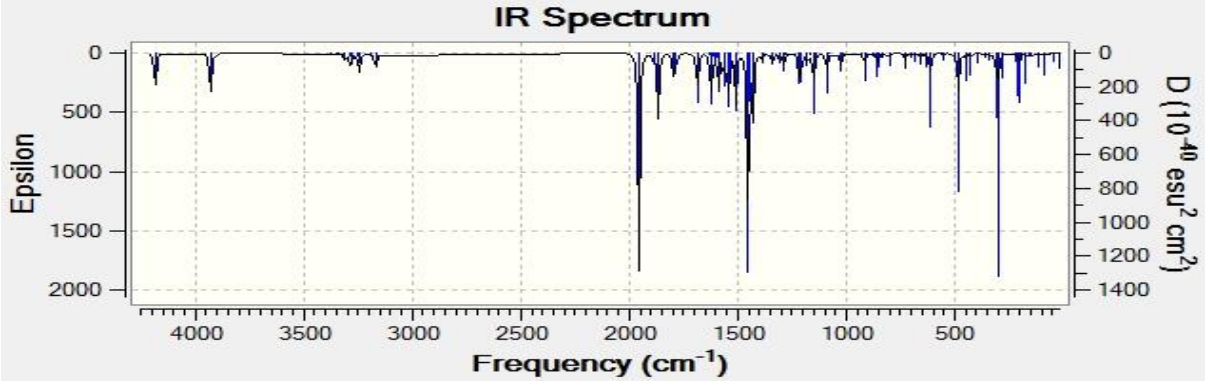



**Fig.4.** IR spectrum simulated HF/6-311G(d) level of 3-methyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**1**)

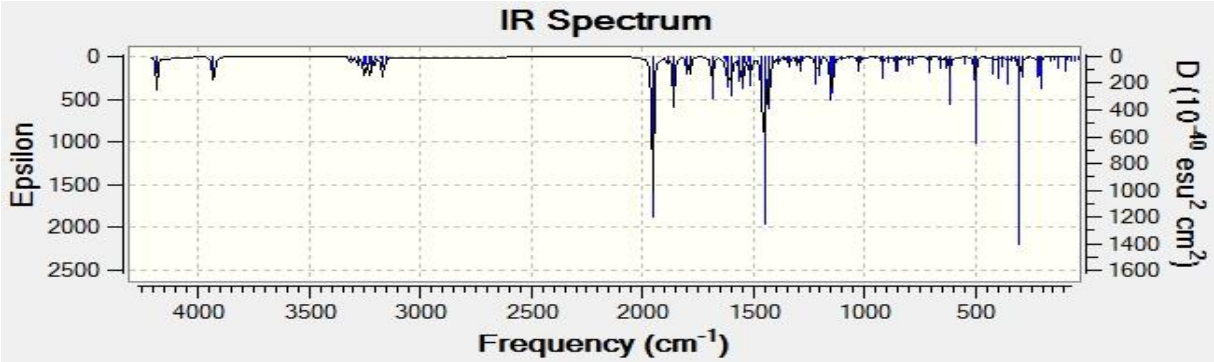



**Fig.5.** IR spectrum simulated HF/6-311G(d) level of 3-*n*-propyl -4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**2**)

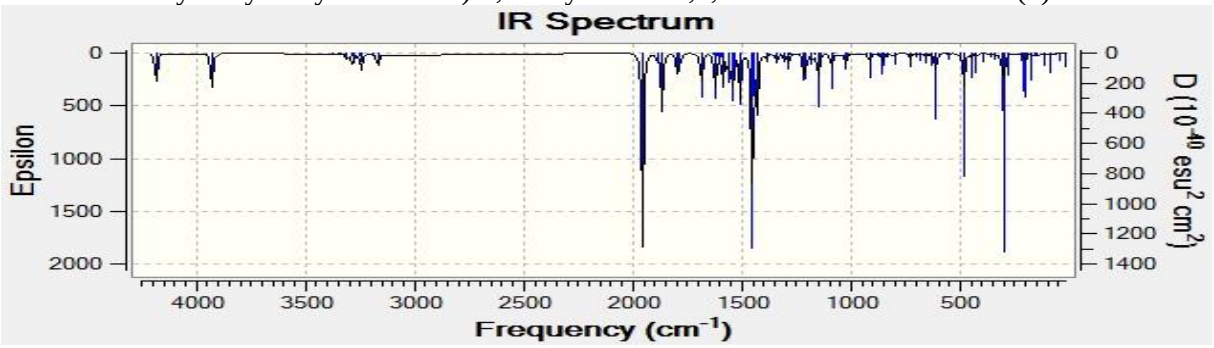


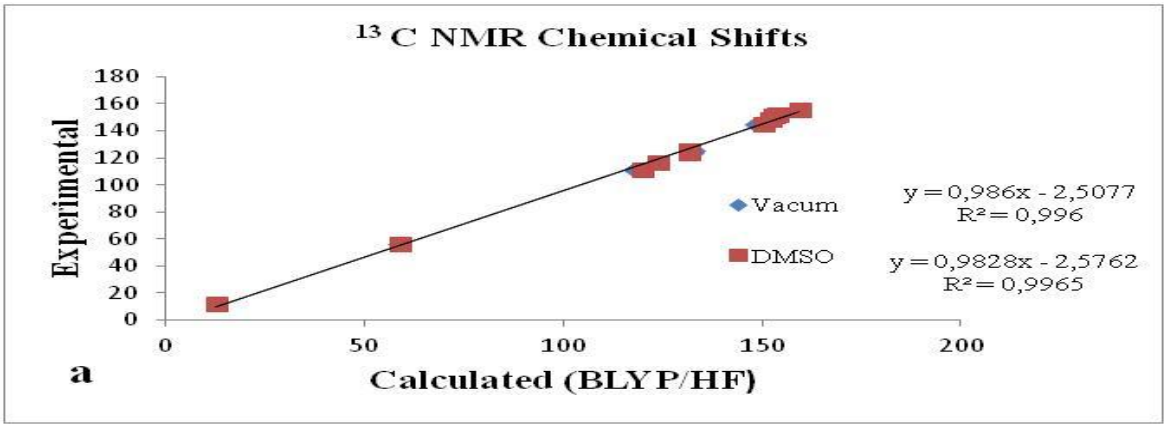

**Fig.6.** IR spectrum simulated HF/6-311G(d) level of 3-*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**2**)

### 3.3 $^{13}$C and $^{1}$H NMR Chemical Shiftsand Regression Analyses

The $^{1}$H and $^{13}$C NMR chemical shifts of the title compounds in gase phase and in DMSO solventhave been calculated by using the DFT (B3LYP) and Hartree Fock (HF)methods with 6-311G(d,p) basis set. The $R^2$ values of compounds **1** and **2** were evaluated and $^{13}$C and $^{1}$H NMR chemical shift values of the compounds **1** and **2**were plotted graphics (Fig**. 7**and**8).**$^{13}$C and $^{1}$H NMR chemical shift values of the compounds **1** and **2** given in Table **5**and**6**. Theoretical and experimental between $^{13}$C and $^{1}$H NMR chemical shifts ratios of compounds **1** and **2** were observed a linear correlation except for NH proton by $R^2$ because N-H proton of 4,5-dihydro-1*H*-1,2,4-triazol-5-one ring was displayed the acidic character (Fig. **7** and **8**). The calculated $^{13}$C and $^{1}$H NMR chemical shifts values for the mentioned compounds are in a very good agreement with the experimental data [1]

**Table 5.** The calculated $^{13}C$ and $^{1}H$ NMR isotropic chemical shifts of 3-methyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (1, 2) (with respect to TMS, all values in ppm).

| Nucleus | $\delta_{Exp.}$ | $\delta_{cal.}$DFT | Different | $\delta_{cal.}$DFT (DMSO) | Different | $\delta_{cal.}$HF (Vacum) | Different | $\delta_{cal.}$HF (DMSO) | Different |
|---|---|---|---|---|---|---|---|---|---|
| **C1** | 144,86 | 148,30 | -3,44 | 150,26 | -5,40 | 139,02 | 5,84 | 141,47 | 3,39 |
| **C2** | 152,05 | 152,72 | -0,67 | 153,76 | -1,71 | 141,92 | 10,13 | 142,94 | 9,11 |
| **C3** | 150,85 | 152,53 | -1,68 | 153,13 | -2,28 | 143,76 | 7,09 | 144,56 | 6,29 |
| **C4** | 125,47 | 132,95 | -7,48 | 131,59 | -6,12 | 116,82 | 8,65 | 115,71 | 9,76 |
| **C5** | 123,23 | 132,38 | -9,15 | 131,70 | -8,47 | 123,69 | -0,46 | 123,35 | -0,12 |
| **C6** | 148,71 | 152,72 | -4,01 | 152,09 | -3,38 | 135,38 | 13,33 | 134,35 | 14,36 |
| **C7** | 155,41 | 158,23 | -2,82 | 159,32 | -3,91 | 143,66 | 11,75 | 144,21 | 11,20 |
| **C8** | 110,91 | 117,57 | -6,66 | 119,81 | -8,90 | 104,14 | 6,77 | 106,03 | 4,88 |
| **C9** | 116,31 | 123,49 | -7,18 | 123,93 | -7,62 | 116,57 | -0,26 | 117,25 | -0,94 |
| **C10** | 11,81 | 12,72 | -0,91 | 12,72 | -0,91 | 0,82 | 10,99 | 0,90 | 10,91 |
| **C11** | 56,28 | 58,66 | -2,38 | 59,04 | -2,76 | 41,68 | 14,60 | 42,04 | 14,24 |
| **H12** | 11,64 | 6,80 | 4,84 | 7,26 | 4,38 | 6,04 | 5,60 | 6,45 | 5,19 |
| **H13** | 9,49 | 10,06 | -0,57 | 9,99 | -0,50 | 9,23 | 0,26 | 9,19 | 0,30 |
| **H14** | 7,23 | 7,15 | 0,08 | 7,17 | 0,06 | 7,10 | 0,13 | 7,19 | 0,04 |
| **H15** | 6,86 | 6,47 | 0,39 | 6,92 | -0,06 | 6,17 | 0,69 | 6,63 | 0,23 |
| **H16** | 7,37 | 7,88 | -0,51 | 7,97 | -0,60 | 7,75 | -0,38 | 7,88 | -0,51 |
| **H17** | 2,24 | 2,24 | 0,00 | 3,84 | -1,60 | 1,79 | 0,45 | 1,94 | 0,30 |
| **H18** | 2,24 | 1,97 | 0,27 | 4,60 | -2,36 | 1,64 | 0,60 | 1,95 | 0,29 |
| **H19** | 2,24 | 2,24 | 0,00 | 3,25 | -1,01 | 1,80 | 0,44 | 1,69 | 0,55 |
| **H20** | 3,81 | 3,77 | 0,04 | 2,36 | 1,45 | 3,28 | 0,53 | 3,27 | 0,54 |
| **H21** | 3,81 | 3,12 | 0,69 | 2,36 | 1,45 | 3,25 | 0,56 | 3,30 | 0,51 |
| **H22** | 3,81 | 4,56 | -0,75 | 2,03 | 1,78 | 2,43 | 1,38 | 2,62 | 1,19 |
| **H23** | 9,65 | 3,56 | 6,09 | 4,53 | 5,12 | 5,65 | 4,00 | 3,54 | 6,11 |



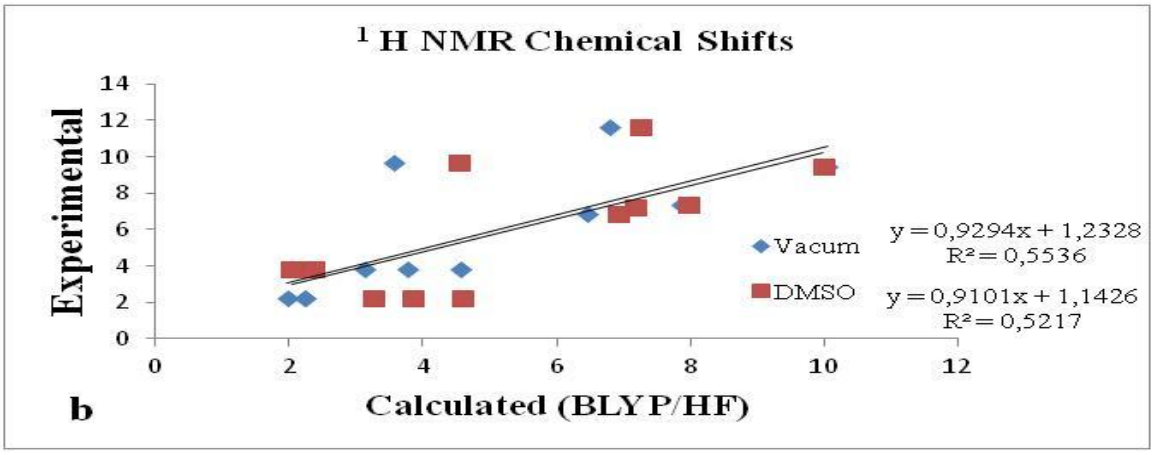



**Fig.7.** The correlation $^{13}C$ (a) and $^{1}H$ (b) NMR isotropic chemical shifts of 3-methyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**1**)

**Table 6.** The calculated and experimental $^{1}H$ NMR isotropic chemical shifts of 3-*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**2**) (with respect to TMS, allvalues in ppm).

| Nucleus | $\delta_{Exp.}$ | $\delta_{cal.}$DFT (Vacum) | Different | $\delta_{cal.}$DFT (DMSO) | Different | $\delta_{cal.}$HF (Vacum) | Different | $\delta_{cal.}$HF (DMSO) | Different |
|---|---|---|---|---|---|---|---|---|---|
| **H14** | 11,78 | 6,90 | 4,88 | 6,45 | 5,33 | 6,73 | 5,05 | 7,38 | 4,40 |
| **H15** | 9,47 | 10,13 | -0,66 | 9,2 | 0,27 | 9,96 | -0,49 | 10,06 | -0,59 |
| **H16** | 7,23 | 7,16 | 0,07 | 7,2 | 0,03 | 7,82 | -0,59 | 7,18 | 0,05 |
| **H17** | 6,85 | 6,48 | 0,37 | 6,64 | 0,21 | 6,90 | -0,05 | 6,93 | -0,08 |
| **H18** | 7,36 | 7,91 | -0,55 | 7,89 | -0,53 | 8,46 | -1,10 | 8,02 | -0,66 |
| **H19** | 2,60 | 2,97 | -0,37 | 2,15 | 0,45 | 2,73 | -0,13 | 3,04 | -0,44 |
| **H20** | 2,60 | 2,45 | 0,15 | 1,73 | 0,87 | 2,40 | 0,20 | 2,53 | 0,07 |
| **H21** | 1,65 | 1,66 | -0,01 | 1,24 | 0,41 | 1,99 | -0,34 | 1,81 | -0,16 |
| **H22** | 1,65 | 1,65 | 0,00 | 0,75 | 0,90 | 1,46 | 0,19 | 1,59 | 0,06 |
| **H23** | 0,92 | 0,68 | 0,24 | 0,7 | 0,22 | 1,41 | -0,49 | 0,91 | 0,01 |
| **H24** | 0,92 | 0,86 | 0,06 | 0,59 | 0,33 | 1,21 | -0,29 | 0,98 | -0,06 |
| **H25** | 0,92 | 0,89 | 0,03 | 0,51 | 0,41 | 1,19 | -0,27 | 0,62 | 0,30 |
| **H26** | 3,81 | 3,13 | 0,68 | 3,3 | 0,51 | 3,92 | -0,11 | 4,59 | -0,78 |
| **H27** | 3,81 | 3,78 | 0,03 | 3,27 | 0,54 | 3,97 | -0,16 | 3,85 | -0,04 |
| **H28** | 3,81 | 4,55 | -0,74 | 2,62 | 1,19 | 3,15 | 0,66 | 3,27 | 0,54 |
| **H29** | 9,74 | 3,56 | 6,18 | 3,54 | 6,20 | 3,37 | 6,37 | 4,53 | 5,21 |

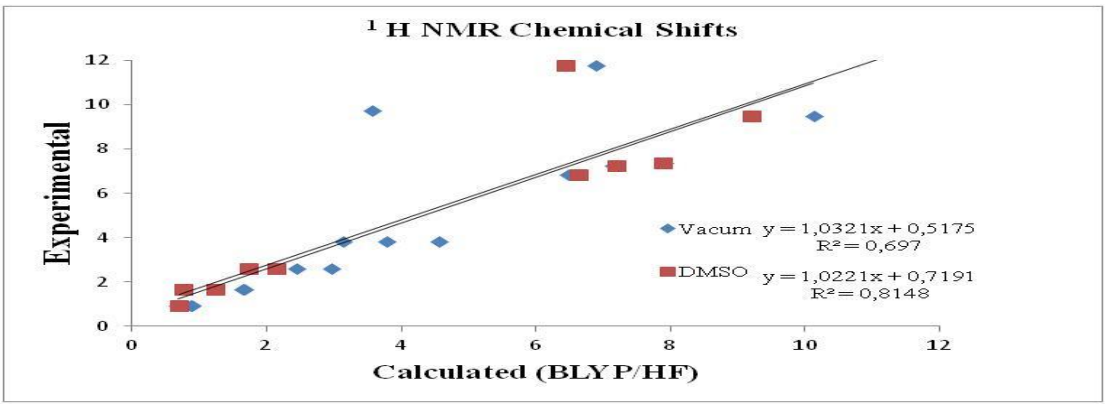
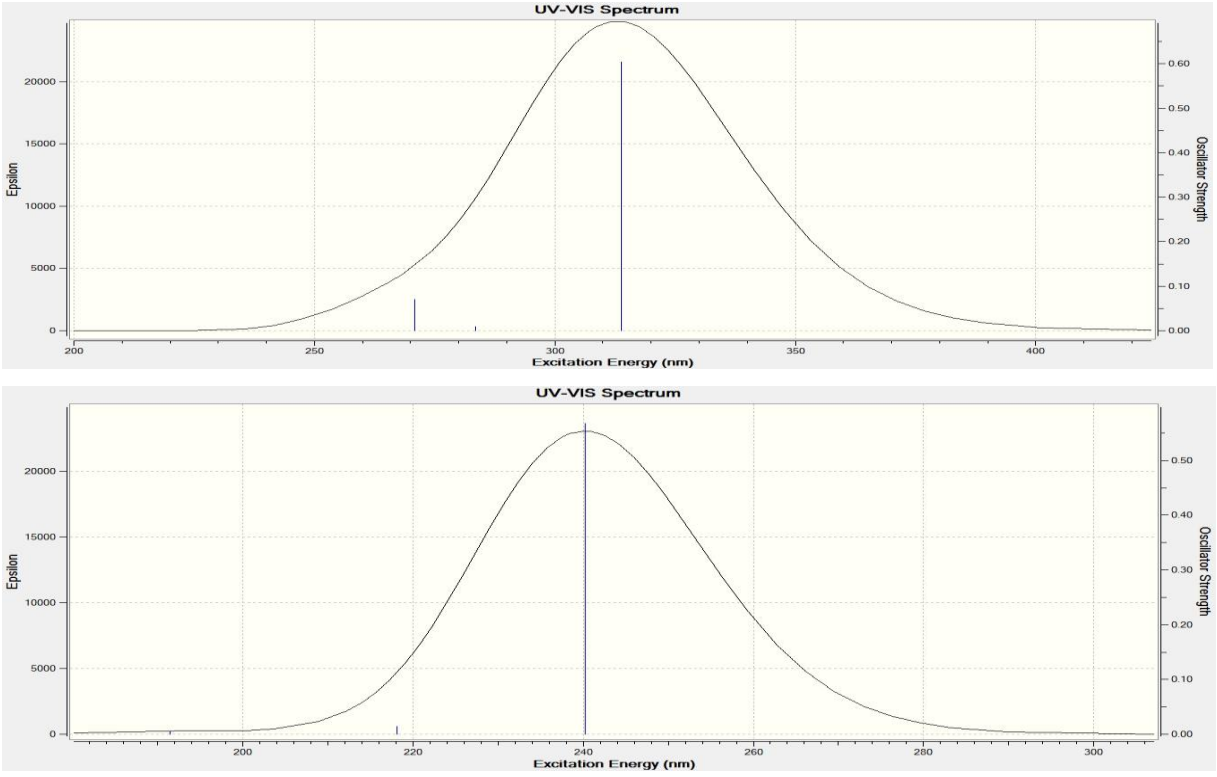



**Fig.8.** The correlation $^{1}$H NMR isotropic chemical shifts of 3-*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**2**)

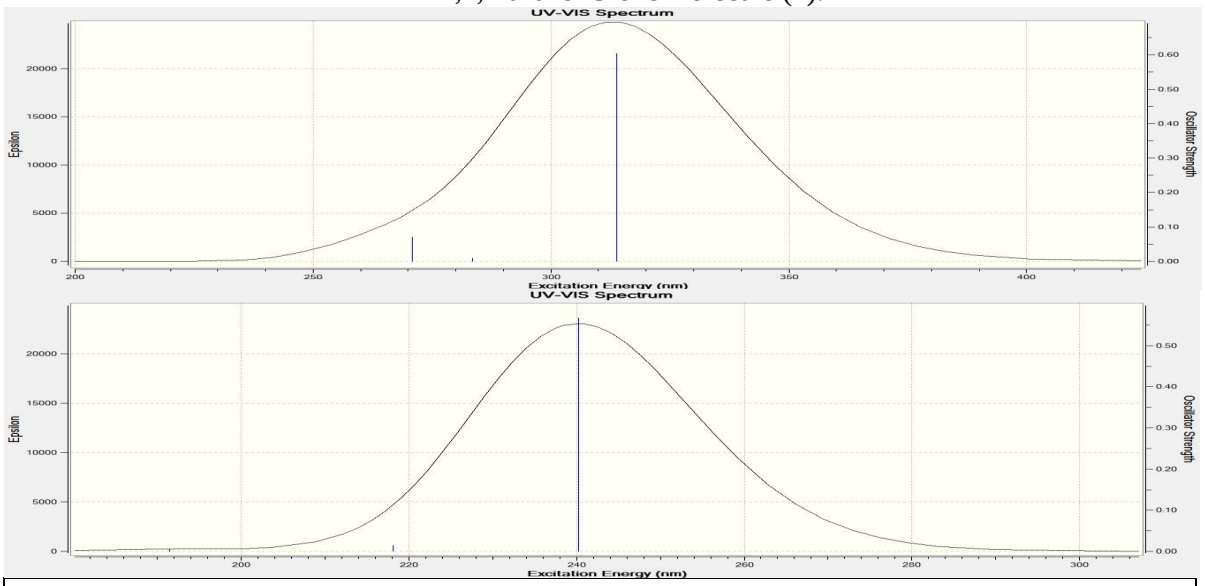
### 3.4 UV-vis. Spectroscopy and HOMO-LUMO Analyses

The experimental absorption wavelenghts [1] of the compounds **1**and **2** in ethanol solvent have been observed 332,308, 234,220 nm and 312, 286, 234, 216 nm respectively. The excitation energies, oscillator strengths (*f*) and absorption wavelengths (λ) of UV–Vis electron absorption spectroscopy [8] of the title molecules have been calculated in ethanol solvent by using B3LYP/HF methods with 6-311G(d,p) basis set and are presented in Figure **9** and **10**. The calculated electron absorption wavelengths for the compounds **1** and **2** were found as 313,74/240,30283,46/218,12, 270,86/191,49 and 314,16/223,27, 284,08/242,45, 271,44/194,15 nm in ethanol solvent, respectively. Furthermore, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)have been simulated for compounds **1** and **2**have been determined. In our study, HOMO and LUMO energies and their 3D plots of the compounds **1** and **2**are shown in Fig **11** and **12**.



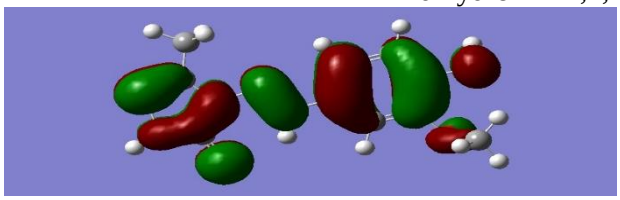
| λ (nm)B3LYP/HF | Excitation Energy (eV) B3LYP/HF | *f* (oscillator strengths) B3LYP/HF |
|---|---|---|
| 313.74/240.30 | 3.9518/5.1596 | 0.6044/0.5670 |
| 283.46/218.12 | 4.3740/5.6841 | 0.0092/0.0141 |
| 270.86/191.49 | 4.5774/6.4749 | 0.0700/0.0059 |

**Fig.9.** The calculated absorption wavelength (λ), excitation energies and oscillator strengths (*f*) and UV-vis spectrums (B3LYP/HF) of 3-methyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**1**).

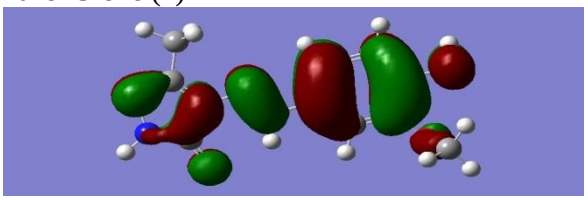



| λ (nm)B3LYP/HF | Excitation Energy (eV) B3LYP/HF | *f* (oscillator strengths) B3LYP/HF |
|---|---|---|
| 314.16/223.27 | 3.9466/5.5532 | 0.5643/0.4944 |
| 284.08/242.45 | 4.3644/5.6756 | 0.0261/0.0256 |
| 271.44/194.15 | 4.5677/6.0143 | 0.0730/0.0092 |

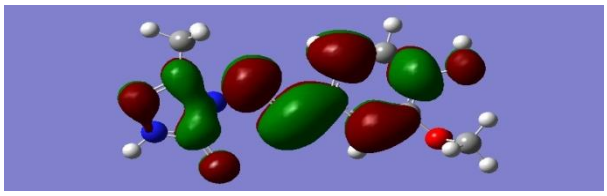
**Fig. 10.** The calculated absorption wavelength (λ), excitation energies and oscillator strengths (*f*) and UV-vis spectrums (B3LYP/HF) of 3-*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**2**)



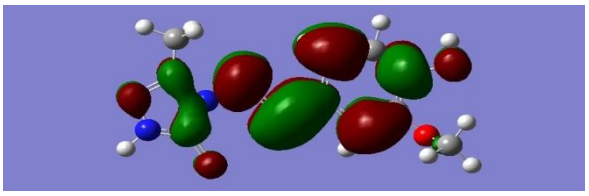
$E_{HOMO}$ (B3LYP) :-0.21738 Hatree



$E_{HOMO}$ (HF) : -0.30472 Hatree

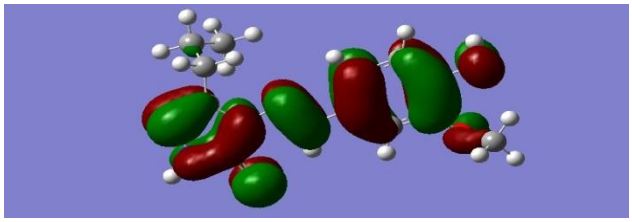


$E_{LUMO}$ (B3LYP) : -0.05835 Hatree

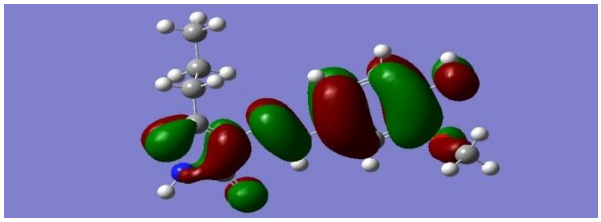


$E_{LUMO}$ (HF) : 0.08773 Hatree

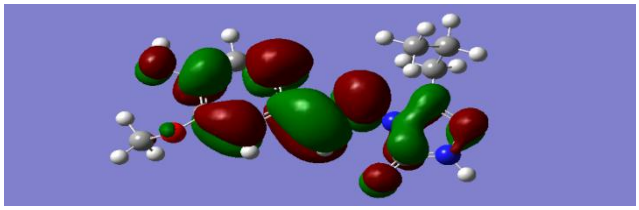
**Fig.11.** 3D plots of HOMO and LUMO energiesof 3-methyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**1**) at the B3LYP/HF 6-311G(d) level.



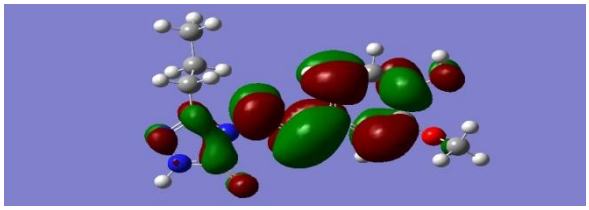
$E_{HOMO}$ (B3LYP) :-0.05786Hatree



$E_{HOMO}$ (HF) : -0,30466 Hatree



$E_{LUMO}$ (B3LYP) : -0,21696 Hatree



$E_{LUMO}$ (HF) : 0.08787 Hatree

**Fig. 12.** 3D plots of HOMO and LUMOenergies of3-*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**2**) at the B3LYP/HF 6-311G(d) level.

### 3.5 Atomic Charges, Thermodynamic Properties and Dipole Moments

The calculated Mulliken atomic charges [9] and resultsof thermodynamic parameter by using B3LYP/HF 6-311G(d) methods of compounds **1** and **2** in gase phase are listed in (Table**7** and **8**), respectively.The electronegative N24, N25, N26, N27, O28, O29,O30 and N30, N31, N32, N33, O34, O35,O36 atoms have negative atomic charge values. The atomic charges of these atoms were calculated as -0.313/-0.380, -0.221/-0.286, -0.364/-0.469, -0.215/-0.277, -0.393/-0.530, -0.366/-0.487, -0.357/-0.447 and -0.312/-0,379, -0.226/-0.276, -0.392/-0.531, -0.366/-0.487, -0.357/-0.447 for compound **1**and **2**, respectively. The C1, C2, C3, C6, C7 atoms surrounded with electronegative atoms have positive atomic charge values for compounds **1** and **2**. These values were found as 0.294/0.396 and 0.342/0.450 (C1) 0.534/0.728 and 0.532/0.723 (C2), 0.138/0.241 and 0.128/0.242 (C3) 0.134/0.217 and 0.137/0.217 (C6), 0.162/2.238 and 0.163/0.239 (C7) a.u. for compounds **1** and **2,** respectively. The C2 atom which is surrounded with three electronegative atoms (N, N, O), C1 atom surrrounded with two electronegative atoms (N, N) have the highest positive charges values. All hydrogen atoms of these compounds **1** and **2** have positive atomic charge values.Total energy values and dipole moments of above mentioned compounds were calculated by using B3LYP/HF 6-311G(d,p) methods. The calculates energy values and dipole moment values are given in Table**7**and**8.**

**Table 7.** The calculated thermodynamic properties of 3-methyl/n-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**1** and **2**)

| **Parameter** | **Value Compound 1** | **Value Compound 2** |
|---|---|---|
| **Thermal energy, E (cal/mol K)** | **Dft/Hf** | **Dft/Hf** |
| Elektronic | 0.000/0.000 | 0.000/0.000 |
| Transnational | 0.889/0.889 | 0.889/0.889 |
| Rotational | 0.889/0.889 | 0.889/0.889 |
| Vibrational | 152.989/163.499 | 185.478/203.087 |
| Total | 154.767/165.277 | 187.256/204.864 |
| **Dipole Moment D (Debye)** | **Dft/Hf** | **Dft/Hf** |
| $\mu_x$ | 1.7702/1.424 | 0.565/-0.941 |
| $\mu_y$ | 3.3397/3.607 | 4.134/3.579 |
| $\mu_z$ | 1.3008/1.540 | 1.720/-1.811 |
| $\mu_{Toplam}$ | 3.9974/4.1730 | 4.518/4.120 |
| **Zero-Point Vibrational energy (kcal/mol)** | **Dft/Hf** 144.18425 /155.23268 | **Dft/Hf** 178.37675/193.19008 |
| **Sum of electronic and zero-point Energy** | **Dft/Hf** -871.024275/-865.828355 | **Dft/Hf** -949.495778/-943.855302 |

| | | |
|---|---|---|
| **(Hartree/Particle)** | | |
| **Sum of electronic and thermal Energies (Hartree/Particle)** | **Dft/Hf** -871.007411/-865.812349 | **Dft/Hf** -949.481628/-943.836698 |
| **Sum of electronic and thermal Enthalpies (Hartree/Particle)** | **Dft/Hf** -871.006467/-865.811405 | **Dft/Hf** -949.480684/-949.480684 |
| **Sum of electronic and thermal Free Energies (Hartree/Particle)** | **Dft/Hf** -871.069886/-871. 069886 | **Dft/Hf** -949.537383/-949.537383 |
| **Rotational constants (GHZ)** | **Dft/Hf** | **Dft/Hf** |
| **A** | 1.1547317 | 0.6982621 |
| **B** | 0.1680958 | 0.1589898 |
| **C** | 0.1492125 | 0.1328035 |
| **B3LYP:** -871.25404745 **a.u.** | | |
| **HF:** -866.07573362 **a.u.** | | |

**Table 8.**The Mulliken atomic charges of 3-methyl/*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule (**1** and **2**)

| **Atoms Compound 1** | **Charges (a.u.)** | | **Atoms Compound 2** | **Charges (a.u.)** | |
|---|---|---|---|---|---|
| | **DFT** | **HF** | | **DFT** | **HF** |
| **C1** | 0.294 | 0.396 | **C1** | 0,342 | 0,450 |
| **C2** | 0.534 | 0.728 | **C2** | 0,532 | 0,723 |
| **C3** | 0.138 | 0.241 | **C3** | 0,128 | 0,242 |
| **C4** | -0.158 | -0.181 | **C4** | -0,163 | -0,186 |
| **C5** | -0.048 | -0.076 | **C5** | -0,048 | -0,076 |
| **C6** | 0.134 | 0.217 | **C6** | 0,134 | 0,217 |
| **C7** | 0.162 | 0.238 | **C7** | 0,163 | 0,239 |
| **C8** | -0.104 | -0.10 | **C8** | -0,107 | -0,106 |
| **C9** | -0.024 | -0.039 | **C9** | -0,019 | -0,037 |
| **C10** | -0.245 | -0.182 | **C10** | -0,201 | -0,153 |
| **C11** | -0.115 | -0.003 | **C11** | -0,231 | -0,204 |
| **H12** | 0.249 | 0.250 | **C12** | -0,291 | -0,242 |
| **H13** | 0.141 | 0.165 | **C13** | -0,114 | -0,003 |
| **H14** | 0.102 | 0.107 | **H14** | 0,249 | 0,259 |
| **H15** | 0.092 | 0.098 | **H15** | 0,142 | 0,166 |
| **H16** | 0.100 | 0.111 | **H16** | 0,102 | 0,107 |
| **H17** | 0.132 | 0.122 | **H17** | 0,091 | 0,097 |
| **H18** | 0.132 | 0.122 | **H18** | 0,107 | 0,114 |
| **H19** | 0.132 | 0.127 | **H19** | 0,135 | 0,128 |
| **H20** | 0.117 | 0.097 | **H20** | 0,141 | 0,126 |
| **H21** | 0.119 | 0.099 | **H21** | 0,121 | 0,116 |
| **H22** | 0.094 | 0.072 | **H22** | 0,109 | 0,104 |
| **H23** | 0.253 | 0.262 | **H23** | 0,110 | 0,116 |
| **N24** | -0.313 | -0.380 | **H24** | 0,108 | 0,104 |
| **N25** | -0.221 | -0.286 | **H25** | 0,110 | 0,090 |
| **N26** | -0.364 | -0.469 | **H26** | 0,094 | 0,087 |
| **N27** | -0.215 | -0.277 | **H27** | 0,117 | 0,098 |
| **O28** | -0.393 | -0.530 | **H28** | 0,119 | 0,073 |
| **O29** | -0.366 | -0.487 | **H29** | 0,253 | 0,099 |

| Atoms Compound 1 | Charges (a.u.) | | Atoms Compound 2 | Charges (a.u.) | |
|---|---|---|---|---|---|
| | DFT | HF | | DFT | HF |
| **O30** | -0.357 | -0.447 | **N30** | -0,312 | -0,379 |
| | | | **N31** | -0,226 | -0,284 |
| | | | **N32** | -0,373 | -0,482 |
| | | | **N33** | -0,211 | -0,276 |
| | | | **O34** | -0,392 | -0,531 |
| | | | **O35** | -0,366 | -0,487 |
| | | | **O36** | -0,357 | -0,447 |

## 4 CONCLUSION

The molecular structure, vibrational wavenumbers, the electronic absorption maximum wavelenghts, the HOMO, LUMO, atomic charges and thermodynamic parameters of the synthesized 3-methyl/*n*-propyl-4-(3-methoxy-4-hydroxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule have been calculated by using HF/6-311G(d,p) and DFT/6-311G(d,p) levels.The calculated theoretical vibrational frequencies and UV spectroscopic parameters are consistent with the experimental data.

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