JOTCSA
Journal of the Turkish Chemical Society
Section: A
Chemistry
TURKISH CHEMICAL SOCIETY

*(This article was presented to the 28th National Chemistry Congress and submitted to JOTCSA as a full manuscript)*

# Theoretical and Spectroscopic Studies of (*E*)-3-Benzyl-4-((4-Isopropylbenzylidene)-Amino)-1-(Morpholinomethyl)-1*H*-1,2,4-triazol-5(4*H*)-one Molecule

Gül Kotan[1*], Haydar Yüksek[2]

[1]Vocational School, Kafkas University, 36100, Kars, Turkey.
[2]Department of Chemistry, Kafkas University, 36100, Kars, Turkey.

**Abstract:** In this study, (*E*)-3-benzyl-4-((4-isopropylbenzylidene)-amino)-1-(morpholinomethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (**1**) was synthesized by the reaction of 3-benzyl-4-(4-isopropylbenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one with morpholine and formaldehyde. The structure of compound **1** was determined by FT-IR, $^{1}$H-NMR, $^{13}$C-NMR spectral data. Then, the synthesized compound **1** was optimized by using the B3LYP/6-31G (d,p) and HF/6-31G (d,p) basis sets. $^{1}$H-NMR and $^{13}$C-NMR isotropic shift values, IR absorption frequencies, bond angles, bond lengths, HOMO-LUMO energy, electronegativity, and Mulliken charges were calculated theoretically by using the program package Gaussian G09W. In addition, IR, $^{1}$H-NMR, $^{13}$C-NMR theoretical spectral data were compared with certain experimental data.

**Keywords:** Mannich bases, HOMO-LUMO energy, B3LYP 631G (d,p), HF 631G (d,p), Gaussian 09W.

**Submitted:** July 01, 2016. **Revised:** September 19, 2016. **Accepted:** September 20, 2016.

**Cite this:** Kotan G, Yüksek H. Theoretical and Spectroscopic Studies of (E)-3-Benzyl-4-((4-Isopropylbenzylidene)-Amino)-1-(Morpholinomethyl)-1H-1,2,4-triazol-5(4H)-one Molecule. JOTCSA. 2016;3(3):381–92.

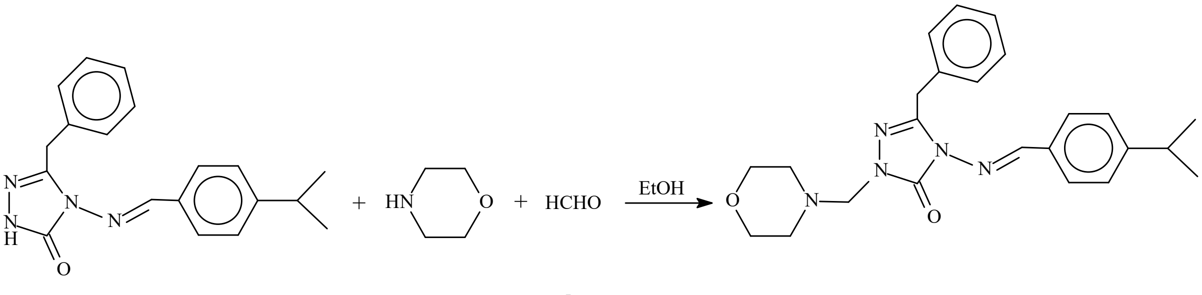
**DOI:** 10.18596/jotcsa.08773.

*Corresponding author. E-mail: gulkemer@hotmail.com.

## INTRODUCTION

Mannich bases have applications the field of medicinal chemistry, the product synthetic polymers, the petroleum industry, as products used in water treatment, cosmetics, the dyes industry, *etc* [1]. On the other hand, quantum chemical calculation methods have widely been used to theoretically predict the structural, spectroscopic, thermodynamic, and electronic properties of molecular systems. The quantum chemical calculation methods provide support for experimental structural and spectroscopic studies [2–7].

In this study, (*E*)-3-benzyl-4-((4-isopropylbenzylidene)-amino)-1-(morpholinomethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (**1**) molecule, which was obtained from the reaction of 3-benzyl-4-(4-isopropylbenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one with morpholine and formaldehyde (**Scheme 1**). The compound **1** was optimized by using the B3LYP/6-31G (d,p) and HF/6-31G (d,p) basis sets [8,9]. This optimized structure was used to research the other different theoretical properties of the main compound.$^1$H-NMR and $^{13}$C-NMR isotropic shift values were calculated by the method of GIAO using the program package Gaussian G09W [9]. Experimental and theoretical values were inserted into the graphic according to equitation δ exp=a+b. δ calc. The standard error values were found via SigmaPlot program with regression coefficient of a and b constants. Then, they were compared with certain experimental data, which are shown to be accurate. The veda4f program was used in defining IR data calculated theoretically [10]. IR absorption frequencies of analyzed molecule were calculated by two methods. Infrared spectra were composed by using the data obtained from both methods. IR absorption frequencies were multiplied by the appropriate adjustment factors B3LYP / 631G(d,p) 0.9688 and HF/631G (d, p) 0.9059 [11]. Furthermore, bond angles, bond lengths, the highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies, electronegativity and Mulliken charges of this compound was found.



**Scheme 1**

### MATERIALS AND METHODS

**Experimental: The synthesis of *((E)-3-benzyl-4-((4-isopropylbenzylidene)-amino)-1-(morpholinomethyl)-1H-1,2,4-triazol-5(4H)-one* (1):** 3-Benzyl-4-(4-ethylbenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazole-5-one (5 mmol) was dissolved in absolute ethanol and to this solution were added formaldehyde (%37, 10 mmol) and morpholine (6 mmol). The reaction mixture was refluxed for 4 hours. The mixture was left at room temperature overnight. Then, the mixture was cooled in the -18 $^0$C refrigerator. The solid formed was obtained by filtration, washed with cold ethanol and recrystallized from ethanol. Melting points were checked on WRS-2A Microprocessor Melting-Point Apparatus. The FTIR spectra were measured on an Alpha-P Bruker FT-IR Spectrometer. $^1$H- and $^{13}$C-NMR spectra were recorded in deuteriated dimethyl sulfoxide with TMS as internal standard on a Bruker 400 MHz spectrometer, respectively. Yield 89%; m.p: 120 $^0$C; FTIR (KBr, cm$^{-1}$): 1692 (C=O), 1602, 1586 (C=N), 835 (1,4-disubstituted benzenoid ring), 731 and 696 (monosubstitued benzenoid ring) cm$^{-1}$. $^1$H-NMR (400 MHz, DMSO) δ (ppm): 1.22 (d, 6H, 2C$\underline{H}_3$ ; *J*=6.80 Hz), 2.58-2.60 (m, 4H, C$\underline{H}_2$NC$\underline{H}_2$), 2.95 (heptet, 1H, C$\underline{H}$(CH$_3$)$_2$; J=6.80 Hz), 4.09 (s, 2H, C$\underline{H}_2$Ph), 4.57 (s, 2H, NC$\underline{H}_2$N), 3.55-3.58 (m, 4H, C$\underline{H}_2$OC$\underline{H}_2$), 7.21-7.25 (m, 1H, ArH), 7.30-7.35(m, 4H, ArH), 7.37 (d, 2H, ArH; J=8.40 Hz), 7.72 (d, 2H, ArH; J=8.40 Hz), 9.62 (s, 1H, N=C$\underline{H}$), $^{13}$C-NMR: δ 23.53 (2CH$_3$), 30.92 ($\underline{C}$H$_2$Ph), 33.45 ($\underline{C}$H(CH$_3$)$_2$), 49.99 ($\underline{C}$H$_2$N$\underline{C}$H$_2$), 66.03(N$\underline{C}$H$_2$N + $\underline{C}$H$_2$O$\underline{C}$H$_2$), [126.77, 126.99 (2C), 127.89(2C), 128.49(2C), 128.67(2C), 131.01, 135.65, 144.91] (ArC), 150.30 (Triazole C$_3$), 152.39 (N=$\underline{C}$H), 154.21(Triazole C$_5$).

**Methods:** The quantum chemical calculations were carried out with density functional theory (DFT) and Hartree-Fock (HF) methods using 6-31G (d,p) basis set at the Gaussian 09W program package on a computing system [9]. Firstly, the compound **1** was optimized by using the B3LYP/6-31G (d,p) and HF/6-31G (d,p) basis sets [8,9]. Thus, the most stable geometric conformer of compound **1** was obtained. Then, $^1$H-NMR and $^{13}$C-NMR isotropic shift values were calculated with method of GIAO. The veda4f program was used in defining IR data [10]. Otherwise, bond angles, bond lengths, the HOMO-LUMO energy, electronegativity and Mulliken charges of compound were calculated theoretically on the computer.

## Theoretical Calculations

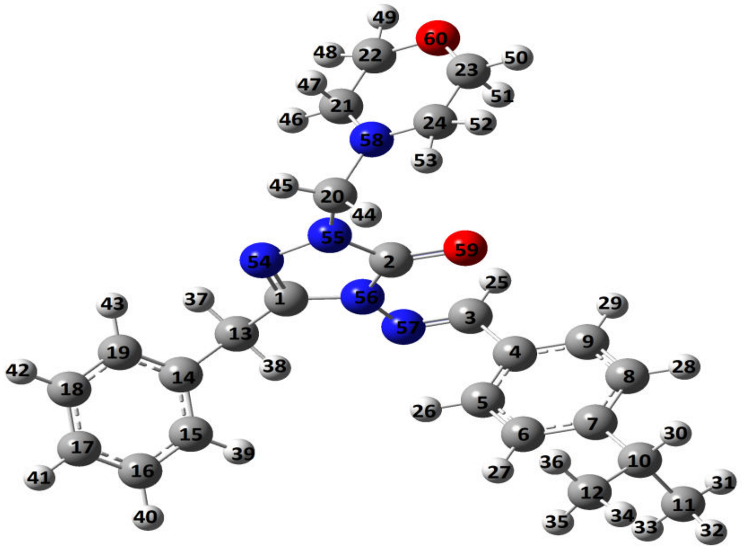


**Figure 1.** Optimized geometry of the molecule **1.**

**Table 1.** The calculated and experimental $^{13}C$ and $^{1}H$-NMR/NMR DMSO(B3LYP/ HF 6-31G(d,p)) isotropic chemical shifts of the molecule (δ/ppm)

| No | Exp. | B3LYP | Diff. | B3LYP/ DMSO | Diff./ DMSO | HF | Diff. | HF/ DMSO | Diff./ DMSO |
|---|---|---|---|---|---|---|---|---|---|
| **C1** | 144,91 | 149,46 | 150,46 | -4,55 | -5,55 | 144,48 | 146,67 | 0,43 | -1,76 |
| **C2** | 154,21 | 152,26 | 152,86 | 1,95 | 1,35 | 147,15 | 147,68 | 7,06 | 6,53 |
| **C3** | 152,39 | 154,54 | 155,44 | -2,15 | -3,05 | 148,87 | 149,88 | 3,52 | 2,51 |
| **C4** | 131,01 | 137,23 | 136,10 | -6,22 | -5,09 | 126,57 | 125,53 | 4,44 | 5,48 |
| **C5** | 127,89 | 128,23 | 127,64 | -0,34 | 0,25 | 123,30 | 122,85 | 4,59 | 5,04 |
| **C6** | 126,99 | 128,62 | 129,24 | -1,63 | -2,25 | 123,38 | 123,44 | 3,61 | 3,55 |
| **C7** | 150,30 | 154,39 | 156,54 | -4,09 | -6,24 | 148,11 | 149,77 | 2,19 | 0,53 |
| **C8** | 126,99 | 131,66 | 132,17 | -4,67 | -5,18 | 120,69 | 121,07 | 6,30 | 5,92 |
| **C9** | 127,89 | 136,06 | 136,44 | -8,17 | -8,55 | 130,22 | 130,63 | -2,33 | -2,74 |
| **C10** | 33,45 | 47,66 | 47,50 | -14,21 | -14,05 | 29,47 | 29,23 | 3,98 | 4,22 |
| **C11** | 23,53 | 33,10 | 32,44 | -9,57 | -8,91 | 20,27 | 19,81 | 3,26 | 3,72 |
| **C12** | 23,53 | 32,90 | 32,66 | -9,37 | -9,13 | 20,27 | 19,81 | 3,26 | 3,72 |
| **C13** | 30,92 | 42,49 | 42,18 | -11,57 | -11,26 | 27,94 | 27,49 | 2,98 | 3,43 |
| **C14** | 135,65 | 140,47 | 140,64 | -4,82 | -4,99 | 130,02 | 130,35 | 5,63 | 5,30 |
| **C15** | 128,67 | 132,30 | 132,42 | -3,63 | -3,75 | 126,49 | 126,42 | 2,18 | 2,25 |
| **C16** | 128,49 | 131,27 | 131,74 | -2,78 | -3,25 | 124,57 | 124,81 | 3,92 | 3,68 |
| **C17** | 126,77 | 129,55 | 129,82 | -2,78 | -3,05 | 123,26 | 123,53 | 3,51 | 3,24 |
| **C18** | 128,49 | 131,38 | 131,47 | -2,89 | -2,98 | 124,62 | 124,86 | 3,87 | 3,63 |
| **C19** | 128,67 | 130,71 | 130,57 | -2,04 | -1,90 | 126,45 | 126,39 | 2,22 | 2,28 |
| **C20** | 66,03 | 74,30 | 74,05 | -8,27 | -8,02 | 56,28 | 56,12 | 9,75 | 9,91 |
| **C21** | 49,99 | 58,50 | 58,28 | -8,51 | -8,29 | 41,27 | 40,95 | 8,72 | 9,04 |
| **C22** | 66,03 | 73,89 | 73,73 | -7,86 | -7,70 | 55,76 | 55,61 | 10,27 | 10,42 |
| **C23** | 66,03 | 74,50 | 74,40 | -8,47 | -8,37 | 55,65 | 55,48 | 10,38 | 10,55 |
| **C24** | 49,99 | 59,16 | 58,86 | -9,17 | -8,87 | 40,74 | 40,48 | 9,25 | 9,51 |
| **H25** | 9,62 | 10,99 | 10,93 | -1,37 | -1,31 | 10,31 | 10,27 | -0,69 | -0,65 |
| **H26** | 7,72 | 9,14 | 9,16 | -1,42 | -1,44 | 8,89 | 8,95 | -1,17 | -1,23 |
| **H27** | 7,37 | 8,35 | 8,56 | -0,98 | -1,19 | 7,75 | 7,95 | -0,38 | -0,58 |
| **H28** | 7,37 | 8,01 | 8,20 | -0,64 | -0,83 | 7,90 | 8,11 | -0,53 | -0,74 |
| **H29** | 7,72 | 8,07 | 8,21 | -0,35 | -0,49 | 8,06 | 8,25 | -0,34 | -0,53 |
| **H30** | 2,95 | 3,58 | 3,72 | -0,63 | -0,77 | 2,76 | 2,92 | 0,19 | 0,03 |
| **H31** | 1,22 | 2,89 | 2,05 | -1,67 | -0,83 | 1,48 | 1,41 | -0,26 | -0,19 |
| **H32** | 1,22 | 2,11 | 2,19 | -0,89 | -0,97 | 1,49 | 1,56 | -0,27 | -0,34 |
| **H33** | 1,22 | 2,14 | 2,20 | -0,92 | -0,98 | 1,55 | 1,61 | -0,33 | -0,39 |
| **H34** | 1,22 | 2,06 | 2,01 | -0,84 | -0,79 | 1,49 | 1,42 | -0,27 | -0,20 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **H35** | 1,22 | 2,12 | 2,17 | -0,90 | -0,95 | 1,50 | 1,61 | -0,28 | -0,39 |
| **H36** | 1,22 | 2,09 | 2,16 | -0,87 | -0,94 | 1,48 | 1,56 | -0,26 | -0,34 |
| **H37** | 4,09 | 4,64 | 4,76 | -0,55 | -0,67 | 4,04 | 4,22 | 0,05 | -0,13 |
| **H38** | 4,09 | 4,64 | 4,80 | -0,55 | -0,71 | 4,00 | 4,19 | 0,09 | -0,10 |
| **H39** | 7,34 | 8,37 | 8,56 | -1,03 | -1,22 | 7,86 | 8,06 | -0,52 | -0,72 |
| **H40** | 7,32 | 8,25 | 8,43 | -0,93 | -1,11 | 7,92 | 8,11 | -0,60 | -0,79 |
| **H41** | 7,23 | 8,11 | 8,28 | -0,88 | -1,05 | 7,87 | 8,06 | -0,64 | -0,83 |
| **H42** | 7,32 | 8,20 | 8,34 | -0,88 | -1,02 | 7,94 | 8,12 | -0,62 | -0,80 |
| **H43** | 7,34 | 8,40 | 8,42 | -1,06 | -1,08 | 7,92 | 8,11 | -0,58 | -0,77 |
| **H44** | 4,57 | 4,63 | 4,79 | -0,06 | -0,22 | 3,93 | 4,04 | 0,64 | 0,53 |
| **H45** | 4,57 | 5,23 | 5,27 | -0,66 | -0,70 | 4,62 | 4,67 | -0,05 | -0,10 |
| **H46** | 2,59 | 3,81 | 3,80 | -1,22 | -1,21 | 2,52 | 2,46 | 0,07 | 0,13 |
| **H47** | 2,59 | 3,13 | 3,23 | -0,54 | -0,64 | 2,06 | 2,19 | 0,53 | 0,40 |
| **H48** | 3,56 | 4,34 | 4,57 | -0,78 | -1,01 | 3,55 | 3,65 | 0,01 | -0,09 |
| **H49** | 3,56 | 4,48 | 4,35 | -0,92 | -0,79 | 3,29 | 3,30 | 0,27 | 0,26 |
| **H50** | 3,56 | 4,51 | 4,61 | -0,95 | -1,05 | 3,38 | 3,46 | 0,18 | 0,10 |
| **H51** | 3,56 | 4,51 | 4,49 | -0,95 | -0,93 | 3,64 | 3,72 | -0,08 | -0,16 |
| **H52** | 2,59 | 3,33 | 3,46 | -0,74 | -0,87 | 2,46 | 2,49 | 0,13 | 0,10 |
| **H53** | 2,59 | 3,27 | 3,37 | -0,68 | -0,78 | 2,45 | 2,46 | 0,14 | 0,13 |

## The relation between R$^2$ values of the compound 1

B3LYP/631G(d,p): $^{13}$C: 0.9977, $^{1}$H: 0.9853; HF/631G(d,p): $^{13}$C: 0.9960, $^{1}$H: 0.9867, B3LYP/631G(d,p) (DMSO): $^{13}$C: 0.9974, $^{1}$H: 0.9921; HF/631G(d,p) (DMSO): $^{13}$C: 0.9954, $^{1}$H: 0.9874. There were such relationships between R$^2$ values of the compound. Found standard error rate and a, b constants regression values were calculated according to formula exp =a +b. δ calc Eq. These values for compound were shown in Table 2.

**Table 2.** The correlation data for chemical shifts of the molecule.

| | **$^{13}$C** | | | | **$^{1}$H** | | | |
|---|---|---|---|---|---|---|---|---|
| | **R$^2$** | **S. error** | **a** | **b** | **R$^2$** | **S. error** | **a** | **b** |
| **DFT** | 0.9977 | 2.2456 | 1.0745 | -13.6269 | 0.9853 | 0.3195 | 0.9766 | -0.7337 |
| **HF** | 0.9960 | 2.9582 | 0.9715 | 7.4501 | 0.9867 | 0.3035 | 0.9070 | 0.2378 |
| | **$^{13}$C (DMSO)** | | | | **$^{1}$H(DMSO)** | | | |
| | **R$^2$** | **S. error** | **a** | **b** | **R$^2$** | **S. error** | **a** | **b** |
| **DFT** | 0.9974 | 2.4004 | 1.0650 | -12.7398 | 0.9921 | 0.2346 | 0.9610 | -0.7073 |
| **HF** | 0.9954 | 3.0914 | 0.9629 | 8.1616 | 0.9874 | 0.2953 | 0.8937 | 0.2124 |

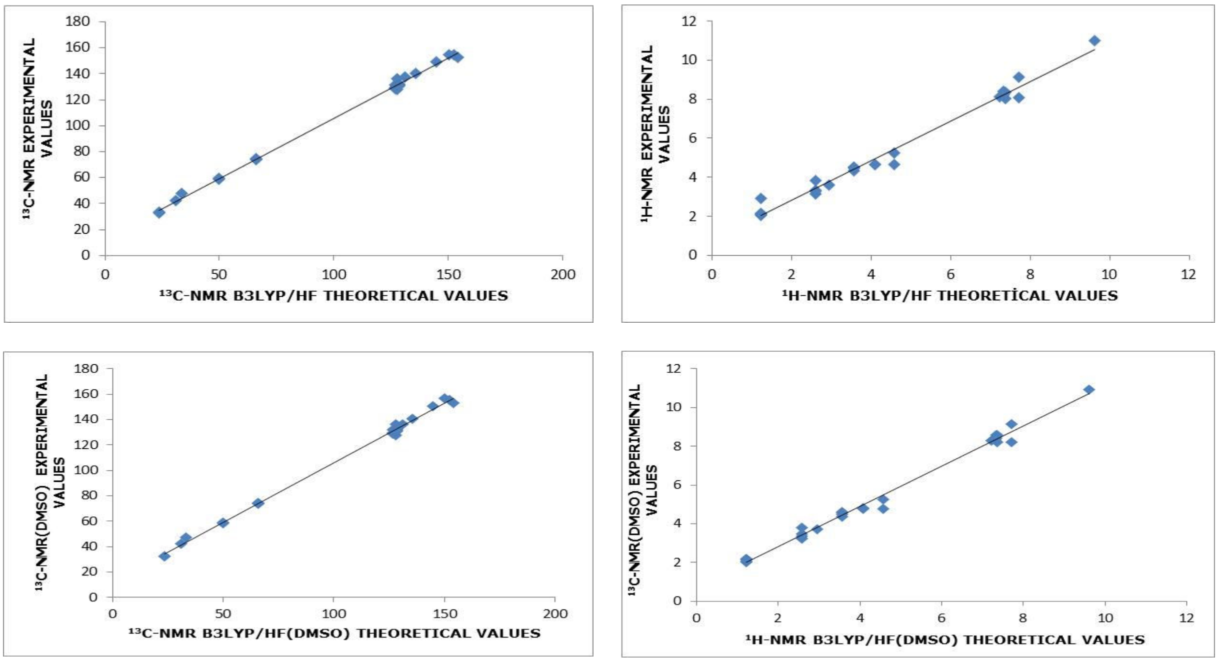


**Figure 2.** The correlation graphs for chemical shifts of the molecule.

## Vibration frequency of the compound

Theoretical IR values were calculated with the Veda 4f program and scalar values were obtained. Negative frequencies were not found in the data. This shows that the structure of the compound is stable. IR spectra were drawn with obtained values according to HF and DFT method (Figure 3). Theoretical IR values were compared with the experimental counterparts. The result of this comparison were found to correspond to each other. Experimental carbonyl peak (C=O) was found in 1692 cm$^{-1}$ and theoretical (C=O) peak was found in 1735 cm$^{-1}$.

**Table 3.** The calculated frequencies values of the molecule.

| Vibration Types | Experimental | Scaled dft | Scaled hf |
|---|---|---|---|
| τ HCOC(16) | 626 | 602 | 560 |
| τ ONNC(12) | 696 | 670 | 623 |
| τ HCCC(11) | 731 | 704 | 685 |
| τ HCCC(50) | 835 | 819 | 764 |
| ν NC(10) | 1586 | 1419 | 1423 |
| ν NC(32) | 1602 | 1614 | 1519 |
| ν OC(76) | 1692 | 1735 | 1635 |

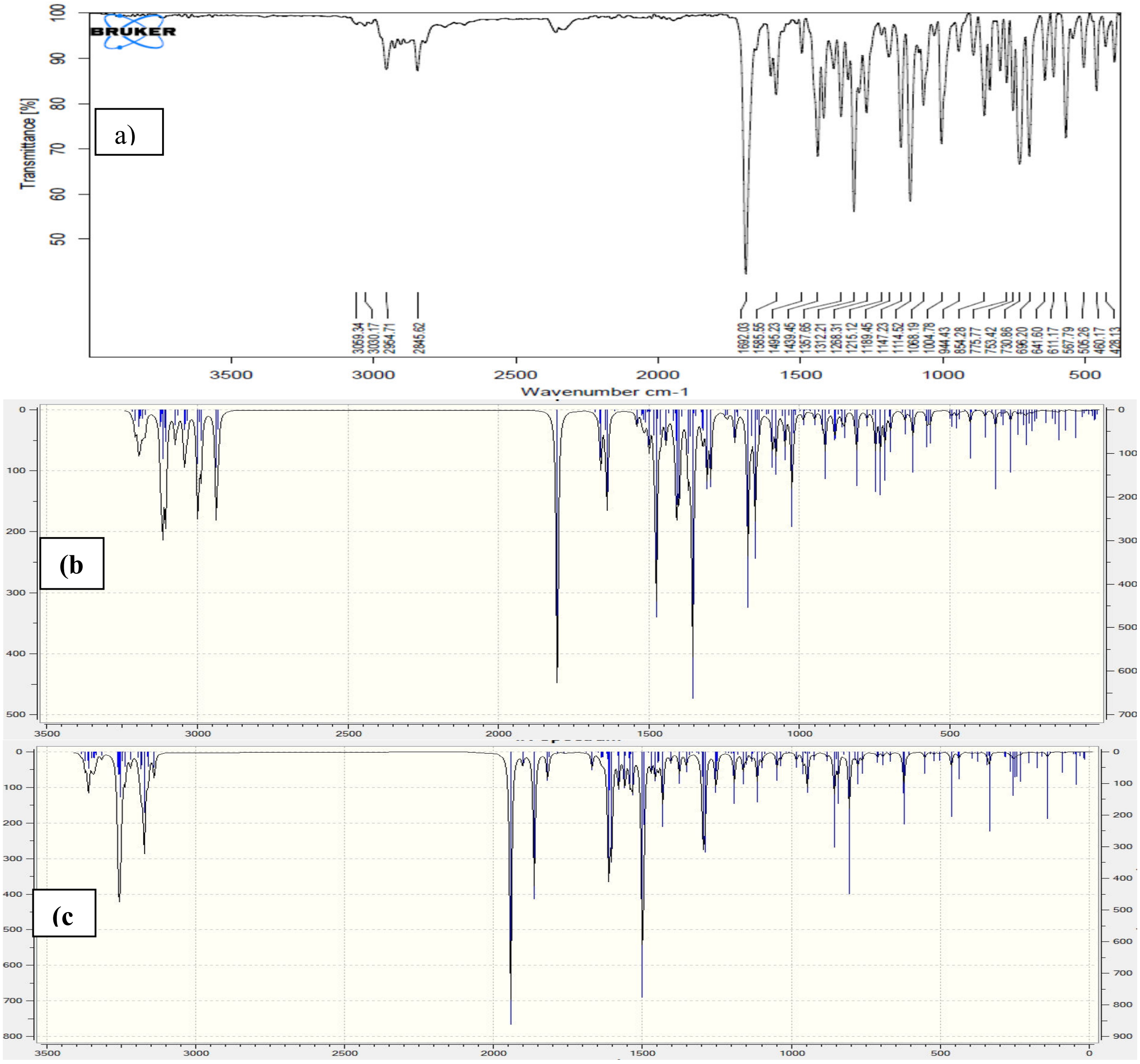


**Figure 3.** Experimental **(a)** and theoretical IR spectra and simulation with DFT/B3LYP/6-31G(d,p)**(b)** and HF/B3LYP/6-31G(d,p)**(c)** levels of the molecule.

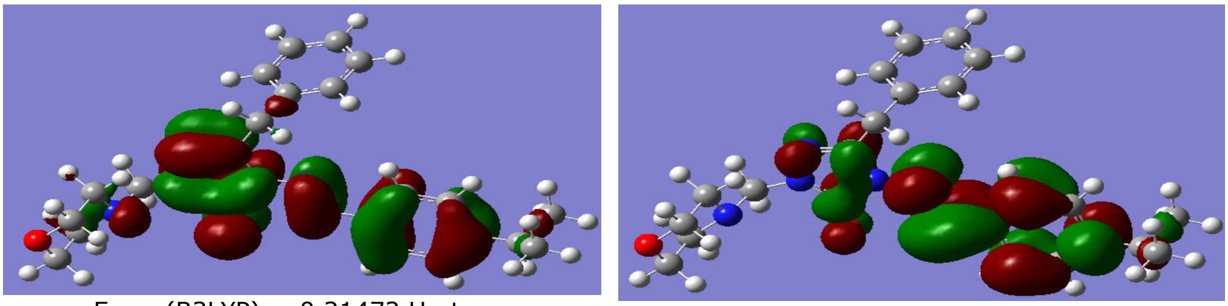
**Table 4.** Calculated bond angles B3LYP/HF 6-31G(d,p) of the molecule.

| | **Bond Angles** | **B3LYP** | **HF** | | **Bond Angles** | **B3LYP** | **HF** |
|---|---|---|---|---|---|---|---|
| **1** | N(54)-C(1)-N(56) | 111.37 | 111.11 | **45** | C(7)-C(8)-C(9) | 121.17 | 120.89 |
| **2** | N(54)-N(55)-C(2) | 113.24 | 112.51 | **46** | C(8)-C(9)-H(29) | 119.87 | 119.46 |
| **3** | N(54)-N(55)-C(20) | 122.00 | 121.29 | **47** | C(8)-C(9)-C(4) | 120.67 | 120.86 |
| **4** | C(20)-N(55)-C(2) | 124.58 | 126.14 | **48** | C(7)-C(10)-C(11) | 111.84 | 111.87 |
| **5** | N(55)-C(2)-O(59) | 129.07 | 128.82 | **49** | C(7)-C(10)-C(12) | 111.79 | 111.87 |
| **6** | O(59)-C(2)-N(56) | 128.87 | 128.35 | **50** | C(7)-C(10)-H(30) | 106.97 | 106.92 |
| **7** | C(2)-N(56)-N(57) | 130.61 | 131.01 | **51** | H(30)-C(10)-C(11) | 107.43 | 107.31 |
| **8** | C(1)-N(56)-N(57) | 121.23 | 121.10 | **52** | C(10)-C(11)-H(31) | 111.27 | 111.47 |
| **9** | N(56)-C(1)-C(13) | 124.00 | 121.98 | **53** | C(10)-C(11)-H(32) | 110.55 | 110.44 |
| **10** | N(54)-C(1)-C(13) | 124.60 | 126.89 | **54** | C(10)-C(11)-H(33) | 111.32 | 111.11 |
| **11** | C(1)-C(13)-H(37) | 106.28 | 107.85 | **55** | C(10)-C(12)-H(34) | 110.58 | 110.44 |
| **12** | C(1)-C(13)-H(38) | 109.06 | 107.90 | **56** | C(10)-C(12)-H(35) | 111.28 | 111.47 |
| **13** | H(37)-C(13)-H(38) | 107.85 | 105.83 | **57** | C(10)-C(12)-H(36) | 111.26 | 111.11 |
| **14** | H(37)-C(13)-C(14) | 109.96 | 110.59 | **58** | H(34)-C(12)-H(35) | 107.65 | 107.69 |
| **15** | H(38)-C(13)-C(14) | 109.53 | 110.62 | **59** | H(34)-C(12)-H(36) | 108.17 | 108.13 |
| **16** | C(13)-C(14)-C(15) | 120.63 | 120.62 | **60** | H(35)-C(12)-H(36) | 107.73 | 107.84 |
| **17** | C(13)-C(14)-C(19) | 120.46 | 120.57 | **61** | H(31)-C(11)-H(32) | 108.17 | 108.13 |
| **18** | C(14)-C(15)-H(39) | 119.43 | 119.68 | **62** | H(31)-C(11)-H(33) | 107.76 | 107.84 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **19** | C(14)-C(15)-C(16) | 120.66 | 120.69 | **63** | H(32)-C(11)-H(33) | 107.60 | 107.69 |
| **20** | H(39)-C(15)-C(16) | 119.89 | 119.62 | **64** | N(55)-C(20)-H(44) | 106.24 | 106.00 |
| **21** | C(15)-C(16)-C(17) | 120.09 | 120.10 | **65** | N(55)-C(20)-H(45) | 106.58 | 106.44 |
| **22** | C(15)-C(16)-H(40) | 119.76 | 119.78 | **66** | N(55)-C(20)-N(58) | 113.05 | 116.83 |
| **23** | H(40)-C(16)-C(17) | 120.13 | 120.10 | **67** | C(20)-N(58)-C(24) | 112.57 | 115.07 |
| **24** | C(16)-C(17)-H(41) | 120.20 | 120.19 | **68** | C(20)-N(58)-C(21) | 113.26 | 115.52 |
| **25** | H(41)-C(17)-C(18) | 120.19 | 120.19 | **69** | N(58)-C(21)-H(46) | 109.17 | 112.00 |
| **26** | C(16)-C(17)-C(18) | 119.60 | 119.61 | **70** | N(58)-C(21)-H(47) | 111.31 | 109.23 |
| **27** | C(17)-C(18)-H(42) | 120.06 | 120.11 | **71** | H(46)-C(21)-H(47) | 107.63 | 107.60 |
| **28** | C(17)-C(18)-C(19) | 120.20 | 120.10 | **72** | H(46)-C(21)-C(22) | 110.13 | 109.78 |
| **29** | H(42)-C(18)-C(19) | 119.73 | 119.78 | **73** | H(47)-C(21)-C(22) | 109.12 | 109.32 |
| **30** | C(18)-C(19)-H(43 | 120.10 | 119.62 | **74** | C(21)-C(22)-H(48) | 109.41 | 109.60 |
| **31** | N(55)-N(54)-C(1) | 105.17 | 105.65 | **75** | C(21)-C(22)-H(49) | 110.58 | 110.63 |
| **32** | N(56)-N(57)-C(3) | 118.60 | 119.77 | **76** | H(48)-C(22)-H(49) | 108.70 | 108.61 |
| **33** | N(57)-C(3)-H(25) | 121.93 | 122.12 | **77** | C(21)-C(22)-O(60) | 111.33 | 110.95 |
| **34** | H(25)-C(3)-C(4) | 117.88 | 117.33 | **78** | H(48)-C(22)-O(60) | 106.54 | 106.93 |
| **35** | C(3)-C(4)-C(5) | 122.70 | 122.78 | **79** | H(49)-C(22)-O(60) | 110.19 | 110.04 |
| **36** | C(3)-C(4)-C(9) | 118.82 | 118.64 | **80** | C(22)-O(60)-C(23) | 110.78 | 112.39 |
| **37** | C(4)-C(5)-C(6) | 120.45 | 120.31 | **81** | O(60)-C(23)-H(50) | 106.61 | 106.94 |
| **38** | C(4)-C(5)-H(26) | 118.87 | 119.47 | **82** | O(60)-C(23)-H(51) | 110.27 | 110.04 |
| **39** | H(26)-C(5)-C(6) | 120.66 | 120.21 | **83** | H(50)-C(23)-H(51) | 108.78 | 108.60 |
| **40** | C(5)-C(6)-H(27) | 118.99 | 119.14 | **84** | O(60)-C(23)-C(24) | 111.35 | 111.00 |
| **41** | C(5)-C(6)-C(7) | 121.37 | 121.46 | **85** | H(52)-C(24)-N(58) | 109.00 | 109.34 |
| **42** | H(27)-C(6)-C(7) | 119.62 | 119.39 | **86** | H(53)-C(24)-N(58) | 112.21 | 111.83 |
| **43** | C(6)-C(7)-C(8) | 117.85 | 117.89 | **87** | C(23)-C(24)-N(58) | 109.27 | 109.00 |
| **44** | C(7)-C(8)-H(28) | 119.37 | 120.15 | **88** | H(52)-C(24)-H(53) | 107.98 | 107.62 |

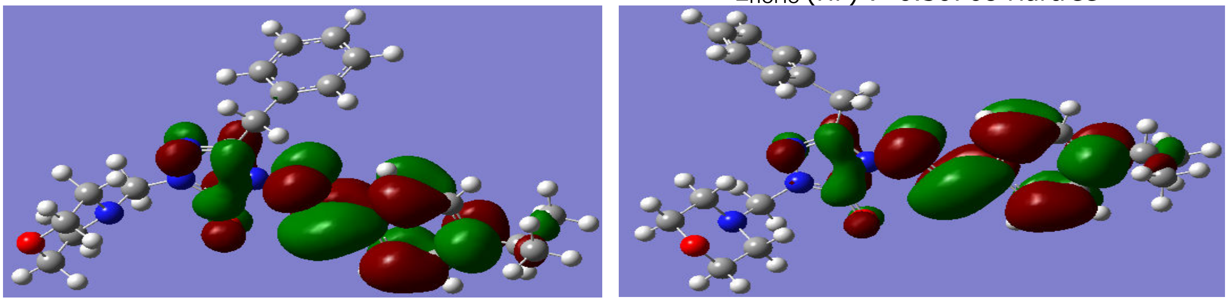
**Table 5.** The calculated bond lengths B3LYP/HF 6-31G(d,p) of the molecule.

| **Bond Lengths** | | **B3LYP** | **HF** | **Bond Lengths** | | **B3LYP** | **HF** |
|---|---|---|---|---|---|---|---|
| **1** | C(1)-C(13) | 1.49 | 1.49 | **32** | C(8)-C(9) | 1.39 | 1.38 |
| **2** | C(1)-N(54) | 1.30 | 1.26 | **33** | C(9)-H(29) | 1.08 | 1.07 |
| **3** | C(1)-N(56) | 1.38 | 1.38 | **34** | C(4)-C(9) | 1.40 | 1.38 |
| **4** | N(54)-N(55) | 1.39 | 1.37 | **35** | C(7)-C(10) | 1.52 | 1.52 |
| **5** | N(55)-C(2) | 1.37 | 1.34 | **36** | C(10)-H(30) | 1.10 | 1.09 |
| **6** | C(2)-N(56) | 1.41 | 1.38 | **37** | C(10)-C(11) | 1.54 | 1.53 |
| **7** | C(2)-O(59) | 1.22 | 1.20 | **38** | C(11)-H(31) | 1.09 | 1.09 |
| **8** | N(56)-N(57) | 1.37 | 1.36 | **39** | C(11)-H(32) | 1.10 | 1.08 |
| **9** | C(13)-H(37) | 1.09 | 1.08 | **40** | C(11)-H(33) | 1.09 | 1.08 |
| **10** | C(13)-H(38) | 1.09 | 1.08 | **41** | C(10)-C(12) | 1.54 | 1.53 |
| **11** | C(13)-C(14) | 1.52 | 1.51 | **42** | C(12)-H(34) | 1.09 | 1.08 |
| **12** | C(14)-C(15) | 1.40 | 1.39 | **43** | C(12)-H(35) | 1.09 | 1.08 |
| **13** | C(15)-H(39) | 1.09 | 1.08 | **44** | C(12)-H(36) | 1.09 | 1.08 |
| **14** | C(15)-C(16) | 1.39 | 1.38 | **45** | N(55)-C(20) | 1.44 | 1.42 |
| **15** | C(15)-H(40) | 1.09 | 1.07 | **46** | C(20)-H(44) | 1.09 | 1.08 |
| **16** | C(16)-C(17) | 1.39 | 1.38 | **47** | C(20)-H(45) | 1.10 | 1.08 |
| **17** | C(17)-H(41) | 1.09 | 1.07 | **48** | C(20)-N(58) | 1.45 | 1.42 |
| **18** | C(17)-C(18) | 1.39 | 1.38 | **49** | N(58)-C(24) | 1.46 | 1.45 |
| **19** | C(18)-H(42) | 1.09 | 1.07 | **50** | C(21)-H(46) | 1.09 | 1.09 |
| **20** | C(18)-C(19) | 1.39 | 1.38 | **51** | C(21)-H(47) | 1.10 | 1.08 |
| **21** | C(19)-H(43) | 1.08 | 1.08 | **52** | C(21)-C(22) | 1.52 | 1.51 |
| **22** | N(57)-C(3) | 1.29 | 1.26 | **53** | C(22)-H(48) | 1.09 | 1.08 |
| **23** | C(3)-H(25) | 1.09 | 1.07 | **54** | C(22)-H(49) | 1.10 | 1.09 |
| **24** | C(3)-C(4) | 1.46 | 1.47 | **55** | C(22)-O(60) | 1.42 | 1.40 |
| **25** | C(4)-C(5) | 1.40 | 1.39 | **56** | O(60)-C(23) | 1.42 | 1.40 |
| **26** | C(5)-H(26) | 1.08 | 1.07 | **57** | C(23)-H(50) | 1.09 | 1.09 |
| **27** | C(5)-C(6) | 1.39 | 1.38 | **58** | C(23)-H(51) | 1.10 | 1.08 |
| **28** | C(6)-H(27) | 1.09 | 1.07 | **59** | C(23)-C(24) | 1.52 | 1.52 |
| **29** | C(6)-C(7) | 1.40 | 1.39 | **60** | C(24)-H(52) | 1.09 | 1.08 |
| **30** | C(7)-C(8) | 1.39 | 1.39 | **61** | C(24)-H(53) | 1.10 | 1.09 |
| **31** | C(8)-H(28) | 1.08 | 1.07 | **62** | C(24)-N(58) | 1.46 | 1.45 |



$E_{HOMO}$ (B3LYP) : -0.21472 Hartree

$E_{HOMO}$ (HF) : -0.30768 Hartree



$E_{LUMO}$ (B3LYP) : -0.05370 Hartree

$E_{LUMO}$ (HF) : 0.08899 Hartree

**Figure 4.** HOMO-LUMO energy calculated with DFT/B3LYP/6-31G(d,p) and HF/B3LYP/6-31G(d,p) levels of the molecule.

**Table 6.** The calculated Mulliken charge data with B3LYP/HF 6-31G(d,p) of the molecule

| | DFT | HF | | DFT | HF | | DFT | HF |
|---|---|---|---|---|---|---|---|---|
| **C1** | 0.541 | 0.611 | **C21** | -0.048 | -0.028 | **H41** | 0.085 | 0.149 |
| **C2** | 0.846 | 1.100 | **C22** | 0.052 | 0.110 | **H42** | 0.087 | 0.151 |
| **C3** | 0.112 | 0.181 | **C23** | 0.054 | 0.118 | **H43** | 0.098 | 0.149 |
| **C4** | 0.083 | -0.086 | **C24** | -0.045 | -0.033 | **H44** | 0.138 | 0.155 |
| **C5** | -0.101 | -0.111 | **H25** | 0.157 | 0.227 | **H45** | 0.105 | 0.167 |
| **C6** | -0.127 | -0.176 | **H26** | 0.106 | 0.177 | **H46** | 0.123 | 0.120 |
| **C7** | 0.151 | 0.022 | **H27** | 0.083 | 0.150 | **H47** | 0.082 | 0.123 |
| **C8** | -0.144 | -0.156 | **H28** | 0.084 | 0.152 | **H48** | 0.092 | 0.122 |
| **C9** | -0.122 | -0.144 | **H29** | 0.094 | 0.164 | **H49** | 0.102 | 0.102 |
| **C10** | -0.130 | -0.154 | **H30** | 0.091 | 0.124 | **H50** | 0.101 | 0.103 |
| **C11** | -0.305 | -0.314 | **H31** | 0.110 | 0.122 | **H51** | 0.095 | 0.124 |
| **C12** | -0.305 | -0.314 | **H32** | 0.102 | 0.114 | **H52** | 0.084 | 0.135 |
| **C13** | -0.287 | -0.272 | **H33** | 0.103 | 0.110 | **H53** | 0.108 | 0.108 |
| **C14** | 0.126 | 0.002 | **H34** | 0.102 | 0.114 | **N54** | -0.350 | -0.334 |
| **C15** | -0.123 | -0.141 | **H35** | 0.104 | 0.118 | **N55** | -0.388 | 0.592 |
| **C16** | -0.085 | -0.145 | **H36** | 0.110 | 0.122 | **N56** | -0.436 | -0.641 |
| **C17** | -0.085 | -0.151 | **H37** | 0.130 | 0.168 | **N57** | -0.322 | -0.333 |
| **C18** | -0.084 | -0.145 | **H38** | 0.141 | 0.167 | **N58** | -0.425 | -0.624 |
| **C19** | -0.115 | -0.141 | **H39** | 0.082 | 0.140 | **O59** | -0.550 | -0.679 |
| **C20** | 0.121 | 0.192 | **H40** | 0.085 | 0.150 | **O60** | -0.485 | -0.641 |

## RESULTS AND DISCUSSION

In this work, geometric parameters and spectroscopic parameters such as IR, $^{1}$H-NMR and $^{13}$C-NMR spectra of (E)-3-benzyl-4-((4-isopropylbenzylidene)-amino)-1-(morpholinomethyl)-1H-1,2,4-triazol-5(4H)-one were calculated by density functional theory (DFT) and Hartree-Fock (HF) methods with the 631G(d,p) basis set. Obtained spectroscopic parameters were compared with experimental data. The chemical shifts in the calculated $^{1}$H-NMR and $^{13}$C-NMR and IR vibrational frequencies were found to be compatible with the experimental data. Theoretical and experimental carbon and proton chemical shifts ratios between according to a, b, and $R^2$ values, a linear correlation were observed. Furthermore, IR vibrational frequencies for experimental carbonyl peak (C=O) in 1692 $cm^{-1}$ and theoretically (C=O) peak in 1735 $cm^{-1}$ were observed. The negative frequency in the IR data was not found. This result shows that the structure of compound was shown to be stable. In addition, the minimum-energy geometry structure in obtained optimization results was determined bond lengths of the molecule. The bond length of the molecule investigated theoretically to see the agreement with experimental data of the molecule C-C bond lengths and the C-H bond of length in the benzene ring in the literature was found to be registered in accordance with the data. Finally, bond angles, the HOMO-LUMO energy, electronegativity and Mulliken charges are calculated theoretically by using the B3LYP/6-31G (d,p) and HF/6-31G (d,p) basis sets.

## REFERENCES

1. Tramontini M, Angiolini L. Mannich Bases: Chemistry and Uses. CRC Press; 1994. 289 p.

2. Yüksek H, Gürsoy O, Cakmak I, Alkan M. Synthesis and GIAO NMR calculations for some new 4,5-dihydro-1H-1,2,4-triazol-5-one derivatives: comparison of theoretical and experimental 1H and 13C chemical shifts. Magn Reson Chem. 2005;43(May):585–7. DOI: 10.1002/mrc.1591. .

3. Yüksek H, Cakmak I, Sadi S, Alkan M, Baykara H. Synthesis and GIAO NMR Calculations for Some Novel 4-Heteroarylidenamino-4,5-dihydro-1H-1,2,4-triazol-5-one Derivatives: Comparison of Theoretical and Experimental 1Hand 13C- Chemical Shifts. Int J Mol Sci. 2005;6(6):219–29. doi:10.3390/i6060219.

4. Yüksek H, Alkan M, Bahçeci Ş, Cakmak I, Ocak Z, Baykara H, et al. Synthesis, determination of pKa values and GIAO NMR calculations of some new 3-alkyl-4-(p-methoxybenzoylamino)-4,5-dihydro-1H-1,2,4-triazol-5-ones. J Mol Struct. 2008;873(1-3):142–8. DOI: 10.1016/j.molstruc.2007.03.016.

5. Yüksek H, Alkan M, Cakmak I, Ocak Z, Bahçeci S, Calapoglu M, et al. Preparation, GIAO NMR calculations and acidic properties of some novel 4,5-dihydro-1H-1,2,4-triazol-5-one derivatives with their antioxidant activities. Int J Mol Sci. 2008 Jan 8;9(1):12–32. PMCID: PMC2635600.

6. Gökce H, Bahçeli S, Akyildirim O, Yüksek H, Kol ÖG. The Syntheses, Molecular Structures, Spectroscopic Properties (IR, Micro– Raman, NMR and UV–vis) and DFT Calculations of Antioxidant 3– alkyl–4–[3–methoxy–4–(4–methylbenzoxy)benzylidenamino]–4,5–dihydro– 1H–1,2,4–triazol–5–one Molecules. Lett Org Chem. 2013;10:395–441. DOI: 10.2174/15701786113109990001.

7. Gökce H, Akyildirim O, Bahçeli S, Yüksek H, Kol ÖG. The 1-acetyl-3-methyl-4-[3-methoxy-4-(4-methylbenzoxy)benzylidenamino]-4,5- dihydro-1H-1,2,4-triazol-5-one molecule investigated by a joint spectroscopic and quantum chemical calculations. J Mol Struct. 2014;1056-1057(1):273–84. DOI: 10.1016/j.molstruc.2013.10.044.

8. Frisch MJ, Trucks GW, Schlegel GE, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09. Wallingford CT: Gaussian, Inc.; 2009.

9. Wolinski K, Hinton JF, Pulay P. Efficient Implementation of the Gauge-Independent Atomic Orbital Method for NMR Chemical Shift Calculations. J Am Chem Soc [Internet]. 1990 Nov;112(d):8251–60. DO:10.1021/ja00179a005.

10. Jamroz MH. Vibrational Energy Distribution Analysis VEDA 4. Warsaw; 2010.

11. Merrick JP, Moran D, Radom L. An evaluation of harmonic vibrational frequency scale factors. J Phys Chem A. American Chemical Society; 2007;111(45):11683–700. DOI: 10.1021/jp073974n.

## Türkçe Öz ve Anahtar Kelimeler

# Theoretical and Spectroscopic Studies of (*E*)-3-Benzyl-4-((4-Isopropylbenzylidene)-Amino)-1-(Morpholinomethyl)-1*H*-1,2,4-triazol-5(4*H*)-one Molecule

Gül Kotan, Haydar Yüksek

**Öz:** Bu çalışmada, (*E*)-3-benzil-4-((4-izopropilbenziliden)-amino)—(morfolinometil)-1*H*-1,2,4-triazol-5(4*H*)-on (**1**) bileşiği, 3-benzil-4-(4-izopropilbenzilidenamino)-4,5-dihidro-1*H*-1,2,4-triazol-5-on ile morfolin ve formaldehit arasındaki tepkimeden elde edilmiştir. **1** bileşiğinin yapısı FT-IR, $^1$H-NMR, $^{13}$C-NMR spektral verileriyle aydınlatılmıştır. Bunun ardından, sentezlenen **1** bileşiği B3LYP/6-31G (d,p) ve HF/6-31G (d,p) baz setleri kullanılarak en iyi duruma getirilmiştir. $^1$H-NMR ve $^{13}$C-NMR izotropik kayma değerleri, IR soğurma frekansları, bağ açıları, bağ uzunlukları, HOMO-LUMO enerjisi, elektronegatiflik ve Mulliken yükleri teorik olarak Gaussian G09W programı ile hesaplanmıştır. Buna ilave olarak, IR, $^1$H-NMR ve $^{13}$C-NMR teorik spektrumları deneysel verilerle karşılaştırılmıştır.

**Anahtar kelimeler:** Mannich bazları, HOMO-LUMO enerjisi, B3LYP 631G(d,p), HF 631G(d,p), Gaussian 09W.

**Gönderme:** 01 Temmuz 2016. **Düzeltme:** 19 Eylül 2016. **Kabul:** 20 Eylül 2016.