COMPARATION OF THEORETICAL PROPERTIES OF 3-METHYL-4-(3-BENZOXY-4-METHOXYBENZYLIDENAMINO)-4, 5-DIHYDRO-1H-1, 2, 4-TRIAZOL-5-ONE MOLECULE.

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Abstract

3-Methyl-4-(3-benzoxy-4-methoxybenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one molecule was optimized by using the B3LYP/HF 631G(d,p) and B3LYP/HF 6311G(d,p) basis sets. This optimized structures used to calculation of the different theoretical properties of the compound. ¹H-NMR and ¹³C-NMR isotropic shift values were calculated by the method of GIAO using the program package Gaussian G09W. Experimental and theoretical values were inserted into the graphic according to equation of $\delta_{exp}=a+b$. $\delta_{calc}$. The standard error values were found via SigmaPlot program with regression coefficient of $a$ and $b$ constants. The wdu4f program was used in defining IR data. IR absorption frequencies were compared with experimental data. Infrared spectrums were composed by using the data calculated. Additionally, bond lengths, dipole moments, HOMO-LUMO energys, Mulliken charges by using the B3LYP/HF 631G(d,p) and B3LYP/HF 6311G(d,p) basis sets of this compound were theoretically calculated. Finally, theoretical properties of the compound according to two different basis sets were compared.

Introduction:

Schiff base compounds are used as starting materials in the synthesis of important drugs, such as antibiotics and antiallergic, antiphlogistic, and antitumor substances (Barton & Ollis, 1979; Ingold, 1969; Layer, 1963). On the industrial scale, they have a wide range of applications, such as dyes and pigments (Taggi et.al., 2002). Schiff bases have also been employed as ligands for the complexation of metal ions (Aydogan et.al., 2001). Schiff bases are also becoming increasingly important in the dye and plastic industries as well as for the liquidcrystal technology and mechanistic investigation of drugs used in pharmacology, biochemistry and physiology (Casaszar et.al., 1985, Sheikhshoae & Sharif, 2006).

In the past years, by increasing development of computational chemistry, theoretically properties of Schiff bases were investigated. 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 (Yüksek et.al., 2005a; Yüksek et.al., 2005b; Yüksek et.al., 2008a; Yüksek et.al., 2008b; Gökçe et.al., 2013; Gökçe et.al., 2014).

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Experimental data of 3-methyl-4-(3-benzoxy-4-methoxybenzylideno)4,5-dihydro-1H-1,2,4-triazol-5-one molecule was described in the literature (Bahçeci et al., 2016).

In the present paper, theoretical values of compound were calculated theoretically on the computer. Molecule was optimized by using the B3LYP/HF 631G(d,p) and B3LYP/HF 6311G(d,p) basis sets (Frisch et al., 2009; Wolinski, Hilton & Pulay, 1990). Starting from this optimized structure with $^1$H-NMR and $^{13}$C-NMR spectral data (Table 1) and IR spectral values according to GIAO (Wolinski et al., 1990) method was calculated using the method of Gaussian G09W program package in gas phase. Theoretically and experimentally values (Bahçeci et al., 2016) were plotted according to $\exp = a + b \cdot \delta$ Equ. a and b constants regression coefficients with a standard error values were found using the SigmaPlot program (Table 2). The correlation graphs for chemical shifts drawn with $^1$H-NMR, $^{13}$C-NMR and $^1$H-NMR(DMSO), $^{13}$C-NMR(DMSO) spectral data of the molecule (Fig. 3). Theoretically calculated IR data are multiplied with appropriate adjustment factors (Merrick et al., 2007) and the data obtained according to HF and DFT method are formed using theoretical infrared spectrum (Fig. 4, 5). The identification of calculated IR data was used in veda4f program (Jamróz, 2004) (Table 3). Additionally, bond lengths (Table 4), Mulliken charges (Mulliken, 1955) (Table 5), the HOMO (the highest occupied molecular orbitals) - LUMO (lowest unoccupied molecular orbitals) energy (Fig. 5, 6) and dipole moments (Table 6) of this compound was found by using two basis sets.

![Chemical formula of compound](image)

**Figure 1:** Chemical formula of compound

**Methods:**

The quantum chemical calculations were carried out with Density Functional Theory (DFT) and Hartree-Fock (HF) methods using 631G(d,p) and 6311G(d,p) basis set at the Gaussian 09W program package on a computing system (Frisch et al., 2009). Firstly, the compound was optimized by using the B3LYP/HF 631G(d,p) and B3LYP/HF 6311G(d,p) basis sets (Frisch et al., 2009; Wolinski, Hilton & Pulay, 1990). Thus, the most stable geometrical conformer of compound was obtained. Then, $^1$H-NMR and $^{13}$C-NMR isotropic shift values were calculated with method of GIAO (Wolinski et al., 1990). The veda4f program was used in defining IR data (Jamróz, 2004). Otherwise, bond lengths, dipole moments, the HOMO-LUMO energy, and Mulliken charges (Mulliken, 1955) of compound were calculated theoretically on the computer. Theoretical properties of the compound according to two different basis sets were compared.

**Theoretical Calculations:**

![Optimized structure of the molecule](image)

**Figure 2:** The optimized structure of the molecule with DFT/B3LYP/631G(d,p) (1) and DFT/B3LYP/6311G(d,p) (2) levels
There is such a relationship between R

The optimized R² values of the compound with B3LYP/631G(1) level:

The optimized R² values of the compound with B3LYP/6311G(2) level:

There is such a relationship between R² values of the compound. Found standard error rate and a, b constants regression values were calculated according to formuleexpx = a +b. δ calc Eq. These values for compound were shown in the table 2. Theoretical and experimental carbon and proton chemical shifts ratios between acording to a, b ve R² values, liner a correlation were observed.
Table 2: The correlation data for chemical shifts of the molecule

|           | ¹/²C (DMSO) |                   | ¹/²H(DMSO) |                   |
|-----------|-------------|------------------|------------|------------------|
| ²         |             |                  |            |                  |
| DFT/631G | 0.9934      | 2.9357           | 1.0244     | -6.8507          | 0.8617 | 1.1174 | 1.0485 | 0.8687 |
| HF/631G  | 0.9898      | 3.7732           | 0.9869     | 5.8241           | 0.8220 | 1.2678 | 0.9617 | 0.0200 |

1/2 C (DMSO)  
2     | R²       | S. error | a    | b    | ²     | R²       | S. error | a    | b    |
DFT/631G | 0.9936   | 2.9800   | 0.9547 | -14.369 | 0.8437 | 1.1880   | 1.0751   | 0.8786 |
HF/631G  | 0.9885   | 4.0078   | 0.9416 | 0.9226  | 0.8009 | 1.3410   | 0.9589   | 0.1621 |

Figure 3: The correlation graphs for B3LYP/HF 631G(d,p)/6311G(d,p) chemical shifts of the molecule

The vibration frequency of the compound: Theoretically IR values were calculation veda 4f programme and scala values were obtain. Theoretically calculated IR data are multiplied with appropriate adjustment factors respectively 0.9617, 0.8992, 0.9688, 0.9059 for DFT/631G(d,p), HF/631G(d,p) and DFT/6311G(d,p), HF/6311G(d,p) basis sets. The negative frequency in the data was not found. This result, structure of compound were shown stable. IR spectrums were drawn with obtained values according to HF and DFT method. Theoretically IR values were compare with experimentally IR values. The result of this compare were found corresponding with each other of values. Experimentally carbonyl peak (C=O) in 1704, 1730 cm⁻¹ and theoretically (C=O) peak in 1768 cm⁻¹ for 631G(d,p), 1762 cm⁻¹ for 6311G(d,p) were observed.

Table 3: The calculated frequencies values of the molecule optimized with 1 and 2 levels

| Vibration Types | Experimental | Skalab dft(1) | Skalab hf(1) | Skalab dft(2) | Skalab hf(2) |
|-----------------|--------------|---------------|--------------|---------------|--------------|
| τ HCCC(16)      | 700          | 692           | 724          | 682           | 684          |
| τ HCCC(11)      | 771          | 779           | 809          | 797           | 826          |
| τ HCOC(27)      | 1262         | 1268          | 1277         | 1179          | 1197         |
| v NC(34)        | 1603         | 1591          | 1625         | 1613          | 1710         |
| v OC(90)        | 1730, 1704   | 1768          | 1809         | 1762          | 1809         |
| v NH(100)       | 3172         | 3557          | 3556         | 3566          | 3561         |
Figure 4: Experimental (a) and theoretical IR spectrums and simulated with DFT/B3LYP/631G(d,p) (b) and HF/B3LYP/631G(d,p) (c) levels of the molecule.
Figure 5:- Theoretical IR spectrums and simulated with DFT/B3LYP/6311G(d,p) (d) and HF/B3LYP/6311G(d,p) (e) levels of the molecule.

Table 4:- The calculated bond lengths B3LYP/HF 631G(d,p) and B3LYP/HF 6311G(d,p) of the molecule.

| Bond Lengths | DFT/631G | HF/631G | DFT/6311G | HF/6311G |
|--------------|----------|---------|-----------|----------|
| 1 C(1)-N(35) | 1.300    | 1.269   | 1.296     | 1.266    |
| 2 C(1)-N(37) | 1.388    | 1.378   | 1.388     | 1.378    |
| 3 C(1)-C(18) | 1.486    | 1.488   | 1.485     | 1.487    |
| 4 N(35)-N(36)| 1.382    | 1.371   | 1.380     | 1.370    |
| 5 N(36)-H(19)| 1.006    | 0.990   | 1.005     | 0.990    |
| 6 N(36)-C(2) | 1.370    | 1.346   | 1.368     | 1.346    |
| 7 C(2)-O(39) | 1.223    | 1.203   | 1.216     | 1.196    |
| 8 C(2)-N(37) | 1.417    | 1.385   | 1.419     | 1.387    |
| 9 N(37)-N(38)| 1.373    | 1.367   | 1.370     | 1.365    |
| 10 N(38)-C(3)| 1.290    | 1.260   | 1.285     | 1.258    |
| 11 C(3)-H(20)| 1.088    | 1.075   | 1.086     | 1.075    |
| 12 C(3)-C(4) | 1.461    | 1.470   | 1.461     | 1.471    |
| 13 C(4)-C(5) | 1.408    | 1.399   | 1.406     | 1.399    |
| 14 C(4)-C(9) | 1.399    | 1.380   | 1.395     | 1.378    |
| 15 C(5)-H(21)| 1.083    | 1.072   | 1.082     | 1.072    |
| 16 C(5)-C(6) | 1.382    | 1.364   | 1.379     | 1.362    |
| 17 C(6)-O(40)| 1.382    | 1.375   | 1.380     | 1.374    |
| 18 C(6)-C(7) | 1.415    | 1.401   | 1.413     | 1.401    |
| 19 C(7)-O(41)| 1.356    | 1.337   | 1.355     | 1.335    |
| 20 C(7)-C(8) | 1.396    | 1.381   | 1.394     | 1.380    |
| 21 C(8)-H(22)| 1.083    | 1.072   | 1.081     | 1.071    |
| 22 C(8)-C(9) | 1.395    | 1.390   | 1.393     | 1.390    |
| 23 C(9)-H(23)| 1.086    | 1.076   | 1.084     | 1.075    |
| 24 O(40)-C(10)| 1.386   | 1.341   | 1.388     | 1.340    |
| 25 C(10)-O(42)| 1.204   | 1.185   | 1.197     | 1.178    |
| 26 C(10)-C(11)| 1.493   | 1.488   | 1.491     | 1.489    |
| 27 C(11)-C(12)| 1.401   | 1.389   | 1.399     | 1.388    |
| 28 C(11)-C(16)| 1.402   | 1.390   | 1.399     | 1.389    |
| 29 C(12)-H(24)| 1.083   | 1.072   | 1.082     | 1.072    |
| 30 C(12)-C(13)| 1.394   | 1.384   | 1.389     | 1.383    |
| 31 C(13)-H(25)| 1.085   | 1.075   | 1.083     | 1.074    |
| 32 C(13)-C(14)| 1.395   | 1.384   | 1.394     | 1.384    |
| 33 C(14)-H(26)| 1.086   | 1.075   | 1.084     | 1.075    |
| 34 C(14)-C(15)| 1.397   | 1.386   | 1.393     | 1.386    |
| 35 C(15)-H(27)| 1.085   | 1.075   | 1.083     | 1.074    |
| 36 C(15)-C(16)| 1.391   | 1.382   | 1.391     | 1.381    |
| 37 C(16)-H(28)| 1.084   | 1.073   | 1.082     | 1.073    |
|   | Bond          | Distance (Å) | Distance (Å) | Distance (Å) | Distance (Å) |
|---|---------------|--------------|--------------|--------------|--------------|
| 38| C(7)-O(41)   | 1.356        | 1.337        | 1.355        | 1.335        |
| 39| O(41)-C(17)  | 1.422        | 1.402        | 1.423        | 1.402        |
| 40| C(17)-H(29)  | 1.096        | 1.085        | 1.095        | 1.079        |
| 41| C(17)-H(30)  | 1.089        | 1.084        | 1.088        | 1.085        |
| 42| C(17)-H(31)  | 1.096        | 1.079        | 1.094        | 1.085        |
| 43| C(18)-H(32)  | 1.094        | 1.083        | 1.092        | 1.083        |
| 44| C(18)-H(33)  | 1.094        | 1.083        | 1.092        | 1.083        |
| 45| C(18)-H(34)  | 1.090        | 1.080        | 1.089        | 1.080        |

**Figure 6:** HOMO-LUMO energy calculated with DFT/B3LYP/631G(d,p) and HF/B3LYP/631G(d,p) levels of the molecule.

**Figure 7:** HOMO-LUMO energy calculated with DFT/B3LYP/631G(d,p) and HF/B3LYP/631G(d,p) levels of the molecule.
Results and Discussion:

In this work, geometrical parameters and spectroscopic parameters such as IR, $^1$H-NMR and $^{13}$C-NMR spectra of molecule are calculated by Density Functional Theory (DFT) and Hartree-Fock (HF) methods with the 631G(d,p) and 6311G(d,p) two different basis sets. Obtained spectroscopic parameters are compared with experimental data. Furthermore, calculated theoretical data with the 631G(d,p) and 6311G(d,p) basis sets are compared with each other. The chemical shifts in the calculations $^1$H-NMR and $^{13}$C-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 a, b ve R$^2$ values, lineer a correlation were observed.

Furthermore, IR vibrational frequencies experimentally carbonyl peak (C=O) in 1706 cm$^{-1}$ and theoretically (C=O) peak in 1768 cm$^{-1}$ for 631G(d,p), 1762 cm$^{-1}$ for 6311G(d,p) were observed. The negative frequency in the IR data was not found. This result, structure of compound were shown stable. In addition, bond lengths, dipole moments, the HOMO-LUMO energy and Mulliken charges are calculated theoretically by using the B3LYP/HF 631G(d,p) and 6311G(d,p) basis sets.
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