

# Thermodynamic Parameters, NBO Analysis, HOMO-LUMO and MEP Analysis of (5R)-2-Methyl-5-[(2S)-6-Methyl-5-Hepten-2-yl]-1,3-Cyclohexadiene Using HF and DFT Calculations

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**Abstract:** Ginger plant is a well-known spice and flavoring agent which has also been used in traditional medicine in many countries. Ginger contains essential oils including Gingerol and Zingiberene. Zingiberene is a monocyclic sesquiterpene that gives a distinctive flavor to ginger. The quantum theoretical calculations for Zingiberene were performed by using HF/6-31G, HF/6-31G(d), B3LYP/6-31G, B3PW91/6-31G and BLYP/6-31G level. The  $E_{\text{HOMO-1}}$ ,  $E_{\text{LUMO}}$ ,  $E_{\text{LUMO+1}}$ , HOMO-LUMO energy gap ( $E_g$ ), and dipole moment ( $\mu_D$ ) obtained for Zingiberene. According to the calculated HOMO and LUMO energies, molecular properties such as Ionisation Potential (I), Electron affinity (A), chemical hardness ( $\eta$ ), electronic chemical potential ( $\mu$ ) and electrophilicity ( $\omega$ ) obtained and also show that charge transfer occurs in Zingiberene. The frontier molecular orbitals (FMOs) and molecular electrostatic potentials (MEPs), the chemical shielding tensors (CS), thermodynamic parameters, natural charge and NBO analysis were investigated for title structure by theoretical calculations.

**Keywords:** Ginger, Zingiberene, Energy gap, Natural charge, NBO analysis.

## Introduction

Ginger plant is a well-known spice and flavoring agent which has also been used in traditional medicine in many countries. This large seasonal plant is cultivated in Southeast Asia and China, India, and some parts of Africa.

Ginger and turmeric plants have several similar characteristics – both possess pale green flowers and are surrounded by long lanceolate leaves. Ginger has been traditionally used for treatment of headaches, nausea, colds [1], arthritis, rheumatism, muscular discomfort [2], and inflammation [3]. Ginger contains essential oils including Gingerol and Zingiberene. It also contains pungent principles such as Zingerone, Gingerol and Shogaol [4]. Zingiberene, with molecular formula  $C_{15}H_{24}$ , is a monocyclic sesquiterpene that is the predominant constituent of the oil of ginger (*Zingiberofficinale*) [5,6] from

which it gets its name. It can contribute up to 30% of the essential oils in ginger rhizomes.

This is the compound that gives ginger its distinct flavoring. The systematic name of Zingiberene is (5R)-2-Methyl-5-[(2S)-6-methyl-5-hepten-2-yl]-1,3-cyclohexadiene (see Figure 1).

In recent years, computational chemistry has become an important tool for chemists and a well-accepted partner for experimental chemistry [7-12]. Density functional theory (DFT) and Hartree-Fock (HF) methods have become a major tool in the methodological arsenal of computational organic chemists. In the present work, we investigate the energetic and structural properties of the Zingiberene, using HF and DFT calculations. In this study, the optimized geometry, HOMO and LUMO analysis,

chemical tensors, natural charge and NBO analysis were calculated.

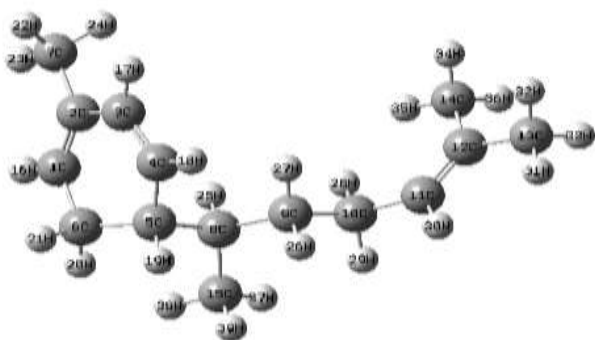


**Figure 1: The theoretical geometric structure of the Zingiberene**

### Computational Method

In this work, we have carried out quantum theoretical calculations of the title compound using HF/6-31G, HF/6-31G(d), B3LYP/6-31G, B3PW91/6-31G and BLYP/6-31G level by the Gaussian 03W program package [13] and calculate its properties. At first we have optimized structure using Gaussian 03W program. We studied the thermodynamic parameters of Zingiberene using five levels, and obtained the energy ( $\Delta E$ ), enthalpies ( $\Delta H$ ), Gibbs free energy ( $\Delta G$ ), entropies ( $S$ ) and constant volume molar heat capacity ( $C_v$ ) of the derivatives [14, 15]. The electronic properties such as energy of the highest occupied molecular orbital ( $E_{HOMO}$ ), energy of the lowest unoccupied molecular orbital ( $E_{LUMO}$ ), HOMO-LUMO energy gap ( $E_g$ ),  $E_{HOMO-1}$ ,  $E_{LUMO+1}$ , natural charges, dipole moment ( $\mu_D$ ) and point group were detected [16].

The optimized molecular structure, HOMO and LUMO surfaces were visualized using GaussView 03 program [17]. Then we were performed NMR calculation using title levels. As a result of these calculations, the NMR parameters such as chemical shift isotropic ( $CS^I$ ) and chemical shift anisotropic ( $CS^A$ ) the is obtained for title structure [14, 18]. The electronic structure of the studied compound were studied by using Natural Bond Orbital (NBO) analysis at the same level in order to understand various second-order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the inter-molecular delocalization or hyper conjugation [15, 19].

### Result and Discussion

The relative energy ( $\Delta E$ ), standard enthalpies ( $\Delta H$ ), entropies ( $\Delta S$ ), Gibbs free energy ( $\Delta G$ ) and constant volume molar heat capacity ( $C_v$ ) values of title compound were obtained by theoretical methods using the five levels to obtain minima of the potential energy. The calculated results in Table 1 show that relative energy, Gibbs free energy and standard enthalpy values of molecule for all levels are negative, therefore we found that molecule is stable. As indicated in Table 1, we found that the maximum stability obtained using B3LYP/6-31G level.

**Table 1: The calculated thermodynamic parameters of Zingiberene using five levels**

|              | $\Delta E(\text{Kcal/mol})$ | $\Delta G(\text{Kcal/mol})$ | $\Delta H(\text{Kcal/mol})$ | $S(\text{cal/molK})$ | $CV(\text{cal/molK})$ |
|--------------|-----------------------------|-----------------------------|-----------------------------|----------------------|-----------------------|
| HF/6-31G     | -364789.140                 | -364828.324                 | -364788.548                 | 133.412              | 59.831                |
| HF/6-31G*    | -364932.929                 | -364972.306                 | -364932.336                 | 134.058              | 60.594                |
| B3LYP/6-31G  | -367408.782                 | -367448.847                 | -367408.190                 | 136.366              | 64.274                |
| B3PW91/6-31G | -367277.888                 | -367318.024                 | -367277.295                 | 136.603              | 64.225                |
| BLYP/6-31G   | -367195.197                 | -367235.731                 | -367194.605                 | 137.939              | 66.260                |

### Electronic Properties

Quantum chemical methods are important to obtain information about molecular structure and electrochemical behavior. The Frontier Molecular Orbitals (FMO) analysis calculated for compound using B3LYP/6-

31+G(d) level [20]. The results of FMO such as  $E_{HOMO}$ ,  $E_{HOMO-1}$ ,  $E_{LUMO}$ ,  $E_{LUMO+1}$  and HOMO-LUMO energy gap ( $E_g$ ) of molecule are summarized in Table 2. The values of energy of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) and their energy

gaps reflect the chemical activity of the molecule [21]. The HOMO can act as an electron donor and the LUMO can act as the electron acceptor. A higher HOMO energy ( $E_{\text{HOMO}}$ ) for the molecule indicates a higher electron-donating ability to an appropriate acceptor molecule with a low-energy empty molecular orbital. The highest value of energy gap for molecule obtained using HF/6-31G(d) level. The calculated values for  $E_{\text{HOMO}}$ ,  $E_{\text{HOMO}-1}$ ,  $E_{\text{LUMO}}$ ,  $E_{\text{LUMO}+1}$  and HOMO–LUMO energy gap ( $E_g$ ) are -8.04, -8.94, 3.83 and 5.38 eV, respectively. The Frontier Molecular Orbitals (FMO) of molecule for

HF/6-31G(d) shown in Figure 2. The HOMO orbital can act as an electron donor and the LUMO orbital can act as the electron acceptor. As shown in Figure 2, charge transfer is taking place within the molecule. According to orbitals pictures (Figure 2), it is found that the HOMO-1 orbital of molecule is localized mainly on C=C of alkene, whereas HOMO orbital is focused on cyclohexadiene. The HOMO→LUMO transition implies an electron density transfer from the phenyl ring to methyl group. Also LUMO+1orbital were localized mainly on the two methyl of alkene.

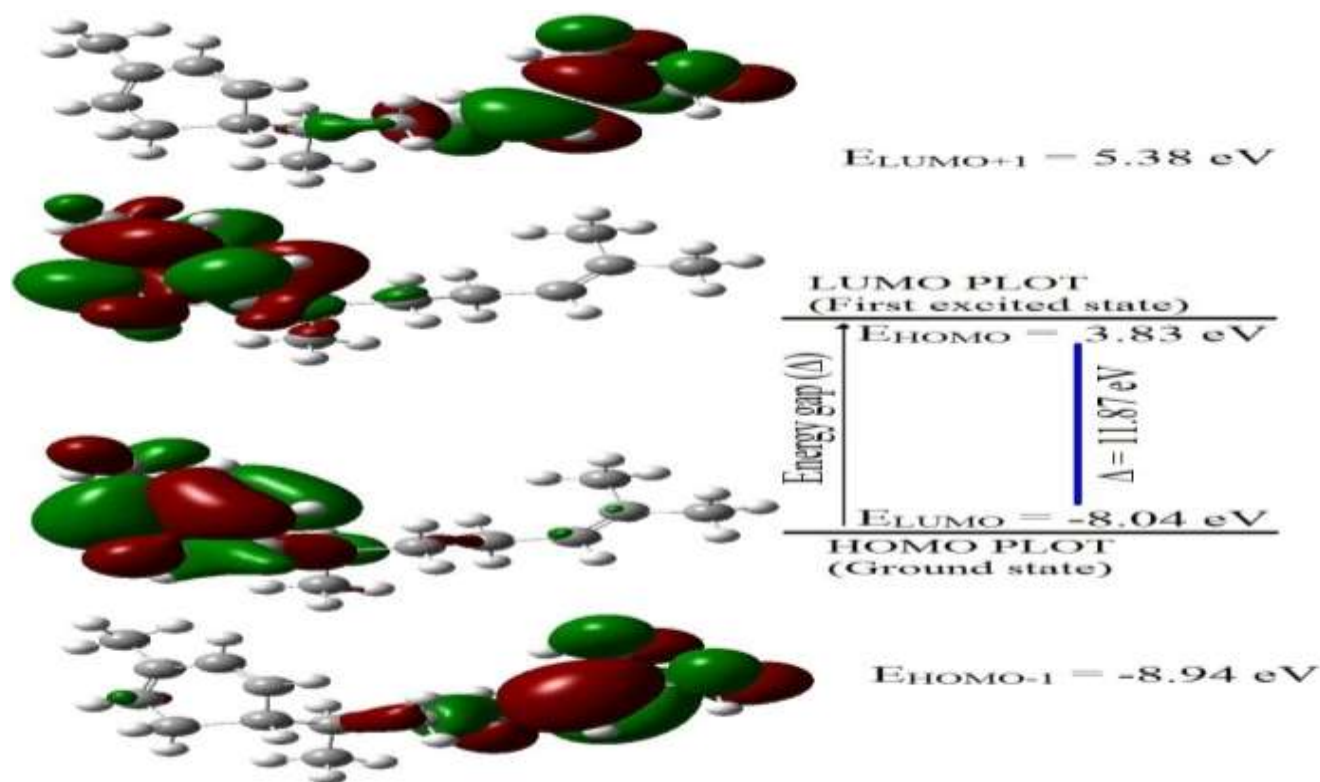


**Figure 2: Frontier molecular orbitals of Zingiberene using HF/6-31G(d) level( $E_g$ : Energy gap between LUMO and HOMO)**

A detail of quantum molecular descriptors of molecule using five levels are summarized in Table 2. The chemical hardness ( $\eta$ ) is important property to measure the molecular stability and reactivity [22, 23].

The electronic chemical potential ( $\mu$ ) is a form of the potential energy that can be absorbed or released during a chemical reaction and that may also change during a phase transition [24], whereas  $I$  is ionization potential and  $A$  is electron affinity. The energy of the HOMO is directly related to the ionization potential and the energy of the LUMO is directly related to the electron affinity [25].

The electrophilicity ( $\omega$ ) measures the stabilization in energy when the system acquires an additional electronic charge from the environment.

The electrophilicity index contains information about both electron transfer (chemical potential) and stability (hardness) and is a better descriptor of global chemical reactivity [26]. Dipole moment ( $\mu_D$ ) is a good measure for the asymmetric nature of a molecule. According Table 2, the biggest and smallest value of dipole moment ( $\mu_D$ ) is obtained using B3PW91/6-31G and HF/6-31G (d), respectively. Also the studied structure has point group of C1 which refers high asymmetry in the structure.

**Table 2: Molecular properties of Zingiberene using five levels**

| Parameter                   | HF/<br>6-31G | HF/<br>6-31G* | B3LYP/<br>6-31G | B3PW91/<br>6-31G | BLYP/<br>6-31G |
|-----------------------------|--------------|---------------|-----------------|------------------|----------------|
| $\mu_D$ (Debye)             | 0.2608       | 0.2024        | 0.2539          | 0.2697           | 0.2457         |
| Point Group                 | C1           | C1            | C1              | C1               | C1             |
| $E_{HOMO}$ (eV)             | -7.97        | -8.04         | -5.49           | -5.55            | -4.47          |
| $E_{LUMO}$ (eV)             | 3.71         | 3.83          | -0.36           | -0.42            | -0.99          |
| $E_{HOMO-1}$ (eV)           | -8.86        | -8.94         | -6.09           | -6.14            | -5.0           |
| $E_{LUMO+1}$ (eV)           | 5.3          | 5.38          | 1.02            | 0.99             | 0.3            |
| $E_g$ (eV)                  | 11.68        | 11.87         | 5.13            | 5.13             | 3.48           |
| $I = -E_{HOMO}$ (eV)        | 7.97         | 8.04          | 5.49            | 5.55             | 4.47           |
| $A = -E_{LUMO}$ (eV)        | -3.71        | -3.83         | 0.36            | 0.42             | 0.99           |
| $\mu = -(I + A)/2$ (eV)     | -2.13        | -2.10         | -2.92           | -2.98            | -2.73          |
| $\eta = (I - A)/2$ (eV)     | 5.84         | 5.93          | 2.56            | 2.56             | 1.74           |
| $\omega = \mu^2/2\eta$ (eV) | 0.39         | 0.37          | 1.66            | 1.73             | 2.14           |

### Molecular Electrostatic Potential (MEP)

Molecular electrostatic potential (MEP) is related to the electronic density and is important in understanding sites for electrophilic attack and nucleophilic reactions [27, 28]. To indicate reactive sites of electrophilic and nucleophilic for title molecule, MEP was calculated at the HF/6-31G, HF/6-31G(d), B3LYP/6-31G, B3PW91/6-31 and BLYP/6-31G level.

Electrostatic potential map shown in Figure 4 characterizes the charge distributions of the molecule as three dimensionally. As shown in Figure 4, the negative regions (red and yellow) of MEP were related to electrophilic reactivity. From the MEP it is clear that the C=C bonds of diene and C=C bond of alkene section are negative charge centers and sites for electrophilic attack. As shown in Fig. 3, the highest and lowest electronic density range obtained with B3PW91/6-31G and HF/6-31G level, respectively.

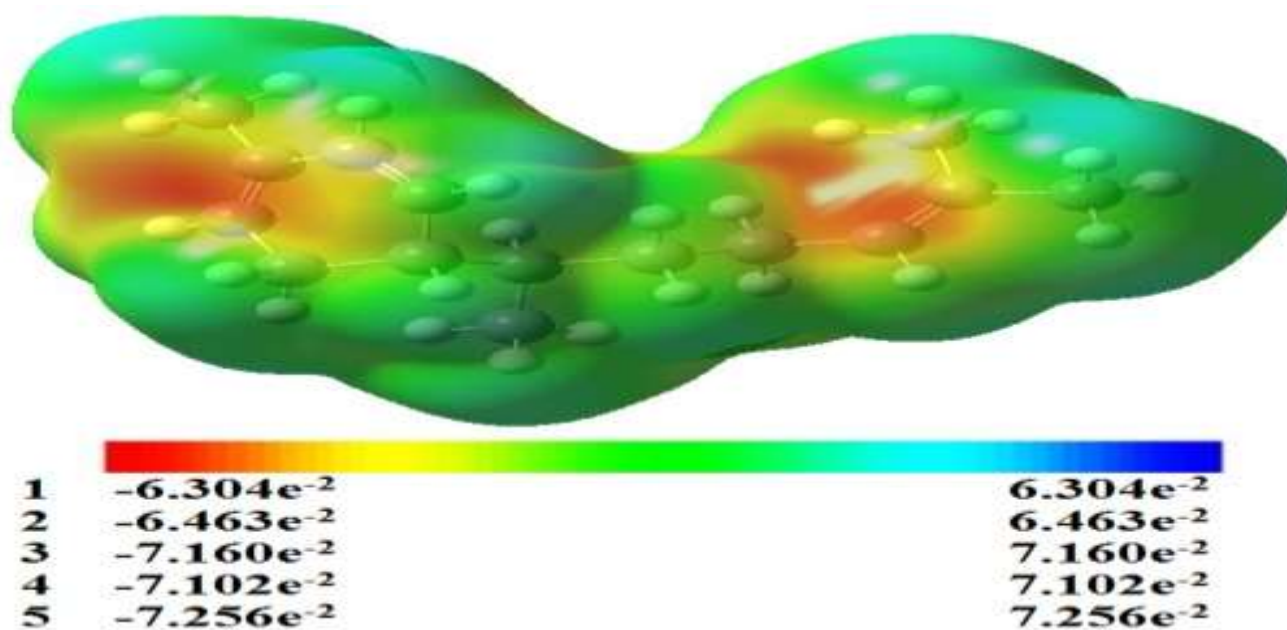


**Figure 3: The molecular electrostatic potential (MEP) surface of Zingiberene using five method such as: (1) HF/6-31G (2)HF/6-31G(d) (3)B3LYP/6-31G (4)B3PW91/6-31G (5)BLYP/6-31G.**

### Atomic Charge

We calculated the charge distributions for equilibrium geometry of molecule by NBO method (natural charge) [29] using five levels that are listed in Table 3. The total charge of the investigated molecule is equal to zero. The calculated results for all

methods reveal that the negative charge is delocalized on carbon, whereas hydrogen atoms have the positive charge.

The biggest values of negative charge, with all methods, are observed for C<sub>7</sub>, C<sub>13</sub>, C<sub>14</sub> and

C<sub>15</sub> (C atoms of methyl groups).The highest values of negative charge for C atoms obtained using B3PW91/6-31G level.

**Table 3: The natural charges (e) for the Zingiberene using five levels**

| Atoms           | HF/6-31G | HF/6-31G* | B3LYP/6-31G | B3PW91/6-31G | BLYP/6-31G |
|-----------------|----------|-----------|-------------|--------------|------------|
| C <sub>1</sub>  | -0.214   | -0.201    | -0.207      | -0.214       | -0.201     |
| C <sub>2</sub>  | -0.051   | -0.055    | -0.056      | -0.061       | -0.056     |
| C <sub>3</sub>  | -0.255   | -0.244    | -0.255      | -0.263       | -0.250     |
| C <sub>4</sub>  | -0.195   | -0.184    | -0.203      | -0.211       | -0.201     |
| C <sub>5</sub>  | -0.269   | -0.253    | -0.283      | -0.295       | -0.280     |
| C <sub>6</sub>  | -0.475   | -0.447    | -0.494      | -0.513       | -0.490     |
| C <sub>7</sub>  | -0.681   | -0.638    | -0.709      | -0.732       | -0.702     |
| C <sub>8</sub>  | -0.239   | -0.227    | -0.247      | -0.260       | -0.243     |
| C <sub>9</sub>  | -0.443   | -0.416    | -0.462      | -0.480       | -0.457     |
| C <sub>10</sub> | -0.465   | -0.435    | -0.487      | -0.506       | -0.482     |
| C <sub>11</sub> | -0.234   | -0.219    | -0.229      | -0.237       | -0.224     |
| C <sub>12</sub> | -0.008   | -0.015    | -0.011      | -0.015       | -0.011     |
| C <sub>13</sub> | -0.684   | -0.640    | -0.711      | -0.735       | -0.704     |
| C <sub>14</sub> | -0.693   | -0.650    | -0.718      | -0.741       | -0.711     |
| C <sub>15</sub> | -0.676   | -0.633    | -0.699      | -0.722       | -0.692     |
| H <sub>16</sub> | 0.277    | 0.215     | 0.230       | 0.238        | 0.226      |
| H <sub>17</sub> | 0.234    | 0.221     | 0.238       | 0.246        | 0.234      |
| H <sub>18</sub> | 0.234    | 0.221     | 0.239       | 0.247        | 0.235      |
| H <sub>19</sub> | 0.243    | 0.228     | 0.252       | 0.263        | 0.250      |
| H <sub>20</sub> | 0.240    | 0.226     | 0.247       | 0.256        | 0.245      |
| H <sub>21</sub> | 0.245    | 0.231     | 0.254       | 0.265        | 0.252      |
| H <sub>22</sub> | 0.235    | 0.221     | 0.244       | 0.253        | 0.242      |
| H <sub>23</sub> | 0.235    | 0.222     | 0.244       | 0.252        | 0.241      |
| H <sub>24</sub> | 0.236    | 0.222     | 0.245       | 0.254        | 0.243      |
| H <sub>25</sub> | 0.240    | 0.226     | 0.247       | 0.259        | 0.244      |
| H <sub>26</sub> | 0.221    | 0.207     | 0.228       | 0.237        | 0.225      |
| H <sub>27</sub> | 0.233    | 0.219     | 0.247       | 0.257        | 0.244      |
| H <sub>28</sub> | 0.227    | 0.214     | 0.234       | 0.243        | 0.232      |
| H <sub>29</sub> | 0.232    | 0.218     | 0.243       | 0.252        | 0.240      |
| H <sub>30</sub> | 0.218    | 0.206     | 0.222       | 0.230        | 0.218      |
| H <sub>31</sub> | 0.233    | 0.220     | 0.241       | 0.249        | 0.239      |
| H <sub>32</sub> | 0.232    | 0.217     | 0.240       | 0.249        | 0.238      |
| H <sub>33</sub> | 0.232    | 0.217     | 0.240       | 0.249        | 0.238      |
| H <sub>34</sub> | 0.235    | 0.220     | 0.243       | 0.252        | 0.241      |
| H <sub>35</sub> | 0.235    | 0.221     | 0.241       | 0.249        | 0.239      |
| H <sub>36</sub> | 0.235    | 0.221     | 0.243       | 0.252        | 0.241      |
| H <sub>37</sub> | 0.230    | 0.217     | 0.240       | 0.249        | 0.238      |
| H <sub>38</sub> | 0.230    | 0.216     | 0.235       | 0.243        | 0.233      |
| H <sub>39</sub> | 0.221    | 0.208     | 0.230       | 0.239        | 0.228      |

## NMR Parameters

Also the NMR parameters such as chemical shift isotropic (CS<sup>I</sup>) and chemical shift anisotropic (CS<sup>A</sup>) for Zingiberene are summarized in Table 4. As can be seen in

Table 4, the CS<sup>I</sup> and CS<sup>A</sup> values of all atoms are positive. As can be seen in Table 4, the lowest values of CS<sup>I</sup> and CS<sup>A</sup> belong to hydrogen atoms.

**Table 4: The NMR parameters (ppm) such as chemical shift isotropic (CS<sup>I</sup>) and chemical shift anisotropic (CS<sup>A</sup>) for Zingiberene using five levels**

| Atoms           | HF/6-31G        |                 | HF/6-31G*       |                 | B3LYP/6-31G     |                 | B3PW91/6-31G    |                 | BLYP/6-31G      |                 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | CS <sup>I</sup> | CS <sup>A</sup> | CS <sup>I</sup> | CS <sup>A</sup> | CS <sup>I</sup> | CS <sup>A</sup> | CS <sup>I</sup> | CS <sup>A</sup> | CS <sup>I</sup> | CS <sup>A</sup> |
| C <sub>1</sub>  | 85.54           | 133.81          | 84.00           | 126.39          | 76.03           | 116.81          | 78.72           | 118.24          | 72.19           | 110.90          |
| C <sub>2</sub>  | 73.27           | 175.48          | 73.09           | 164.55          | 64.22           | 160.41          | 67.62           | 160.58          | 60.12           | 154.58          |
| C <sub>3</sub>  | 77.93           | 152.77          | 77.79           | 142.33          | 70.00           | 138.59          | 72.64           | 139.85          | 66.73           | 132.88          |
| C <sub>4</sub>  | 72.16           | 171.01          | 71.88           | 159.48          | 66.63           | 149.91          | 69.37           | 150.97          | 63.90           | 142.17          |
| C <sub>5</sub>  | 173.64          | 32.66           | 168.59          | 27.73           | 152.40          | 33.96           | 157.19          | 34.80           | 143.77          | 33.98           |
| C <sub>6</sub>  | 184.93          | 10.62           | 178.53          | 10.12           | 165.83          | 13.84           | 169.64          | 13.28           | 158.21          | 15.51           |
| C <sub>7</sub>  | 186.85          | 32.92           | 181.01          | 30.16           | 171.99          | 35.15           | 175.03          | 34.94           | 165.92          | 35.66           |
| C <sub>8</sub>  | 177.01          | 22.66           | 171.93          | 18.92           | 157.12          | 26.59           | 162.35          | 26.84           | 147.84          | 27.33           |
| C <sub>9</sub>  | 175.79          | 34.40           | 170.46          | 30.53           | 157.63          | 27.15           | 161.89          | 27.03           | 150.21          | 26.59           |
| C <sub>10</sub> | 182.16          | 23.76           | 176.28          | 19.85           | 164.31          | 20.36           | 167.97          | 20.68           | 156.96          | 20.23           |
| C <sub>11</sub> | 79.085          | 125.33          | 78.28           | 118.74          | 69.89           | 109.54          | 72.63           | 110.35          | 66.32           | 104.06          |
| C <sub>12</sub> | 75.073          | 162.53          | 75.10           | 153.63          | 65.98           | 145.79          | 69.57           | 145.94          | 61.60           | 139.78          |

|                 |        |       |        |       |        |       |        |       |        |       |
|-----------------|--------|-------|--------|-------|--------|-------|--------|-------|--------|-------|
| C <sub>13</sub> | 182.51 | 39.96 | 176.81 | 37.13 | 167.74 | 41.95 | 170.77 | 41.65 | 161.74 | 42.38 |
| C <sub>14</sub> | 190.74 | 23.65 | 184.66 | 21.65 | 176.76 | 24.22 | 179.50 | 24.18 | 171.06 | 24.34 |
| C <sub>15</sub> | 190.33 | 23.94 | 184.18 | 22.09 | 176.56 | 26.66 | 179.99 | 26.10 | 170.43 | 27.53 |
| H <sub>16</sub> | 27.76  | 2.95  | 27.36  | 3.47  | 27.26  | 3.49  | 27.15  | 3.18  | 27.06  | 3.71  |
| H <sub>17</sub> | 27.21  | 5.00  | 27.00  | 5.41  | 26.66  | 4.36  | 26.53  | 4.22  | 26.48  | 4.25  |
| H <sub>18</sub> | 26.95  | 4.41  | 26.67  | 4.07  | 26.55  | 4.52  | 26.44  | 4.36  | 26.38  | 4.56  |
| H <sub>19</sub> | 32.37  | 7.05  | 31.69  | 6.34  | 31.11  | 5.25  | 31.06  | 5.77  | 30.67  | 4.47  |
| H <sub>20</sub> | 31.70  | 7.64  | 31.02  | 6.96  | 30.55  | 5.88  | 30.47  | 6.39  | 30.16  | 5.18  |
| H <sub>21</sub> | 31.56  | 11.52 | 30.88  | 10.46 | 30.31  | 9.84  | 30.28  | 10.31 | 29.89  | 9.10  |
| H <sub>22</sub> | 31.79  | 10.26 | 31.26  | 9.40  | 30.93  | 8.83  | 30.86  | 9.23  | 30.63  | 8.23  |
| H <sub>23</sub> | 31.93  | 8.60  | 31.27  | 7.75  | 31.25  | 7.06  | 31.14  | 7.44  | 31.01  | 6.47  |
| H <sub>24</sub> | 31.75  | 8.90  | 31.23  | 8.10  | 30.83  | 7.63  | 30.76  | 7.95  | 30.51  | 7.13  |
| H <sub>25</sub> | 32.30  | 5.49  | 31.53  | 5.15  | 30.72  | 5.09  | 30.66  | 5.54  | 30.24  | 4.63  |
| H <sub>26</sub> | 32.78  | 5.99  | 32.09  | 5.54  | 31.61  | 4.86  | 31.58  | 5.23  | 31.22  | 4.40  |
| H <sub>27</sub> | 32.41  | 5.85  | 31.71  | 5.91  | 31.05  | 6.08  | 31.01  | 6.21  | 30.65  | 5.87  |
| H <sub>28</sub> | 31.91  | 7.39  | 31.22  | 7.27  | 30.83  | 7.35  | 30.77  | 7.59  | 30.45  | 6.95  |
| H <sub>29</sub> | 31.88  | 7.33  | 31.25  | 6.69  | 30.60  | 6.18  | 30.57  | 6.53  | 30.20  | 5.72  |
| H <sub>30</sub> | 27.93  | 6.81  | 27.61  | 7.03  | 27.23  | 6.66  | 27.14  | 6.51  | 26.99  | 6.58  |
| H <sub>31</sub> | 31.99  | 8.22  | 31.30  | 7.42  | 31.21  | 6.87  | 31.12  | 7.21  | 30.95  | 6.35  |
| H <sub>32</sub> | 31.89  | 8.82  | 31.35  | 8.03  | 30.96  | 7.69  | 30.91  | 8.01  | 30.64  | 7.22  |
| H <sub>33</sub> | 31.88  | 9.54  | 31.34  | 8.73  | 30.96  | 8.33  | 30.90  | 8.69  | 30.63  | 7.82  |
| H <sub>34</sub> | 32.24  | 9.00  | 31.66  | 8.23  | 31.31  | 7.87  | 31.26  | 8.20  | 30.98  | 7.37  |
| H <sub>35</sub> | 31.62  | 7.65  | 30.97  | 6.98  | 30.73  | 6.34  | 30.66  | 6.61  | 30.42  | 5.87  |
| H <sub>36</sub> | 32.23  | 10.27 | 31.65  | 9.47  | 31.33  | 9.01  | 31.58  | 9.37  | 31.02  | 8.45  |
| H <sub>37</sub> | 32.52  | 9.26  | 31.83  | 8.63  | 31.56  | 8.15  | 31.52  | 8.52  | 31.23  | 7.61  |
| H <sub>38</sub> | 32.51  | 10.05 | 31.83  | 9.37  | 31.55  | 8.34  | 31.51  | 8.73  | 31.21  | 7.77  |
| H <sub>39</sub> | 33.23  | 9.75  | 32.59  | 9.19  | 32.45  | 8.70  | 32.41  | 9.13  | 32.12  | 8.12  |

## NBO Analysis

Natural bond orbital (NBO) analysis is important method for studying intra- and inter-molecular bonding and interaction between bonds [29, 30]. The results of NBO analysis, occupancy and the polarization coefficient amounts of atoms for compound using title levels represented in Table 5. The size of these polarization coefficients shows the importance of the two hybrids in the formation of the bond. As shown in Table 5, for all methods, the calculated bonding orbitals and occupancy summarized for the C<sub>2</sub>-C<sub>7</sub>, C<sub>8</sub>-C<sub>15</sub>, C<sub>12</sub>-C<sub>13</sub> and C<sub>12</sub>-C<sub>14</sub> bonds.

In all methods, the polarization coefficients of C<sub>2</sub>atom and C<sub>7</sub>atom in C<sub>2</sub>-C<sub>7</sub>bond suggest share of contribute C<sub>2</sub> atom is greater than share of C<sub>7</sub>atom. In the bonding orbital C<sub>8</sub>-C<sub>15</sub>, using all methods, the polarization coefficient of C<sub>8</sub> atom is greater than C<sub>15</sub> atom that is shown share of contribute C<sub>8</sub> atom is greater than share of C<sub>15</sub> atom in bond formation. Also in all methods for C<sub>12</sub>-C<sub>13</sub> and C<sub>12</sub>-C<sub>14</sub> bonds, the polarization coefficient of C<sub>12</sub> atom is greater than C<sub>13</sub> and C<sub>14</sub>atoms that it suggest share of contribute C<sub>12</sub> atom is greater than share of C<sub>13</sub> and C<sub>14</sub> atoms.

**Table 5. Calculated natural bond orbitals (NBO) and the polarization coefficient for each hybrid in bonds of Zingiberene using five levels**

|              | Bond (A-B)                              | Occupancy | A                                         | B                         |
|--------------|-----------------------------------------|-----------|-------------------------------------------|---------------------------|
| HF/6-31G     | BD (1) C <sub>2</sub> -C <sub>7</sub>   | 1.98262   | 0.7123 sp <sup>2.16</sup>                 | 0.7019 sp <sup>2.52</sup> |
|              | BD (1) C <sub>8</sub> -C <sub>15</sub>  | 1.98473   | 0.7083 sp <sup>2.91</sup>                 | 0.7059 sp <sup>2.57</sup> |
|              | BD (1) C <sub>12</sub> -C <sub>13</sub> | 1.98105   | 0.7085 sp <sup>2.31</sup>                 | 0.7057 sp <sup>2.51</sup> |
|              | BD (1) C <sub>12</sub> -C <sub>14</sub> | 1.98190   | 0.7078 sp <sup>2.27</sup>                 | 0.7065 sp <sup>2.53</sup> |
| HF/6-31G*    | BD (1) C <sub>2</sub> -C <sub>7</sub>   | 1.98430   | 0.7129 sp <sup>2.16</sup>                 | 0.7013 sp <sup>2.50</sup> |
|              | BD (1) C <sub>8</sub> -C <sub>15</sub>  | 1.98572   | 0.7086 sp <sup>2.98d<sup>0.01</sup></sup> | 0.7056 sp <sup>2.51</sup> |
|              | BD (1) C <sub>12</sub> -C <sub>13</sub> | 1.98235   | 0.7092 sp <sup>2.32</sup>                 | 0.7050 sp <sup>2.49</sup> |
|              | BD (1) C <sub>12</sub> -C <sub>14</sub> | 1.98330   | 0.7084 sp <sup>2.28</sup>                 | 0.7058 sp <sup>2.51</sup> |
| B3LYP/6-31G  | BD (1) C <sub>2</sub> -C <sub>7</sub>   | 1.98259   | 0.7103 sp <sup>2.16</sup>                 | 0.7039 sp <sup>2.47</sup> |
|              | BD (1) C <sub>8</sub> -C <sub>15</sub>  | 1.98387   | 0.7083 sp <sup>2.88</sup>                 | 0.7059 sp <sup>2.55</sup> |
|              | BD (1) C <sub>12</sub> -C <sub>13</sub> | 1.98086   | 0.7067 sp <sup>2.30</sup>                 | 0.7075 sp <sup>2.47</sup> |
|              | BD (1) C <sub>12</sub> -C <sub>14</sub> | 1.98187   | 0.7059 sp <sup>2.25</sup>                 | 0.7083 sp <sup>2.49</sup> |
| B3PW91/6-31G | BD (1) C <sub>2</sub> -C <sub>7</sub>   | 1.98225   | 0.7106 sp <sup>2.15</sup>                 | 0.7036 sp <sup>2.47</sup> |
|              | BD (1) C <sub>8</sub> -C <sub>15</sub>  | 1.98335   | 0.7666 sp <sup>2.87</sup>                 | 0.7054 sp <sup>2.54</sup> |
|              | BD (1) C <sub>12</sub> -C <sub>13</sub> | 1.98050   | 0.7069 sp <sup>2.30</sup>                 | 0.7073 sp <sup>2.47</sup> |
|              | BD (1) C <sub>12</sub> -C <sub>14</sub> | 1.98159   | 0.7061 sp <sup>2.25</sup>                 | 0.7081 sp <sup>2.49</sup> |
| BLYP/6-31G   | BD (1) C <sub>2</sub> -C <sub>7</sub>   | 1.98293   | 0.7099 sp <sup>2.16</sup>                 | 0.7043 sp <sup>2.47</sup> |
|              | BD (1) C <sub>8</sub> -C <sub>15</sub>  | 1.98412   | 0.7081 sp <sup>2.87</sup>                 | 0.7061 sp <sup>2.55</sup> |
|              | BD (1) C <sub>12</sub> -C <sub>13</sub> | 1.98110   | 0.7062 sp <sup>2.30</sup>                 | 0.7080 sp <sup>2.46</sup> |
|              | BD (1) C <sub>12</sub> -C <sub>14</sub> | 1.98225   | 0.7055 sp <sup>2.25</sup>                 | 0.7087 sp <sup>2.49</sup> |

Electron donor orbital, acceptor orbital and the interacting stabilization energy resulting from the second-order micro disturbance theory [31] are reported in Table 6. The electron delocalization from filled NBOs (donors) to the empty NBOs (acceptors) describes a conjugative electron transfer process between them [32, 33]. For each donor (*i*) and acceptor (*j*), the stabilization energy  $E^{(2)}$  associated with the delocalization  $i \rightarrow j$  is estimated.

The resonance energy ( $E^{(2)}$ ) detected the quantity of participation of electrons in the resonance between atoms [29]. The results of the NBO analysis, such as resonance energy ( $E^{(2)}$ ), donor NBO (*i*) and acceptor NBO (*j*), for compound using title levels are listed in Table 6. According to Table 6, with all

method, the greatest resonance energy ( $E^{(2)}$ ) is observed for  $C_1-C_2 \rightarrow C_3-C_4$  and  $C_3-C_4 \rightarrow C_1-C_2$ . The BD(2)  $C_1-C_2$  and BD (2)  $C_3-C_4$  participates as donor and anti-bonding BD\*(2)  $C_3-C_4$  and BD\*(2)  $C_1-C_2$  as acceptor. These results suggest that charge is transferred from  $C_1-C_2$  to  $C_3-C_4$  ( $C_1-C_2 \rightarrow C_3-C_4$ ) and  $C_3-C_4$  to  $C_1-C_2$  ( $C_3-C_4 \rightarrow C_1-C_2$ ). The BD (1)  $C_1-C_6$  participates as donor and the anti-bonding BD\*(1)  $C_2-C_7$  and BD\*(1)  $C_5-C_6$  orbitals acts as acceptor. According to the results observed in Table 5, the resonance energies ( $E^{(2)}$ ) for the transfer of electron density from BD(1)  $C_1-C_6$  to these anti-bonding BD\*(1)  $C_2-C_7$  orbital is greater than BD\*(1)  $C_5-C_6$ . Therefore we found more charge transfer from the bonding orbital BD (1)  $C_1-C_6$  to the anti-bonding orbital BD\*(1)  $C_2-C_7$  [ $C_1-C_6 \rightarrow C_2-C_7$ ].

**Table 6: Second order perturbation theory analysis of Fock matrix in NBO basis threshold for Zingiberene using five levels**

|              | Donor NBO(i)     | Acceptor NBO(j)  | $E^{(2)}$<br>(kcal/mol) | <sup>a</sup> $E(j)-E(i)$ <sup>b</sup> (a.u.) | $F(i, j)$ <sup>c</sup> (a.u.) |
|--------------|------------------|------------------|-------------------------|----------------------------------------------|-------------------------------|
| HF/6-31G     | BD (2) $C_1-C_2$ | BD*(2) $C_3-C_4$ | 16.30                   | 0.59                                         | 0.088                         |
|              | BD (1) $C_1-C_6$ | BD*(1) $C_2-C_7$ | 6.42                    | 1.47                                         | 0.087                         |
|              | BD (1) $C_1-C_6$ | BD*(1) $C_5-C_6$ | 1.15                    | 1.41                                         | 0.036                         |
|              | BD (2) $C_3-C_4$ | BD*(2) $C_1-C_2$ | 17.29                   | 0.61                                         | 0.092                         |
| HF/6-31G*    | BD (2) $C_1-C_2$ | BD*(2) $C_3-C_4$ | 14.93                   | 0.62                                         | 0.086                         |
|              | BD (1) $C_1-C_6$ | BD*(1) $C_2-C_7$ | 6.26                    | 1.49                                         | 0.086                         |
|              | BD (1) $C_1-C_6$ | BD*(1) $C_5-C_6$ | 0.91                    | 1.44                                         | 0.032                         |
|              | BD (2) $C_3-C_4$ | BD*(2) $C_1-C_2$ | 15.85                   | 0.63                                         | 0.090                         |
| B3LYP/6-31G  | BD (2) $C_1-C_2$ | BD*(2) $C_3-C_4$ | 12.88                   | 0.31                                         | 0.056                         |
|              | BD (1) $C_1-C_6$ | BD*(1) $C_2-C_7$ | 4.79                    | 1.02                                         | 0.062                         |
|              | BD (1) $C_1-C_6$ | BD*(1) $C_5-C_6$ | 0.80                    | 0.96                                         | 0.025                         |
|              | BD (2) $C_3-C_4$ | BD*(2) $C_1-C_2$ | 12.90                   | 0.32                                         | 0.058                         |
| B3PW91/6-31G | BD (2) $C_1-C_2$ | BD*(2) $C_3-C_4$ | 13.17                   | 0.31                                         | 0.057                         |
|              | BD (1) $C_1-C_6$ | BD*(1) $C_2-C_7$ | 4.89                    | 1.03                                         | 0.063                         |
|              | BD (1) $C_1-C_6$ | BD*(1) $C_5-C_6$ | 0.92                    | 0.98                                         | 0.027                         |
|              | BD (2) $C_3-C_4$ | BD*(2) $C_1-C_2$ | 13.12                   | 0.32                                         | 0.059                         |
| BLYP/6-31G   | BD (2) $C_1-C_2$ | BD*(2) $C_3-C_4$ | 11.26                   | 0.23                                         | 0.046                         |
|              | BD (1) $C_1-C_6$ | BD*(1) $C_2-C_7$ | 4.32                    | 0.89                                         | 0.055                         |
|              | BD (1) $C_1-C_6$ | BD*(1) $C_5-C_6$ | 0.59                    | 0.84                                         | 0.020                         |
|              | BD (2) $C_3-C_4$ | BD*(2) $C_1-C_2$ | 11.07                   | 0.25                                         | 0.047                         |

<sup>a</sup>  $E^{(2)}$  means energy of hyperconjugative interactions.

<sup>b</sup> Energy difference between donor and acceptor *i* and *j* NBO orbitals.

<sup>c</sup>  $F(i, j)$  is the Fock matrix element between *i* and *j* NBO orbitals.

## Conclusion

In the present study, the quantum theoretical calculations Zingiberene, (5R)-2-Methyl-5-[(2S)-6-methyl-5-hepten-2-yl]-1,3-cyclohexadiene were performed using HF and density functional theory (DFT) methods. The calculated results of thermodynamic parameters such as relative energy, Gibbs free energy and standard enthalpy of molecule for all levels are negative values.

Therefore we found that molecule is stable. The FMO analysis suggests that charge transfer is taking place within the title structure. Also it is found that the HOMO-1 orbital of Zingiberene is localized mainly on C=C of alkene, whereas HOMO orbital is focused on cyclohexadiene. From the MEP it is clear that the C=C bonds of diene and C=C bond of alkene section are negative charge centers and sites for electrophilic attack. The biggest values of negative charge are observed for C atoms of

methyl groups ( $C_7$ ,  $C_{13}$ ,  $C_{14}$  and  $C_{15}$ ). The results of NMR parameters are shown the  $CS^I$  and  $CS^A$  values of all atoms are positive and the lowest values of  $CS^I$  and  $CS^A$  belong to hydrogen atoms. According to the NBO analysis of title structure, the greatest resonance energy ( $E^{(2)}$ ) is observed for  $C_1-C_2 \rightarrow C_3-C_4$  and  $C_3-C_4 \rightarrow C_1-C_2$ .

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