**A DFT STUDY on MOLECULAR STRUCTURE and POSSIBLE CONFORMERS of TARTARIC ACID**

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**Abstract**

In order to determine molecular structure, a conformational analysis of tartaric acid was performed and eight stable conformers were determined. The conformational space of the tartaric acid was scanned using molecular mechanic calculations performed by courtesy of the Spartan08 program. In addition, the most stable structure of tartaric acid that has the lowest energy structure is determined. Geometry optimizations were performed with Becke’s three-parameter hybrid-exchange functional combined with the Lee–Yang–Parr correlation functional (B3LYP) method and the standard 6-311++G(d,p) basis set. The calculated molecular geometry parameters, HOMO-LUMO energies, molecular electrostatic potentials (MEPs) and some thermodynamic parameters were also given for further studies. All these calculations carried out by using Gaussian03W package program.

**Keywords:** DFT, Conformational Analysis, Tartaric Acid, Molecular Thermodynamics

1. **INTRODUCTION**

Tartaric acid has a crystalline structure, colorless organic acid and it has a natural abundance in plants. This acid is used in various industries, especially in the food industry. Also, during the fermentation of the wine potassium, tartaric acid is obtained as a by-product. It is commonly used in sodas, as a sweetener in gelatin, for polishing surface of metals and for the reason of cleaning of the paintings and fabrics [1]. Its consumption is estimated approximately 50.000 to 70.000 tons per year, all over the world markets [2]. Optically active form of tartaric acid has been determined by Patterson and Fourier methods [3]. The hydrogen bonding in the crystal structure of D-tartaric acid determined by using X-Ray diffraction and neutron diffraction methods [4]. Conformational calculations of tartaric acid were carried out by using Ab-initio methods [5]. Experimental studies and Ab-initio calculations of the optical/vibrational/Raman properties of the tartaric acid was studied in some details [6]. The theoretical vibrational frequencies and Potential Energy Distribution (PED) of the L-lysine tartaric acid were calculated by using Density Functional Theory (DFT) method. Beside the calculated frequencies were compared to that of experimentally obtained IR spectra [7].

Because the most of physical and chemical properties of a molecule depend on the molecular structure and several medicinal effects, especially for biologically active molecules, depend on conformational behavior, informations about molecular structure and conformational behavior of a compound are very important [8]. DFT is widely used on molecular structural studies nowadays [9-16]. Due to author knowledge, there is no comprehensive DFT study on molecular structure and conformational behavior of tartaric acid in literature.

In this study, firstly conformational analysis of tartaric acid was performed and then, as a result, eight conformers were determined. Secondly, geometry parameters, Molecules Electrostatic Potentials (MEPs), HOMO-LUMO energies and some thermodynamic properties of the most stable conformer were also presented.

1. **COMPUTATIONAL DETAILS**

In order to establish the stable possible conformations, the conformational space of the tartaric acid was scanned using molecular mechanic calculations performed by courtesy of the Spartan08 program [17]. In the second step, geometry optimizations of the all possible conformers were performed by B3LYP functional with 6-311++G(d,p) basis set. After the determination of the most stable conformer of intersted compound, optimized structural parameters of this conformer were used for the further calculations. Optimizations and frequency calculations were performed by the same level of DFT. In this step, all the calculations were performed using Gaussian03W [18] package program.

1. **RESULTS AND DISCUSSION**
   1. ***Conformational Analysis and Molecular Structure***

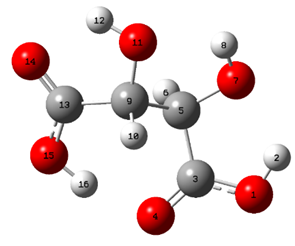
In order to determine the stable conformations of tartaric acid, the combined molecular mechanic and DFT calculations with the B3LYP/6-311++G(d,p) basis set have been used. Firstly, conformational space of tartaric acid was scanned with molecular mechanic calculations. Then, geometry optimizations of these conformers were performed with B3LYP/6-311++G(d,p) level of DFT. The obtained values of these calculations helps us to find the most stable structure. Energy values and dipole moments are shown in Table 1.

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| **Table 1.** Conformer energies and dipole moment values of tartaric acid molecule | | | | | |
| **Conformations** | **Energies (Hartree)** | **Dipole Moment (D)** | **Conformations** | **Energies (Hartree)** | **Dipole Moment (D)** |
| **Conf1** | -607.6037915 | 3.3503 | **Conf5** | -607.5969547 | 1.7204 |
| **Conf2** | -607.5981469 | 3.2322 | **Conf6** | -607.5951956 | 2.1695 |
| **Conf3** | -607.5973040 | 2.7556 | **Conf7** | -607.5933786 | 3.7670 |
| **Conf4** | -607.5971055 | 1.6151 | **Conf8** | -607.5871529 | 4.3422 |

As it is seen in Table 1, the most stable conformer of tartaric acid is the conformer 1 which has a minimum energy (-607.6037915 Hartree). Obtained structures of conformations of tartaric acid are shown in Figure 1.

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**Figure 1.** Possible conformers of tartaric acid molecule



**Figure 2.** The most stable structure of tartaric acid molecule

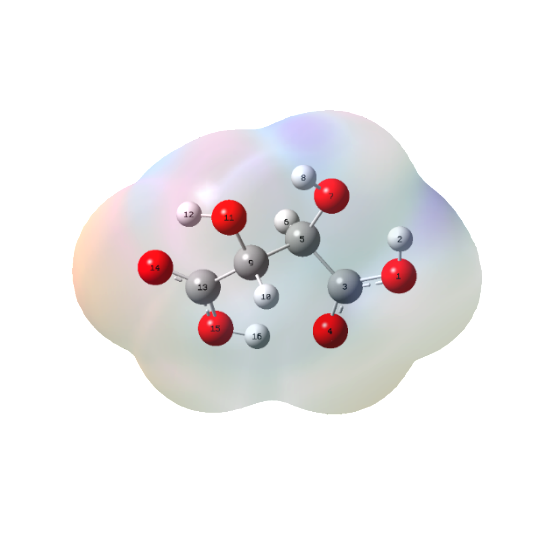
{Kars, 2014 #1}The most stable structure and the atom numbering scheme are shown in Figure 2. Computed bond lengths, bond angles and dihedral angles of the molecule are given in Table 2.

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| **Table 2.** Geometrical parameters of tartaric acid molecule (**R**= Bond Length, **A**= Bond Angles, **D**= Dihedral Angles) | | | | | | | | |
| **Bond Length** | |  | **Bond Angles** | | **Degrees** | **Dihedral Angles** | | **Degrees** |
| **R1** | R(1,2) | 0.971 | **A8** | A(6,5,7) | 110.6443 | **D8** | D(4,3,5,9) | 36.203 |
| **R2** | R(1,3) | 1.325 | **A9** | A(6,5,9) | 108.5445 | **D9** | D(3,5,7,8) | -158.5937 |
| **R3** | R(3,4) | 1.2195 | **A10** | A(7,5,9) | 110.5237 | **D10** | D(6,5,7,8) | 85.0245 |
| **R4** | R(3,5) | 1.5222 | **A11** | A(5,7,8) | 105.9319 | **D11** | D(9,5,7,8) | -35.2365 |
| **R5** | R(4,16) | 1.7237 | **A12** | A(5,9,10) | 109.1193 | **D12** | D(3,5,9,10) | 38.8284 |
| **R6** | R(5,6) | 1.1039 | **A13** | A(5,9,11) | 107.3154 | **D13** | D(3,5,9,11) | 156.9294 |
| **R7** | R(5,7) | 1.4013 | **A14** | A(5,9,13) | 113.9614 | **D14** | D(3,5,9,13) | -83.1668 |
| **R8** | R(5,9) | 1.5677 | **A15** | A(10,9,11) | 109.1104 | **D15** | D(6,5,9,10) | 154.8714 |
| **R9** | R(7,8) | 0.9696 | **A16** | A(10,9,13) | 108.9327 | **D16** | D(6,5,9,11) | -87.0276 |
| **R10** | R(9,10) | 1.0966 | **A17** | A(11,9,13) | 108.304 | **D17** | D(6,5,9,13) | 32.8762 |
| **R11** | R(9,11) | 1.409 | **A18** | A(9,11,12) | 105.9489 | **D18** | D(7,5,9,10) | -83.6178 |
| **R12** | R(9,13) | 1.5448 | **A19** | A(9,13,14) | 119.1255 | **D19** | D(7,5,9,11) | 34.4831 |
| **R13** | R(11,12) | 0.9748 | **A20** | A(9,13,15) | 118.1998 | **D20** | D(7,5,9,13) | 154.3869 |
| **R14** | R(13,14) | 1.2083 | **A21** | A(14,13,15) | 122.6707 | **D21** | D(5,9,11,12) | 121.036 |
| **R15** | R(13,15) | 1.3237 | **A22** | A(13,15,16) | 110.7308 | **D22** | D(10,9,11,12) | -120.8573 |
| **R16** | R(15,16) | 0.9868 | **Dihedral Angles** | | **Degrees** | **D23** | D(13,9,11,12) | -2.4134 |
| **Bond Angles** | | **Degrees** |  |  |  | **D24** | D(5,9,13,14) | -118.0488 |
| **A1** | A(2,1,3) | 107.794 | **D1** | D(2,1,3,4) | -0.1805 | **D25** | D(5,9,13,15) | 62.6516 |
| **A2** | A(1,3,4) | 122.6253 | **D2** | D(2,1,3,5) | -178.5968 | **D26** | D(10,9,13,14) | 119.8532 |
| **A3** | A(1,3,5) | 114.4559 | **D3** | D(1,3,5,6) | 96.8676 | **D27** | D(10,9,13,15) | -59.4464 |
| **A4** | A(4,3,5) | 122.8989 | **D4** | D(1,3,5,7) | -22.5571 | **D28** | D(11,9,13,14) | 1.2965 |
| **A5** | A(3,5,6) | 105.7434 | **D5** | D(1,3,5,9) | -145.3856 | **D29** | D(11,9,13,15) | -178.0031 |
| **A6** | A(3,5,7) | 109.858 | **D6** | D(4,3,5,6) | -81.5438 | **D30** | D(9,13,15,16) | -5.5355 |
| **A7** | A(3,5,9) | 111.4224 | **D7** | D(4,3,5,7) | 159.0315 | **D31** | D(14,13,15,16) | 175.1913 |

* 1. ***Molecular Electrostatic Potentials***

The molecular electrostatic potentials (MEP) are regard as the most significant electrostatic feature to study relation between structure and activity of a molecule. Also, it is an important tool for chemistry to describe different physical and chemical properties.

MEPs were used for investigation of non-covalent interactions (sites with intra and intermolecular interaction) in tartaric acid. In the Figure 3, green parts represent the regions of zero potential while red and blue parts represent the regions of positive and negative electrostatic potential, respectively.



**Figure 3.** MEPs of the tartaric acid molecule

* 1. ***HOMO-LUMO Analysis***

The HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital), which are the main orbitals taking part in chemical reaction, are called as the Frontier Molecule Orbitals (FMOs) [19]. Therefore, HOMO represents the outermost molecule orbital filled by electrons and behaves as an electron donor, while LUMO can be implies as the first empty innermost molecular orbital unfilled by electrons and behaves as an electron acceptor. The energy gap formed between HOMO and LUMO indicates the molecular chemical stability [20]. The energy gap between HOMO and LUMO is a critical parameter to determine molecular electrical transport properties. By using HOMO and LUMO energy values of a molecule, some molecular properties such as the chemical reactivity, kinetic stability, optical polarizability, chemical hardness and softness and electronegativity can be found. The soft molecules are more polarizable than the hard ones. Therefore, for soft molecules to be excites, a small portion of excitation energy is required, whereas for hard ones to be excited, a large amount of excitation energy is required [19]. In this study, using B3LYP/6-311++G(d,p) level of theory HOMO-LUMO energies of structure molecule interest in this work were calculated and shape of these orbitals were drawn, as it is seen in Figure 4, by Gausswiev.

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| (a) E(HOMO) = −0.31657 | (b) E(LUMO) = −0.05223 |

**Figure 4.** (a) HOMO and (b)-LUMO energies of the tartaric acid

Some thermodynamic properties of tartaric acid were given in Table 3.

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| **Table 3.** Thermodynamic parameters of tartaric acid molecule | | | |
| **Thermal energy, E (kcal/mol)** | | **Entropy, S (cal/mol K)** | |
| Electronic | 0.000 | Electronic | 0.000 |
| Translational | 0.889 | Translational | 40.927 |
| Rotational | 0.889 | Rotational | 29.656 |
| Vibrational | 76.950 | Vibrational | 24.278 |
| **Total** | **78.728** | **Total** | **94.861** |
| **Heat capacity, Cv (cal/mol K)** | |  |  |
| Electronic | 0.000 |
| Translational | 2.981 | Zero-point vibrational energy (kcal/mol) | 72.89054 |
| Rotational | 2.981 | Sum of electronic and zero-point energies (Hartree/Particle) | -607.487633 |
| Vibrational | 28.434 | Sum of electronic and thermal free energies (Hartree/Particle) | -607.522458 |
| **Total** | **34.395** |  |  |

1. **CONCLUCION**

DFT calculations on molecular structure and conformational analysis of Tartaric acid were performed for the first time in this study. The calculated energies and dipole moments of eight different conformers and the molecular structural parameters of the most stable conformer were given. The most stable structures energy and dipole moment values were -607.6037915 Hartree and 3.3503 D, respectively. Relationship between structure and activity of the tartaric acid molecule can be studied in terms of MEP. Besides, non-covalent interactions were studied by MEP’s. As seen in the Fig. 3, the negative region is mainly localized on the O14 atom. However, positive region is localized on the H2 and H8 atoms. Thus, we can conclude that these regions are the sites correspond to the hydrogen bondings of tartaric acid. Parameters needed to be known, such as chemical reactivity, kinetic stability, optical polarizability, chemical hardness or softness and electronegativity, can be found by using HOMO-LUMO energies. HOMO and LUMO energy values have been found −0.31657, −0.05223 Hartree and 8.61437 eV and 1.41126 eV respectively that corresponds to 7.19311 eV bandgap value. Some thermodynamic parameters have been given for further researchers in this study.

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