

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

TARTARİK ASİTİN MOLEKÜLER YAPISI VE OLASI KONFERMERLERİ HAKKINDA DFT ÇALIŞMASI

Özet

Tartarik asitin moleküler yapısını belirlemek için konformasyon analizi uygulanmış ve sekiz kararlı konformere sahip olduğu belirlenmiştir. Tartarik asitin konformasyonel uzayı Spartan08 programıyla moleküler mekanik hesaplama ile taranmıştır. Ayrıca, tartarik asit molekülünün en düşük enerjili kararlı yapısı belirlenmiştir. Lee-Yang-Parr korelasyon fonksiyonelli 3 parametrelili Becke karma modeli (B3LYP) ve 6-311++G(d,p) baz seti kullanılarak geometri optimizasyonları

gerçekleştirilmiştir. Hesaplanan moleküler geometri parametreleri, HOMO-LUMO enerjileri, moleküler elektrostatik potansiyel (MEPs) ve bazı termodinamik parametreler de ileri çalışmalar için verilmiştir. Tüm hesaplamalar Gaussian03W paket programı kullanılarak gerçekleştirilmiştir.

Anahtar Kelimeler: DFT, Konformasyon Analizi, Tartarik Asit, Moleküler Termodinamik

1. Introduction

Recently, multi-disciplinary studies involving both theoretical and experimental methods in the fields of chemistry, physics and engineering have become very important for manufacturing new technological tools, for example; development of organic non-linear optical (NLO) materials. Furthermore, Density Functional Theory (DFT) is a widely accepted framework for calculating the properties of ground/excited electronic states in molecules, clusters and solids. In this work, some structural properties of the tartaric acid will be determined.

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, one of the most important organic acids is tartaric acid which provides the taste of juice and wine, as well as supply the low Ph environment needed to prevent microbial deterioration during wine production. The most abundant acid in grape seeds and wine is tartaric acid [1]. By using a high-output UHPLC MS/MS method, tartaric acid has been determined that it exists in grape wine in a high concentration [2]. 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 [3]. Its consumption is estimated approximately 50.000 to 70.000 tons per year, all over the world markets [4]. Optically active form of tartaric acid has been determined by Patterson and Fourier methods [5]. The hydrogen bonding in the crystal structure of D-tartaric acid determined by using X-Ray diffraction and neutron diffraction methods [6]. Conformational calculations of tartaric acid were carried out by using Ab-initio methods [7]. Experimental studies and Ab-initio calculations of the optical/vibrational/Raman properties of the tartaric acid was studied in some details [8]. 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 [9]. Theoretical calculations of vibrational frequencies and potential energy distribution (PDE) for L-lysine×tartaric acid were calculated by B3LYP method. Calculated frequencies were compared to experimentally measured IR spectra. Also, the time-dependent Hartree-Fock calculation of nonlinear optical (NLO) properties and dipole moments were performed too [9].

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, information about molecular structure and conformational behavior of a compound are very important [10]. DFT is widely used on molecular structural studies nowadays [11-18]. 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.

2. 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 [19]. 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 interested 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 [20] package program.

3. Results and Discussion

3.1 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.

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.

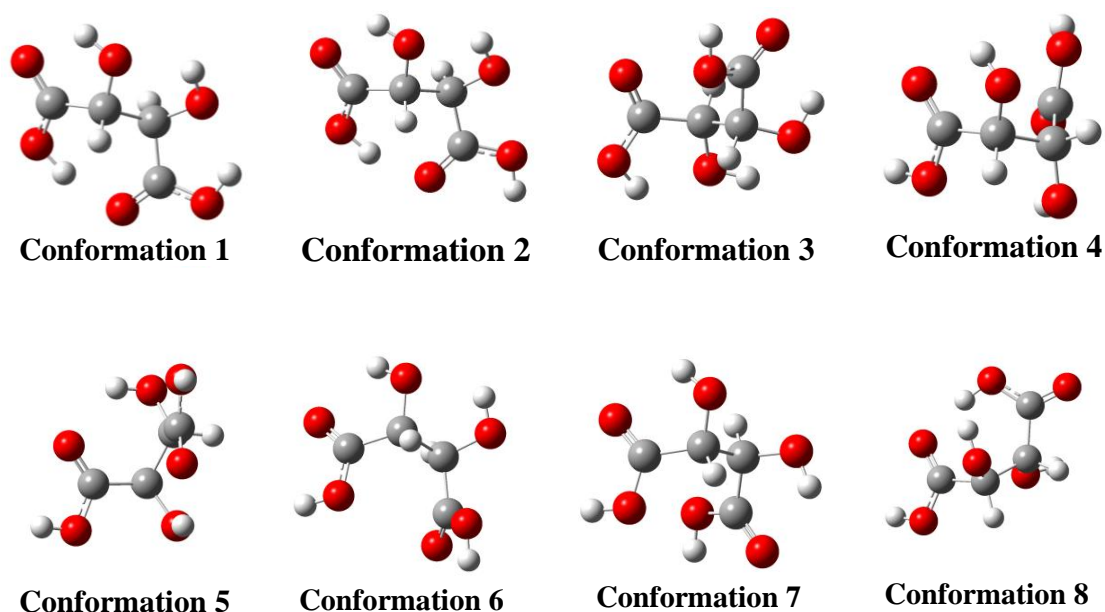


Figure 1. Possible conformers of tartaric acid molecule

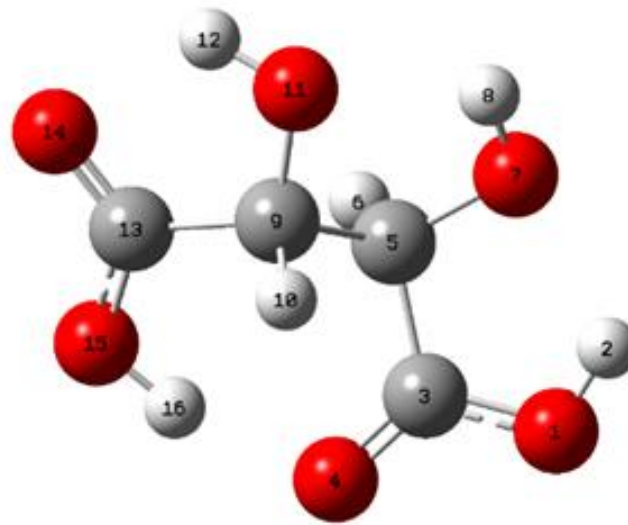


Figure 2. The most stable structure of tartaric acid molecule

The most stable structure and the atom numbering scheme are shown in Figure 2.

3.2 Molecular Electrostatic Potentials

The molecular electrostatic potentials (MEPs) are regarded as the most significant electrostatic feature to study the 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 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.

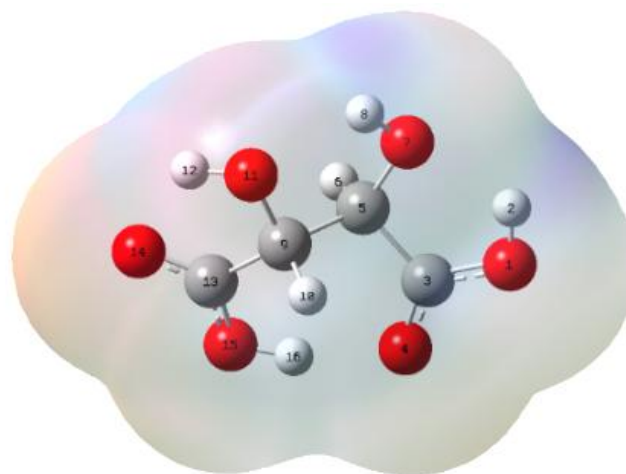


Figure 3. MEPs of the tartaric acid molecule

Computed bond lengths, bond angles and dihedral angles of the molecule are given in Table 2.

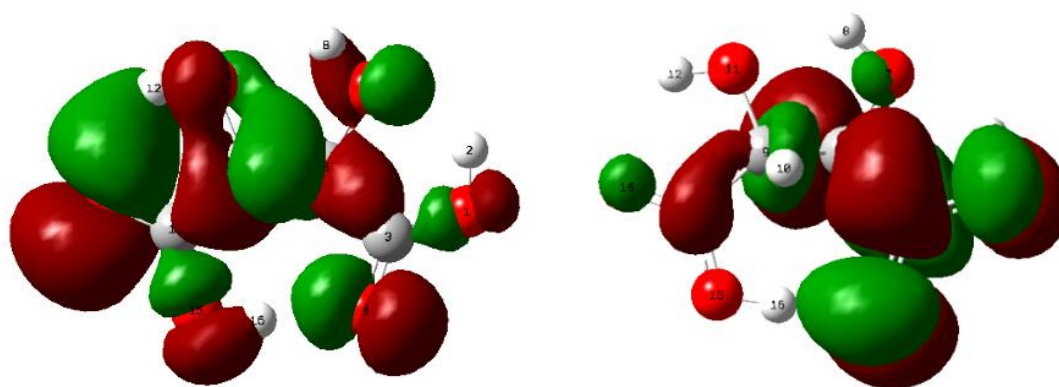
Table 2. Geometrical parameters of tartaric acid molecule (**R**= Bond Length, **A**= Bond Angles, **D**= Dihedral Angles)

Bond Lengths		Angstrom (Å)	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	D25	D(5,9,13,15)	62.6516
A1	A(2,1,3)	107.794	D1	D(2,1,3,4)	-0.1805	D26	D(10,9,13,14)	119.8532
A2	A(1,3,4)	122.6253	D2	D(2,1,3,5)	-	D27	D(10,9,13,15)	-59.4464
A3	A(1,3,5)	114.4559	D3	D(1,3,5,6)	96.8676	D28	D(11,9,13,14)	1.2965
A4	A(4,3,5)	122.8989	D4	D(1,3,5,7)	-22.5571	D29	D(11,9,13,15)	-178.0031
A5	A(3,5,6)	105.7434	D5	D(1,3,5,9)	-	D30	D(9,13,15,16)	-5.5355
A6	A(3,5,7)	109.858	D6	D(4,3,5,6)	-81.5438	D31	D(14,13,15,16)	175.1913
A7	A(3,5,9)	111.4224	D7	D(4,3,5,7)	159.0315			

3.3 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) [21]. 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 [22]. 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 excited, a small portion of excitation energy is required, whereas for hard ones to be excited, a large amount of excitation energy is required [21]. 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.



(a) $E(\text{HOMO}) = -0.31657$

(b) $E(\text{LUMO}) = -0.05223$

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

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

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, C_v (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

4. Conclusion

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 MEPs. Besides, non-covalent interactions were studied by MEPs. 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 band gap value. Some thermodynamic parameters have been given for further researchers in this study.

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