

# DFT Computations, Vibrational Spectra, Topology Analysis And NLO Analysis Of Orotic Acid

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## Abstract

The FT-IR and FT-Raman spectra of Orotic Acid have been recorded and analyzed. The molecular geometry and vibrational wave numbers of the title compound have been calculated by density functional theory (DFT) with 6-311++G (d,p) base set. NBO analysis is used to understand charge transfer interaction existing in the molecule. Using MESP and Topology analyses, the electron distribution and reactive sites on the surface of the compound were examined.

**Keywords** DFT, NBO analysis, MESP, AIM, ELF, LOL, RDG.

## 1. Introduction

Orotic acid (vitamin B13) and its salts are present in the cells and physiological fluids of many living species and which are important components because they act as precursors of pyrimidine nucleosides. Different metal complexes of were explored as bio stimulators of ionic exchange processes in organisms, which are used in medicine. Orotic acid is also a popular topic of study in the fields of food safety and nutrition [1]. Orotic acid's crystal and molecular structures were determined by Takusawaga and Shimada, while Mutikainen [2] looked into the crystal structure of metal complexes.

## 2. Experimental methods

The compound was bought from Sigma Aldrich Chemical Company (USA) and used without any further purification. The FT-IR spectra were obtained in the range 4000-400  $\text{cm}^{-1}$  using a PERKIN ELMER FTIR spectrometer at 1.0  $\text{cm}^{-1}$  resolution using the KBr pellet technique. The FT-Raman spectrum was recorded in the region 3500-50  $\text{cm}^{-1}$  with a BRUKER RFS 100/s 66 V spectrophotometer using KBr pellet technique.

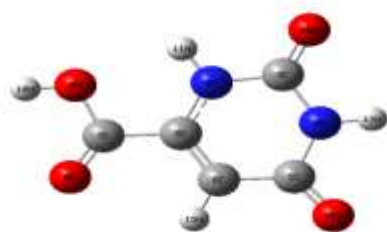
## 3. Computational details

The related vibrational assignments of compound using the Gaussian09 software package with the B3LYP/6-31++G(d,p) calculation. The VEDA4 program was used to create a potential energy distribution, which served as the basis for the vibrational assignments. NBO study on a molecule at the same level using second order perturbation revealed strong evidence of stabilization resulting from the hyperconjugation of particular intramolecular interactions. RDG analysis for analyzing weak interactions, Density of States analysis and topological analysis were carried out using Multiwfn, a multifunctional wave function analysis tool.

## 4. Results and discussion

### 4.1. Molecular geometry

The B3LYP/6-311++G (d,p) was used to calculate the optimized parameters of Orotic acid.



The C<sub>5</sub>-C<sub>7</sub> bond length (1.498 Å) is high compared to other C-C bond lengths because of the electron withdrawing nature of carboxylic acid (-COOH) group attached to the C<sub>5</sub> carbon atom and the presence of C<sub>7</sub>-H<sub>10</sub>...O<sub>8</sub> hyperconjugation. The bond length of the C<sub>5</sub>-C<sub>6</sub> bond is 1.349 Å, which is slightly longer than a C=C double bond and confirms the p-electron delocalization. The C<sub>7</sub>-O<sub>9</sub> bond length is 1.201 Å, which is longer than a typical C=O double bond (1.20 Å), but shorter than a normal C-O single bond (1.43 Å). The C<sub>7</sub>-O<sub>8</sub> bond length is 1.353 Å, which is shorter than a normal C-O single bond (1.43 Å). The C<sub>7</sub>-O<sub>9</sub> and C<sub>7</sub>-O<sub>8</sub> carboxyl bond lengths differ from the typical single and double bond lengths, implying that the negative charge and double bond are delocalized (Hernanz 2000). In the uracil ring, the endocyclic bond angles N<sub>4</sub>-C<sub>5</sub>-C<sub>6</sub> and C<sub>3</sub>-N<sub>4</sub>-C<sub>5</sub> are found to be 121.7° and 123.6°, whereas the exocyclic angle of the ring C<sub>3</sub>-N<sub>4</sub>-H<sub>11</sub> and N<sub>4</sub>-C<sub>5</sub>-C<sub>7</sub> are obtained as 116.2° and 117.7° respectively. The increased and decreased angles reveals highly electronegative nitrogen atom present inside the ring. The dihedral angle C<sub>1</sub>-N<sub>2</sub>-C<sub>3</sub>-N<sub>4</sub>, N<sub>2</sub>-C<sub>3</sub>-N<sub>4</sub>-C<sub>5</sub> are 0.0 as well as O<sub>12</sub>-C<sub>3</sub>-N<sub>4</sub>-H<sub>11</sub>, O<sub>12</sub>-C<sub>3</sub>-N<sub>2</sub>-H<sub>13</sub> shows the molecule is planar [3].

### 4.2. Natural bond orbital analysis

NBO analysis is a helpful method for studying charge transfer and conjugation in molecular systems, as well as intra- and intermolecular bonding interactions [4]. On the basis of second-order perturbation, the stabilization energy E<sup>2</sup> is calculated. The charge transfer interaction between molecules inside the ring. The shift from LP1 (N<sub>2</sub>) and (C<sub>5</sub>-C<sub>6</sub>) donor orbitals to (C<sub>3</sub>-C<sub>12</sub>), (C<sub>1</sub>-C<sub>14</sub>), and (C<sub>7</sub>-C<sub>9</sub>) acceptor orbitals, with stabilization energies of 57.37, 19.91, and 16.47 kcal/mol, is crucial for the high stability of Orotic acid. The overlap between (C<sub>6</sub>-H<sub>15</sub>) and (N<sub>4</sub>-C<sub>5</sub>), which has stabilization energy of 6.82 kcal/mol, results in the intramolecular

hydrogen bonding. The greater delocalization interaction between electron donors and electron acceptors is revealed by an increase in the  $E^{(2)}$  value.

### 4.3. Vibrational spectral analysis

The vibrational wavenumbers for Orotic acid at the 6-311++G (d,p) level were calculated using the DFT method. The computed frequencies slightly differ from the experimental values. These variations are expected given that the computed vibrational modes are based on a single gas phase molecule.

#### 4.3.1. C–C vibration

The bands in the range of 1400 and 1650  $\text{cm}^{-1}$  have been described to vibrations of the C-C heterocyclic ring ( Fuson et al., 1956). In the range of 1300-1000  $\text{cm}^{-1}$ , stretching vibrations (C-C) are predictable ( Barnes et al., 1985). In the molecule, the C-C stretching vibrations are observed at 1622, 1312 and 1126  $\text{cm}^{-1}$  in IR and 1649, 1310  $\text{cm}^{-1}$  in Raman and the scaled frequency values at 1618, 1319, 1128  $\text{cm}^{-1}$ . Due to the attachment of nitrogen to the ring the C-C stretching vibrations present inside the ring were muted.

#### 4.3.2. C- N vibration

Finding the ring C-N stretching vibration is a very difficult undertaking because several vibrational modes may combine in this region. The C-N stretching vibration is typically located in the range of 1266–1382  $\text{cm}^{-1}$ (Silverstein 1981). In title molecule, the C-N stretching vibrations are observed at 1451, 1346 and 1312  $\text{cm}^{-1}$  in IR and 1468, 1338 and 1310  $\text{cm}^{-1}$  in Raman and the corresponding calculated value lies at 1464, 1350 and 1319  $\text{cm}^{-1}$ . Due to the  $\text{C}_3\text{-N}_4\text{...O}_{12}$  hydrogen bonding, the increase in wavenumber leads to blue shift which exhibits the NLO activity of the molecule.

#### 4.3.3. C–H vibration

Due to C-H stretching vibrations, the hetero aromatic organic compounds frequently display numerous broad bands in the range of 3100–3000 $\text{cm}^{-1}$  (Silverstein et al., 1981). The C-H in plane bending vibrations, which were observed in the range 1000–1300 $\text{cm}^{-1}$  (Socrates George 2001). In the present Orotic acid molecule, IR band at 3115  $\text{cm}^{-1}$  and a Raman band at 3097  $\text{cm}^{-1}$  and the calculated values at 3134  $\text{cm}^{-1}$  are assigned to C-H stretching vibration. The C-H in plane bending vibration is observed in IR 1258  $\text{cm}^{-1}$  and a band at 1250  $\text{cm}^{-1}$ , 1172  $\text{cm}^{-1}$  in Raman. The range of 1000-750  $\text{cm}^{-1}$  is where the C-H out of plane bending vibrations occurs. The C-H out of plane bending vibration is at 859  $\text{cm}^{-1}$  in IR.

#### 4.3.4. N–H vibration

The stretching absorption of the hetero aromatic molecule with an N-H group occurs between 3500 and 3220  $\text{cm}^{-1}$ (Bellamy 1960). In the current work, N-H stretching vibration is observed at 3502 and 3496  $\text{cm}^{-1}$  in IR and 3496, 3480  $\text{cm}^{-1}$  in Raman and the calculated values at 3505 and 3476  $\text{cm}^{-1}$ . The title molecule's bending N-H vibration is visible band at 1451  $\text{cm}^{-1}$  in the IR spectrum; the predicted value for the N-H bending mode is 1464  $\text{cm}^{-1}$ . The C-N stretching vibrations overlap with this vibration.

### 4.3.5 C=O vibrations

The carbonyl (C=O) group stretching vibration is expected to appear in the region of 1680-1715  $\text{cm}^{-1}$  (James et al., 2008). In Orotic acid, the wavenumber of carbonyl stretching vibration is observed a weak band at 1738  $\text{cm}^{-1}$  and a very strong band at 1704  $\text{cm}^{-1}$  in IR and a weak band at 1709  $\text{cm}^{-1}$  in Raman and the calculated values at 1744, 1709  $\text{cm}^{-1}$ . The small deviation between experimental wavenumbers from the expected range is due to the presence of C<sub>1</sub>-N<sub>2</sub>...O<sub>14</sub> and C<sub>3</sub>-N<sub>4</sub>...O<sub>12</sub> hydrogen bonding.

### 4.4 Molecular electrostatic potential

The molecular electrostatic potential (MESP) of a molecule is related to its dipole moments, partial charges, electro negativity and chemical reactivity. It demonstrates the degree of reactivity by the colours of the regions under electrophilic and nucleophilic assault. The MESP map strongly indicates that the negative potential regions (red) are electrophilic regions; these are primarily due to O atoms and are reflected as a yellowish bob. The maximum positive potential region (blue) is localized on the hydrogen atoms in the hydroxyl group as well as localized over the hydrogen C-H atoms, indicating the probable sites for nucleophilic attack. The MESP map shows that the hydrogen atoms are surrounded by positive potential sites and that the oxygen and nitrogen atoms are present in regions where the negative potential sites are located.

### 4.5 Topology analysis

#### 4.5.1. Atoms in molecule (AIM)

One of the most effective techniques is to take advantage of the topology analysis of charge density or electron density of molecules in the actual space boundaries of the atoms forming a system in order to analyze the properties of the atoms forming a system using the Bader theory of "Atoms in Molecules." AIM is a potent tool for learning about hydrogen bonding and chemical bonds in the molecular system. The parameters for the compound were computed from the AIM analysis electron density, its Laplacian density and its ellipticity. In Orotic acid molecule, the electron density is maximum for C<sub>7</sub>-O<sub>9</sub> (0.424), C<sub>3</sub>-O<sub>12</sub> (0.419) and C<sub>1</sub>-O<sub>14</sub> (0.412) bonds and these bonds have greater negative values of Laplacian electron density -0.167, -0.355 and -0.277 respectively demonstrates its covalent character. The C<sub>5</sub>-C<sub>6</sub> (0.316) atom has a higher value than others in ellipticity, which denotes the bond's instability.

#### 4.5.2. ELF and LOL analysis

The Multiwfn program was used to do the topological analysis of the Localized Orbital Locator LOL and the Electron Localization Function ELF. The ELF color-filled map shows the delocalized electron cloud around a few carbon and nitrogen atoms in blue, the localized bonding around hydrogen atoms in considerable detail, and the non-bonding electrons in red. The LOL color-filled map reveals that the centres of certain hydrogen atoms are white, indicating that a single localized orbital predominates the bonds (exceeds the upper limit 0.8). The valence shell, inner shells of a few carbon atoms, and oxygen atoms of the depleted

region are represented by the blue circles, whereas the high LOL values of the covalent kind of electron depletion zone around the nitrogen atom are represented by the red circles.

#### 4.5.3. RDG analysis

The RDG technique, which uses Multiwfn and the visual molecular dynamics application, is a topological tool that exposes noncovalent interactions such as van der Waals, steric effects and hydrogen bonds. The steric effect can be seen in the red color scatter near the carboxylic group in the RDG isosurface plot, and it can also be seen in the scatter plot between the positive region between 0.05 and 0.01 a.u. Green color scatter indicates the presence of non-covalent van der Waals force H...H inter scatter between 0.01–0.02. The red scatter in the isosurface density plots, which show the non-bonded interactions from the RDG graph. The RDG scatter graph demonstrates the significant steric effect and van der Waals force interaction that take place in the compound.

#### 4.6. Fukui function

One of the greatest ways to understand well-known chemical concepts like electronegativity, electron affinity, ionization potential, chemical potential etc., is through the use of DFT. The atomic descriptors were first used by Kolandaivel et al. to identify the molecule's regionally reactive areas. Dual adjective describes an electrophilic attack negatively as the order  $C6 > O14 > O12 > O9 > N4 > H15 > C5 > H11 > H13 > O8 > H10 > N2$ .

#### 4.7 Nonlinear optical analysis

Finite field approach method is an effective device to fabricate new materials with high NLO response and it has been used to evaluate linear polarizability and hyperpolarizability [5]. The value of dipole moment is calculated as 1.714 Debye. The first and second order hyper polarizability of Orotic acid molecule are equal to  $1.13 \times 10^{-30}$  e.s.u and  $5.43 \times 10^{-39}$  e.s.u.. The calculated first and second order hyper polarizability shows the possibility of nonlinear optical activity of the Orotic acid molecule.

#### 4.9 Second harmonic generation (SHG) analysis

For the title compound the Output signal is 5.35 mV, 2.08 times that of urea and it gives the experimental evidence for the NLO activity.

### 5. Conclusion

The current study reports complete vibrational analysis has been made for proper frequency contributions of Orotic acid. The FT-IR and FT-Raman frequencies of the title compound have been theoretically computed using DFT methods. Vibrational frequencies calculated by DFT level of theory utilizing 6-311++G (d,p) method agree well with experimental results. NBO analysis confirmed the possible hydrogen bonding and intramolecular hyperconjugative interaction enhance the NLO nature of the molecule. The inter molecular interactions were explained by MESP analysis. Using Fukui, ELF, LOL, and RDG the electron distribution and reactive sites on the surface of the molecule were examined. The theoretical first, second and third order NLO properties were calculated using DFT method. The SHG analysis substantiates

the first order theoretical NLO property. It shows the possibility NLO activity present in the molecule.

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