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Molecular Structure, Geometry Properties, HOMO-LUMO, and MEP Analysis of Acrylic Acid Based on DFT Calculations

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ABSTRACT

In this paper, quantum computational chemistry methods were employed to calculate the molecular properties of acyrilic acid. The molecule was optimized at STO-3G basis set using Density Functional Theory (DFT/B3LYP). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the frontier orbitals were obtained using DFT. The energy gap of HOMO–LUMO orbitals has been found to be 5.545 eV. Molecular Electrostatic Potential (MEP) surface analyses were also investigated. In addition, the basic crystal structure properties of acrylic acid were shown via the Crystallographic Information File (CIF). A discussion of the fundamental theory was reported behind the characterization methods.

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1. Introduction

It is a result of the large amount of acrylic acid that is produced globally (the global capacity is roughly 1.7 million tons per year). It serves as the starting point for making polymerization products [1]. Prop-2-enoic acid, another name for acrylic acid, is an organic compound having the formula $C_3H_4O_2$. It possesses the fundamental characteristics of unsaturated carboxylic acids. Acrylic acid is a clear liquid with a strong odor when it is at room temperature. In an industrial setting, acrylic acid is created by oxidizing propene with oxygen [2]. Acrylic acid is a high-volume product and is widely used for the manufacture of polymerization products. Many, including ester and acrylic acids, are most frequently utilized in industrial goods. Dental plates, dentures, and orthopedic cement are among the uses for them in both medicine and dentistry. As a result, people who work in the manufacturing, research, medical, and dental fields may be continuously exposed to acrylic monomers. It is crucial to extensively research the toxicity of acrylic acid because it has been demonstrated that acrylic esters can be converted to acrylic acid [3]. In the 20th century, the frontier molecular orbitals theory (FMO) was frequently employed to explain pericyclic reactions; but very recently several studies have demonstrated the feasibility of cycloaddition processes [4].

In this study, we report results of DFT computations, which is a communly used method for studying chemical reactivity [5]. For the theoretical calculations for molecular structure and spectroscopy, Gaussian 09 software were used for the B3LYP/STO-3G basis set. GaussSum software was also used to calculate the density of state (DOS). CIF file retrieved from the Crystallography Open Database website Unit cell drawings were made with the VESTA program, and XRD graphs were drawn with the ReciprOgraph program. ReciprOgraph is an application to calculate the density of any substance refracted by X-rays.

2. Materials and Methods

Calculations using ab initio and Density Functional Theory (DFT) often demand two primary approaches: "method" (expansion of the multi-electron wavefunction) or selection of exchange-correlation functional). The decisions taken in these key steps for resolving the electronic Schrödinger equation will impact the overall correctness of the outcomes and the ensuing computing expense. The goal of this review is to help theoretical or computational chemists build a solid foundation, especially since many base sets are present in widely used software packages or base set archives. While understanding fundamental set development is not a

requirement for performing quantum chemical calculations, it will be helpful. Choose alternatives for molecular calculations while concentrating on knowledge of more current advancements in the field's design, development, and optimization. The author thinks that doing this will make it possible to better understand the baseset missing mistake in every computation or to get the "right results for the right reason" [6-8]. The following explanation has been purposefully kept brief to refresh the reader on the terminology because detailed descriptions of the functions included in the basic sets and their classification can be found in several sources [9].

3. Results and Discussion

3.1 Optimized Geometry

One method for predicting the three-dimensional spatial arrangement of atoms in a molecule is geometry optimization. The Gaussian 09W package software was employed in this investigation to optimize [10]. Density functional theory (DFT) techniques were used to calculate the compound theoretically. One of the variation-correlation functionals utilized in DFT computations most commonly is B3LYP. It contains Yang, and Parr's correlation functional as well as Becke's three-parameter change functional [11, 12].

The Avogadro program was used to simulate the optimal structure of the examined chemical, which is depicted in Figure 1 [13, 14]. The GaussSum tool was used to carry out the energy optimization processes for the optimized chemical, and the results are depicted in Figure 2 [15]. According to DFT optimization energy profile (Figure 2), relevant optimization steps are colored: black for the initial optimization step, green other optimization steps, and red for the final optimization step.

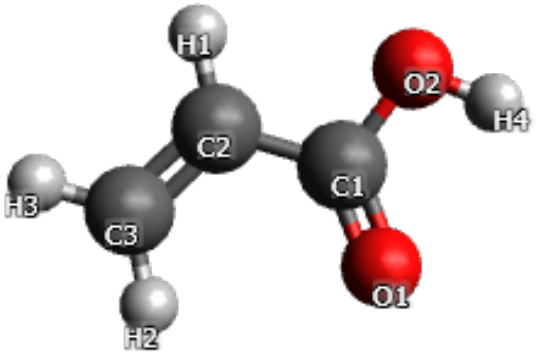

Figure 1. Optimize structure of acrylic acid

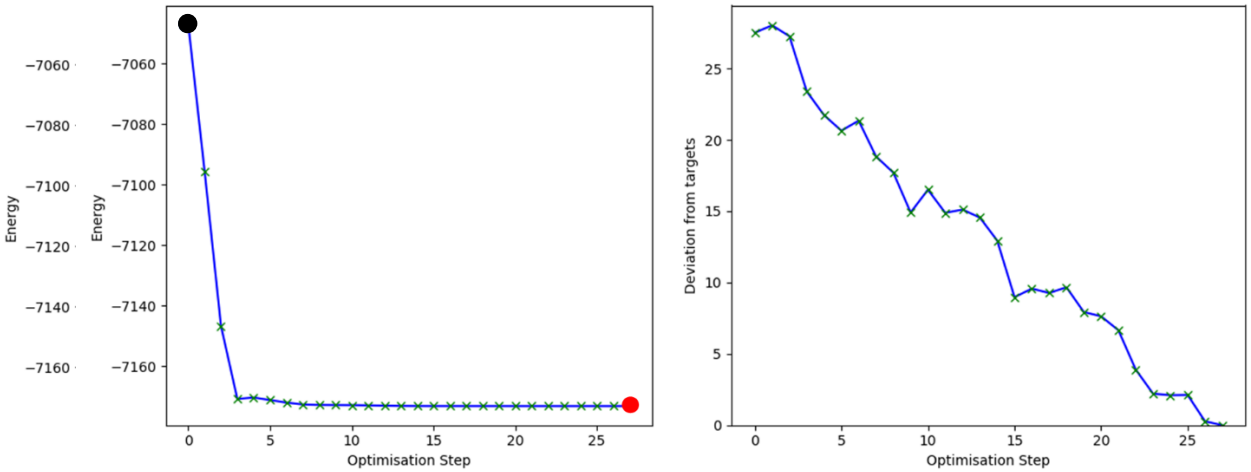

Figure 2. DFT optimization energy profile and deviation from targets for acrylic acid

We have the ability to conduct molecular docking studies and investigate sigma-pi interactions [16]. Natural Bonding Orbital (NBO) Analysis examines the molecules' interactions in charge transfer and intermolecular bonding

[17]. NBO, which offers details on intramolecular charge transfer interactions originating from the overlapping of the bonding and antibonding orbitals, was carried out to explore the internal electronic mobility of the complex. The electronic distribution between the HOMO and LUMO orbitals as a result of charge transfers was also revealed by NBO analysis. The HOMO-LUMO energy gap is made possible by significant charge transfers between the donor and acceptor atoms, and the complex exhibits a high degree of kinetic stability, according to the NBO study [18]. The natural bond orbital (NBO) analysis of acrylic acid was used to determine the bonding lengths within the molecule. The bond lengths were presented in Figure 3 and summarized in Table 1.

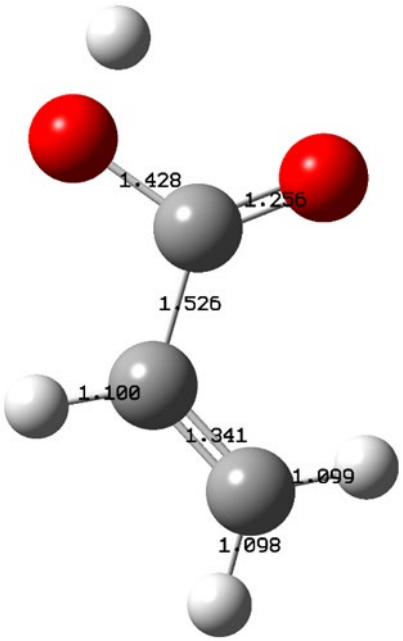

Figure 3. Natural Bond Orbital (NBO) analysis of acrylic acid

Table 1. Bond properties of acrylic acid

	Type	Start Atom	End Atom	Bond Order	Length (Å)
Bond 1	C-C	C1	C2	1	1.526
Bond 2	C-O	C1	O1	2	1.256
Bond 3	C-O	C1	O2	1	1.428
Bond 4	C-C	C2	C3	2	1.341
Bond 5	C-H	C2	H1	1	1.100
Bond 6	C-H	C3	H2	1	1.099
Bond 7	C-H	C3	H3	1	1.098
Bond 8	O-H	O2	H4	1	1.029

3.2 Molecular Electrostatic Potential (MEP) Surface

One of the methods that might be useful in the design of linear receptors is the Molecular Electrostatic Potential (MEP) Surface Analysis [19, 20]. Scientific studies have rationally utilized molecular electrostatic potential (MEP) maps for more than three decades [21]. The surface analysis of the Molecular Electrostatic Potential (MEP)

was discovered using GaussView software. The charge distributions of molecules are shown in three dimensions on the molecular electrostatic potential surface. We can see variably charged areas of the molecule thanks to these surface examinations. Molecular electrostatic potential shows the electronic density and is useful in recognition sites for electrophilic attack and nucleophilic reactions as well as hydrogen bonding interactions. The negative areas (red color) of MEP were related to electrophilic reactivity and the positive areas (blue color) ones to nucleophilic reactivity shown in Figure 4 [22]. The lowest unoccupied orbital is confined in an electrophilic zone in accordance with FMO theory because electrons from this orbital are extremely reactive and prepared to take part in a reaction [23].

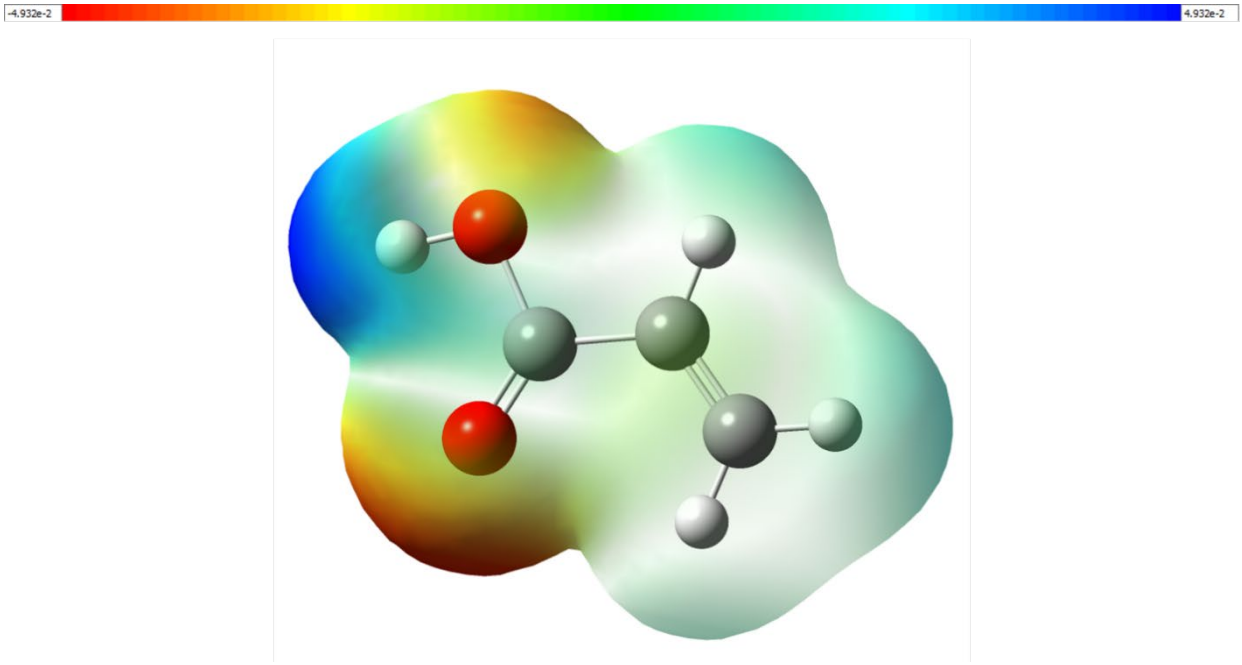

Figure 4. Molecular Electrostatic Potential of acrylic acid

3.3 HOMO-LUMO and Electronic Density of States (DOS) Analysis

According to the molecular orbital theory, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) are found in every molecule. The HOMO and LUMO orbitals can sometimes be referred to as prime orbitals due to their significant involvement in chemical processes. The chemical stability of the molecule is shown by the difference between the HOMO and LUMO energy values [24, 25]. The lower the energy difference (ΔE) and the simpler the interaction and reaction of the reactants, the closer the energy levels of the interacting molecular orbitals are to one another. Estimating the low and high electron density areas of a molecule is necessary for a better understanding of many chemical processes. Frontier molecular orbital analysis is a powerful practical model for describing the chemical reactivity of organic species because it is useful in predicting the electrophilic and nucleophilic areas of organic compounds [26, 27]. The lowest unoccupied orbital is confined in an electrophilic zone in accordance with FMO theory because electrons from this orbital are extremely reactive and prepared to take part in a reaction [28]. Its primary and most significant characteristic is HOMO energy. The HOMO electrons travel more easily when the HOMO energy is higher. The activity of the compounds improves as the electron mobility increases. The LUMO energy levels are determined by the electron acceptor capacity. The more activity, the lower the LUMO energy. Additionally, the energy gap between a molecule's LUMO and HOMO protons, E, is equal to this gap's value [29]. This parameter is used to compute the reactivity attribute. The more favorable the activity of the molecules, the higher the softness value and the lower the hardness value. Activity qualities are greatly influenced electronegativity characteristics by chemical potential. In addition, the Density of States (DOS) calculation presents the HOMO-LUMO energy range of the acrylic acid molecule. The spectrum in Figure 5 illustrates the distribution of available states at various energy levels and Figure 5 also displays HOMO-LUMO energy range of the acrylic acid. The DOS spectrum explains the contribution of electrons to the conduction and valence bands [30].

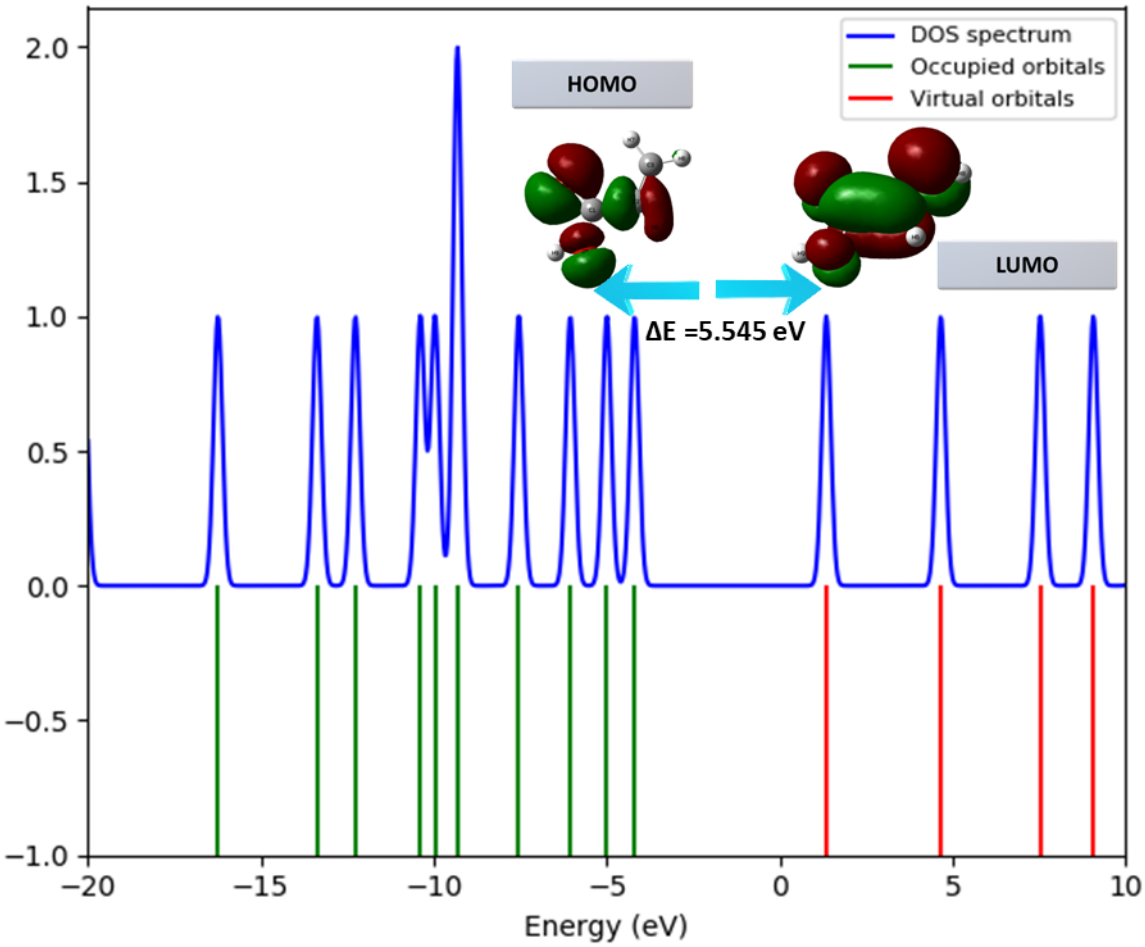

Figure 5. HOMO-LUMO structure with the energy level diagram and the density of states (DOS) with the contribution of acrylic acid

3.4 Crystal Properties

Acrylic acid ($C_3H_4O_2$) belongs to the space group Ibam, which has the number 72. It has a structure with orthorhombic symmetry [31]. a=9.952 Å, b=11.767 Å, and c=6.206 Å make up the lattice parameters, where α=β=γ=90°. The volume of a single cell is V = 726.7548 $Å^3$, taken from the Crystallography Open Database (CIF document [32]: 2008185 [33]). A CIF file enables to get the structure that needs to be investigated. VESTA is a 3D visualization tool for crystal morphologies, electron and nuclear densities, and structural models [34]. In Figure 6, red atoms stand for O, brown atoms for C, and white atoms for H atoms. It displays unit cell drawings created with VESTA [35]. An application called ReciprOgraph can determine the intensities of any material that has been diffracted with X-rays [36]. Figure 7 shows XRD graph created with the ReciprOgraph tool [37].

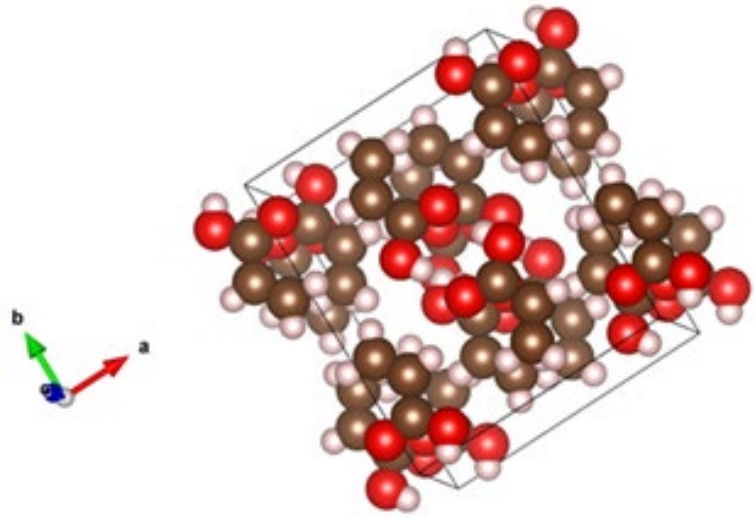

Figure 6. Crystal structure of acrylic acid

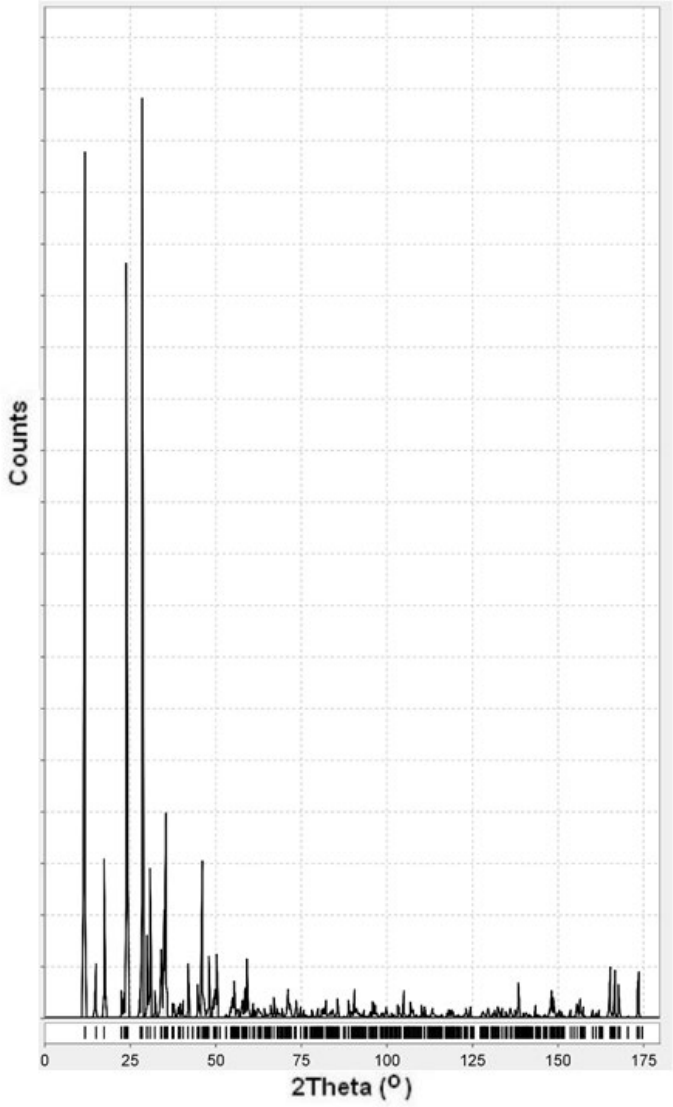

Figure 7. X-ray Diffraction (XRD) pattern of acrylic acid

4. Conclusions

This present study reports the structural, electrical, chemical and biological activities of acrylic acid. This compound plays a significant role in the medicinal and biochemical field. The reactivity of the molecules was predicted through a computational study based on density functional theory (DFT/B3LYP) using the STO-3G basis set. It could correctly classify the compounds according to their reactivity, too. The changes in biochemical and biological activity are extremely noticeable. 3D molecular surface maps were drawn in order to obtain information about negative (electrophilic attack) and positive (nucleophilic attack) regions. Moreover, the global reactivity descriptors have been calculated by the help of HOMO and LUMO energies to determine chemical stability. When we examine the structure of the acrylic acid molecule, the less active sites of HOMO are visible, but the active parts of LUMO appear larger. The energy range was seen as 5.545 eV. This value explains the eventual charge transfer interaction with the molecule, which influences the biological activity of the compound. DFT method has employed to investigate the analysis of the title compound, with a specific focus on its ground state, which corresponds to the minimum energy state. The energy gap impacts the chemical reactivity and kinetic stability of the molecule. The relatively high value of ΔE indicates that the title compound presents high chemical stability and it has low reactivity. Then, when the state density was examined, the peak interval was observed. The composite geometry optimization, geometry parameters, and minimal molecular energy range were all obtained In the optimized energy step, there is a sudden decrease between 0 and 5, and it remains constant between 5 and 25. The bond lengths of acrylic acid were also determined according to the

NBO analysis. The DFT method has proven to be one of the most accurate methods for the computation of the electronic structure as reported in literature.

Ethics in Publishing

There are no ethical issues regarding the publication of this study.

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