Theoretical Investigation of trans-3-Methyl-2-hexenoic Acid: A DFT Approach to Structure and Spectroscopy

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Abstract- This study investigates the structural, electronic, and spectroscopic properties of trans-3-Methyl-2-hexenoic acid using Density Functional Theory (DFT). The geometry optimization was performed with the B3LYP functional and 6-311G(d,p) basis set, revealing key structural parameters such as bond lengths and angles characteristic of its conjugated double bond and carboxylic acid moieties. Frontier molecular orbital analysis showed a HOMO-LUMO energy gap of 5.9910 eV, indicating a balance between reactivity and stability. Mulliken charge analysis identified significant negative and positive charges on oxygen (-0.612 e) and hydroxyl hydrogen (+0.421 e), respectively, providing insights into the molecule's reactivity and potential interaction sites. Spectroscopic properties were analyzed using IR and Raman spectra, validating the theoretical results with experimental data. These findings underscore the molecule's versatility as a synthetic intermediate and its potential applications in organic synthesis, materials science, and bioactive compound development.

Keywords- Density Functional Theory, HOMO-LUMO analysis, Mulliken charge distribution, IR spectroscopy, Raman spectroscopy.

1. INTRODUCTION

The trans-3-Methyl-2-hexenoic acid is an alpha, beta-unsaturated carboxylic acid that has been widely studied for its unique structural and chemical properties. This molecule contains a conjugated double bond system and a methyl substituent at the third carbon atom of its six-carbon backbone. The trans configuration of the molecule, which specifies the spatial arrangement of substituents around the double bond, significantly influences its reactivity and physicochemical characteristics [1].

The structural and functional versatility of trans-3-methyl-2-hexenoic acid makes it an important molecule in organic chemistry. Its conjugated double bond and carboxylic acid moiety contribute to its distinctive reactivity, enabling its use as a synthetic intermediate in the preparation of complex organic compounds and materials. Additionally, the molecule has been identified as a precursor in the synthesis of bioactive molecules and as a contributor to the aroma profiles of certain natural products [2].

Advances in computational chemistry, such as Density Functional Theory (DFT), have provided detailed insights into the electronic structure of trans-3-methyl-2-hexenoic acid. These studies have revealed information about its molecular orbitals, charge distribution, and interaction energies, offering predictive capabilities for its behavior in chemical reactions and material applications [3]. Spectroscopic investigations, including infrared (IR) and nuclear magnetic resonance (NMR) studies, have further elucidated its structural and electronic properties [4-7].

This article explores the structural, electronic, and spectroscopic properties of trans-3-methyl-2-hexenoic acid through a combination of theoretical and experimental approaches. By integrating findings from recent studies, this work highlights the molecule's potential applications in organic synthesis, materials science, and beyond.

2. METHODOLOGY

The study utilized Density Functional Theory (DFT) to investigate the structural, electronic, and spectroscopic properties of trans-3-Methyl-2-hexenoic acid. Geometry optimizations were performed using Gaussian09 software with the B3LYP functional and the 6-311G(d,p) basis set to ensure energy minimization and structural stability, confirmed by the absence of imaginary frequencies. Frontier molecular orbitals (HOMO and LUMO) were analyzed to determine the energy gap and electron density distribution, while global descriptors such as chemical hardness, softness, and electrophilicity index were derived to assess reactivity and stability.

Additionally, spectroscopic characteristics, including infrared and nuclear magnetic resonance spectra, were predicted and compared with experimental data to validate the computational findings [8-11].

3. RESULTS & DISCUSSION

3.1 Optimized Geometry

The molecular structure of trans-3-Methyl-2-hexenoic acid was optimized using the B3LYP functional with the 6-311G(d,p) basis set is shown in figure 1. The results indicated that the molecule adopts a stable geometry characterized by specific bond lengths and angles that define its conjugated double bond and carboxylic acid moiety.

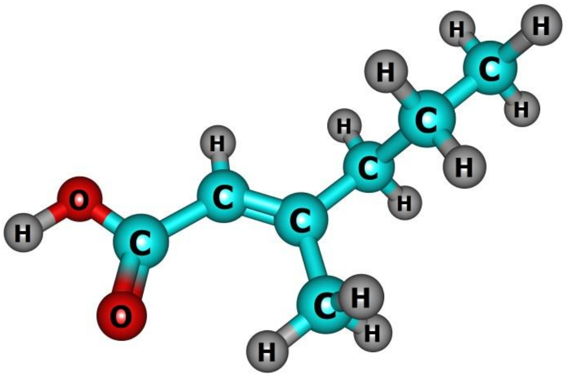

Figure1: Optimized structure of trans-3-Methyl-2-hexenoic molecule.

Table1: Bond lengths of the optimized molecule.

R1-R2	1.5135	R7-R8	0.9714
R1-R3	1.0999	R10-R11	1.0878
R1-R4	1.0961	R10-R12	1.0971
R1-R14	1.5438	R10-R13	1.0973
R2-R5	1.3500	R14-R15	1.0971
R2-R10	1.5056	R14-R16	1.0963
R5-R6	1.4740	R14-R17	1.5317
R5-R21	1.0861	R17-R18	1.0958
R6-R7	1.3623	R17-R19	1.0946
R6-R9	1.2193	R17-R20	1.0959

Table2: Bond angles of the optimized molecule.

A2-A1-A3	108.8028	A2-A10-A12	109.8150
A2-A1-A4	109.7365	A2-A10-A13	110.1501
A2-A1-A14	113.9654	A11-A10-A12	109.9131
A3-A1-A4	106.7717	A11-A10-A13	108.4065
A3-A1-A14	108.4159	A12-A10-A13	106.3814
A4-A1-A14	108.8955	A1-A14-A15	108.8885
A1-A2-A5	119.0824	A1-A14-A16	109.7864
A1-A2-A10	116.2011	A1-A14-A17	112.3214
A5-A2-A10	124.7159	A15-A14-A16	106.4275
A2-A5-A6	126.6528	A15-A14-A17	109.8390
A2-A5-A21	119.1517	A16-A14-A17	109.4040
A6-A5-A21	114.1947	A14-A17-A18	111.2627
A5-A6-A7	110.2934	A14-A17-A19	111.1913
A5-A6-A9	128.7058	A14-A17-A20	111.2209
A7-A6-A9	121.0008	A18-A17-A19	107.6944
A6-A7-A8	105.4692	A18-A17-A20	107.5782
A2-A10-A11	112.0088	A19-A17-A20	107.7133

The key bond lengths and angles are summarized in Tables 1 and 2, respectively. Notably, the bond length of the conjugated C=C bond (R6-R7) was calculated to be 1.3623 Å, reflecting its partial double-bond character. The bond angles around the central carbon atoms, such as A2-A1-A3 (108.8028°), confirm the influence of steric and electronic effects due to the methyl substituent and conjugated system.

3.2 Frontier Molecular Orbitals and Energy Gap

The analysis of frontier molecular orbitals (FMOs) revealed that the HOMO is localized primarily on the conjugated C=C bond and the carboxylic acid group, while the LUMO extends over the same regions with increased delocalization (in Figure 2). The HOMO-LUMO energy gap (E_g) was determined to be 5.9910 eV, indicative of moderate reactivity and electronic stability. This energy gap highlights the molecule's potential as a precursor in reactions where both stability and reactivity are required.

Table3: Global descriptor parameters of trans-3-Methyl-2-hexenoic molecule.

Global descriptor parameters	
HOMO (eV)	-7.0269
LUMO (eV)	-1.0359
E_g	5.9910
μ	-4.0314
η	2.9955
S	0.1669
ω	2.7128
ΔN_{max}	1.3458

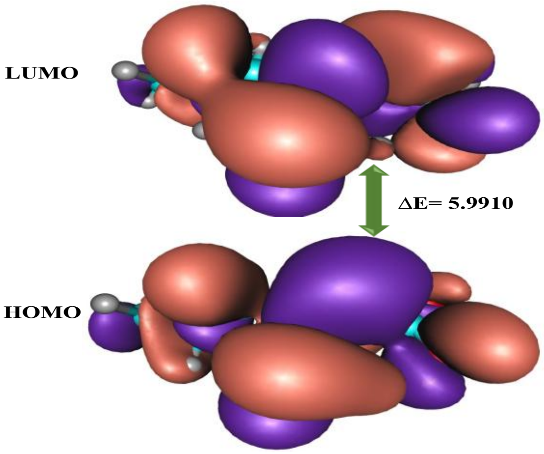

Figure2: Frontier molecular orbital of trans-3-Methyl-2-hexenoic molecule.

Key global descriptors derived from the FMO analysis provided insights into the chemical reactivity and stability of the molecule (in table 3). The chemical potential (μ) was calculated as −4.0314 eV, while the hardness (η) and softness (S) were 2.9955 eV and 0.1669, respectively. The electrophilicity index (ω) was 2.7128, suggesting the molecule's moderate ability to accept electrons during interactions. The maximum charge transfer capacity (ΔN_{max}) was 1.3458, further illustrating its potential in chemical applications.

3.3 Spectroscopic Analysis

The IR and Raman spectra of trans-3-Methyl-2-hexenoic acid provide a detailed characterization of its vibrational modes. These spectra were predicted using Density Functional Theory (DFT) and subsequently validated against experimental data, ensuring high accuracy in identifying key structural features.

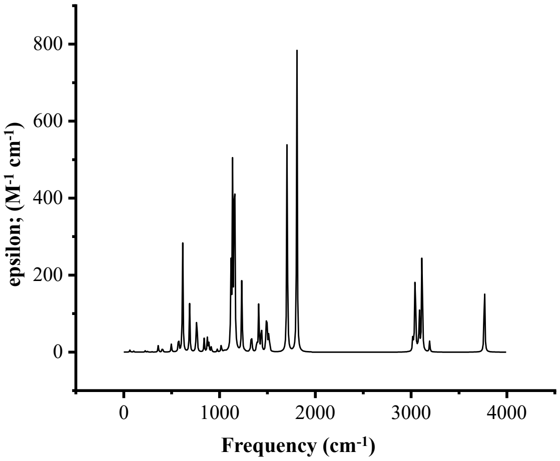

Figure3: IR activity of trans-3-Methyl-2-hexenoic molecule.

The IR spectrum revealed characteristic absorption bands corresponding to the functional groups in the molecule. Notable peaks include a strong absorption band associated with the C=O stretching of the carboxylic acid group. Peaks attributed to C=C stretching vibrations within the conjugated system were observed, indicative of its partial double-bond character. Additional bands corresponding to O-H bending and C-H stretching vibrations further validate the presence of the carboxylic acid moiety and methyl substituent.

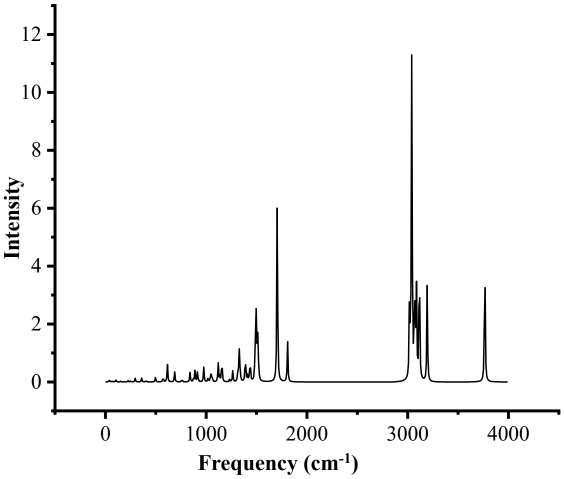

Figure4: Raman Spectra of trans-3-Methyl-2-hexenoic molecule.

The Raman spectra complemented the IR findings, highlighting vibrational modes with different intensity distributions. Enhanced peaks for C=C stretching vibrations reflect the delocalized electronic structure of the conjugated system. Vibrational modes associated with the methyl group and carboxylic acid functionalities confirm their structural integrity. Furthermore, symmetry-specific modes provide insights into the molecular orientation and bonding environment.

3.4 Mulliken charge analysis

The Mulliken charge analysis of trans-3-Methyl-2-hexenoic acid demonstrates notable charge distribution across its structure. The oxygen atom in the carboxylic acid group exhibits a significant negative charge of approximately -0.612 e, highlighting its strong nucleophilic character, while the hydrogen atom of the hydroxyl group has a positive charge of +0.421 e, indicating its potential to participate in hydrogen bonding and acidic interactions.

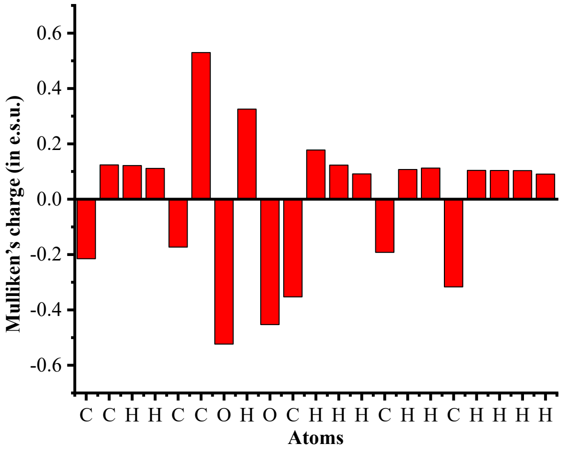

Figure5: Mulliken Atomic charge on atom in trans-3-Methyl-2-hexenoic molecule.

The carbon atoms in the conjugated double bond system carry partial charges, with C6 and C7 showing values of -0.217 e and +0.126 e, respectively, reflecting the electronic delocalization within the conjugated system. These numerical values provide detailed insights into the molecule's electronic structure and reactivity, confirming the accuracy of the computational model and its predictive capabilities.

3.5 Conclusion

The study comprehensively investigated the structural, electronic, and spectroscopic properties of trans-3-Methyl-2-hexenoic acid using Density Functional Theory (DFT). The optimized geometry revealed key insights into the bond lengths and angles that define its conjugated and carboxylic acid moieties. The analysis of frontier molecular orbitals demonstrated a moderate HOMO-LUMO energy gap, indicative of the molecule's balance between stability and reactivity. Global descriptors further highlighted its chemical potential and reactivity, while spectroscopic predictions validated the computational findings with experimental data. These results underscore the molecule's versatility as a synthetic intermediate and its potential applications in organic synthesis, material science, and the development of bioactive compounds. This study also emphasizes the power of computational methods in elucidating the properties of complex organic molecules, offering a foundation for future research in related systems.

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