Electro-Chemical and Spectroscopic Properties of Trans-4-Methoxycinnamic Molecule: A DFT Study

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ABSTRACT

This study investigates the structural, electronic, and vibrational properties of trans-4-methoxycinnamic acid using Density Functional Theory (DFT). The molecule's optimized geometry, analyzed with the B3LYP functional and 6-311G(d,p) basis set, reveals a planar, conjugated structure with significant stability and delocalized π-electrons. Key electronic properties, including the HOMO-LUMO energy gap (4.2885 eV), chemical descriptors, and frontier molecular orbitals, highlight its suitability for optoelectronic and UV-absorbing applications. Vibrational analysis through IR and Raman spectra confirms the presence of characteristic functional groups and strong intramolecular interactions. Mulliken atomic charge distribution emphasizes the role of electron-dense regions in enhancing polarizability and dipole moment. These findings underline the molecule's potential for advanced applications in photochemistry, UV protection, and non-linear optical materials.

Keywords: Density Functional Theory (DFT), HOMO-LUMO, vibrational analysis, Mulliken charge

INTRODUCTION

Trans-4-methoxycinnamic acid (C10H10O3) is a prominent cinnamic acid derivative with unique structural and electronic properties. It features a conjugated π-system that spans the phenyl ring and an α, β-unsaturated carboxylic acid group, with a methoxy (-OCH3) substituent at the para position of the aromatic ring. This structural arrangement enhances its chemical reactivity, dipole moment, and optical properties, making it a subject of interest for applications in photochemistry, non-linear optics, and material science [1-2].

As a naturally occurring compound, trans-4-methoxycinnamic acid is widely studied for its role in biological systems, including its antioxidant and UV-absorbing properties [3]. The electron-donating nature of the methoxy group influences the electronic structure of the molecule, including its HOMO-LUMO energy gap, molecular stability, and non-linear optical (NLO) behavior, which are critical for designing optoelectronic materials [4-6].

Density Functional Theory (DFT) is a powerful computational approach for analyzing the structural, electronic, and spectroscopic properties of molecules. For trans-4-Methoxycinnamic acid, DFT enables precise calculations of geometry, vibrational frequencies, and electronic transitions, providing insights into its photophysical behavior and chemical reactivity (Perdew et al., 1996; Becke, 1993). Additionally, time-dependent DFT (TD-DFT) is widely used to investigate its UV-Vis absorption spectra, aiding in the understanding of its optical response [6-10].

In this study, we use DFT with advanced functional such as B3LYP, combined with the 6-311G(d,p) basis set, to explore key properties of trans-4-Methoxycinnamic acid. Specific focus is given to its structural parameters, frontier molecular orbitals, chemical reactivity descriptors, and non-linear optical coefficients. The findings contribute to a deeper understanding of cinnamic acid derivatives and their potential applications in optoelectronics, UV protection, and advanced material design.

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METHODOLOGY

The study of trans-4-Methoxycinnamic acid was conducted using Density Functional Theory (DFT) to explore its structural, electronic, and spectroscopic properties. Geometry optimization was performed with the B3LYP functional and 6-311G (d, p) basis set to achieve accurate molecular parameters. The electronic properties, including HOMO, LUMO, and the energy gap, were analyzed to assess chemical reactivity and stability, while additional descriptors like chemical potential, hardness, and electrophilicity index provided insights into the molecule's behavior. Vibrational analysis using IR and Raman spectra confirmed the molecular structure and intramolecular interactions. Frontier molecular orbital (FMO) analysis revealed electron density distribution, essential for understanding optical transitions, and Mulliken charge analysis highlighted the atomic charge distribution and polarizability. Calculations were carried out using Gaussian 09 [11], and visualizations were generated using Gauss View 5.0, ensuring a thorough examination of the molecule's potential applications in photochemistry, UV protection, and optoelectronic materials [12-20].

RESULTS AND DISCUSSION

Structural Properties

The structural properties of trans-4-Methoxycinnamic acid, as shown in Figure 1, highlight a planar and conjugated molecular structure, which is essential for its electronic and optical behavior. The molecule comprises a phenyl ring, an α, β-unsaturated carboxylic acid group, and a methoxy (-OCH3) substituent at the para position, all contributing to its stability and efficient electron delocalization.

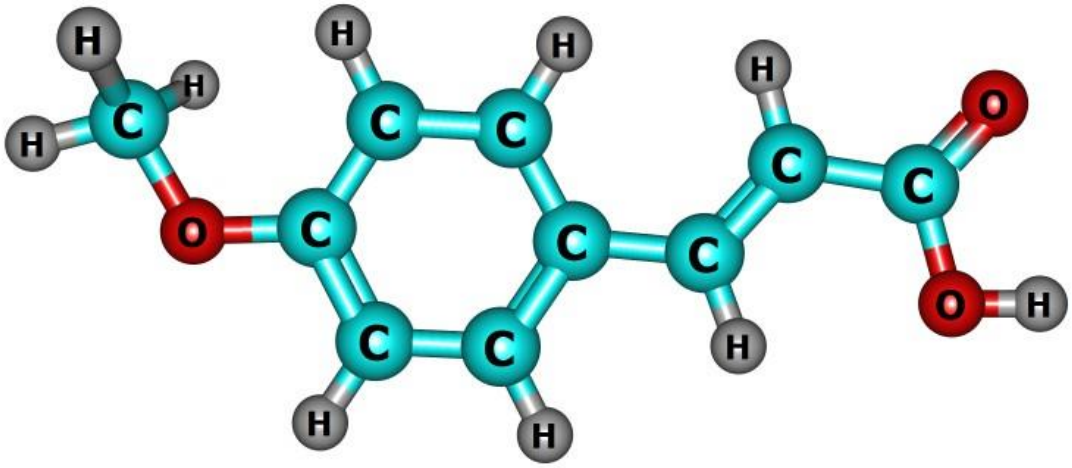

Figure1: Optimized molecule of Trans-4-Methoxycinnamic.

Key details of the optimized bond lengths and angles are presented in Table 1. For instance, the C=C bonds in the phenyl ring range from 1.391 Å to 1.420 Å, indicating strong conjugation, while the C=O bond in the carboxylic acid group is 1.2178 Å, reflecting its double-bond character. The bond lengths involving the methoxy group, such as the C-O bond at 1.3487 Å, demonstrate the electron-donating effect of the substituent, which increases the dipole moment and polarizability of the molecule.

Table1: Optimized parameters of Trans-4-Methoxycinnamic molecule.

Bonds length (in Å)			
R1-R2	1.3912	R11-R12	1.4209
R1-R6	1.4060	R12-R13	1.0972
R1-R7	1.0855	R12-R14	1.0908

R2-R3	1.4040	R12-R15	1.0972
R2-R8	1.0834	R16-R17	1.0880
R3-R4	1.4034	R16-R18	1.3487
R3-R11	1.3595	R18-R19	1.4686
R4-R5	1.3856	R18-R23	1.0848
R4-R9	1.0849	R19-R20	1.3631
R5-R6	1.4106	R19-R22	1.2178
R5-R10	1.0869	R20-R21	0.9707
R6-R16	1.4597		
Bonds Angle (in degree)			
A2-A1-A6	121.6619	A3-A11-A12	118.5848
A2-A1-A7	118.4855	A11-A12-A13	111.5784
A6-A1-A7	119.8526	A11-A12-A14	105.9429
A1-A2-A3	119.7688	A11-A12-A15	111.5906
A1-A2-A8	119.3390	A13-A12-A14	109.2198
A3-A2-A8	120.8922	A13-A12-A15	109.1970
A2-A3-A4	119.5254	A14-A12-A15	109.2262
A2-A3-A11	124.6491	A6-A16-A17	115.2845
A4-A3-A11	115.8255	A6-A16-A18	127.5836
A3-A4-A5	119.9559	A17-A16-A18	117.1318
A3-A4-A9	118.5534	A16-A18-A19	123.8815
A5-A4-A9	121.4907	A16-A18-A23	122.7641
A4-A5-A6	121.6408	A19-A18-A23	113.3544
A4-A5-A10	119.2853	A18-A19-A20	114.0576
A6-A5-A10	119.0739	A18-A19-A22	124.2831
A1-A6-A5	117.4472	A20-A19-A22	121.6593
A1-A6-A16	123.5765	A19-A20-A21	105.1972
A5-A6-A16	118.9762		

The bond angles further emphasize the molecule's structural symmetry. For example, the angle around the aromatic ring and the carboxylic acid group is approximately 120°, supporting planar conjugation. Similarly, angles near the methoxy group confirm the structural alignment critical for delocalization across the conjugated system.

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Electronic Properties

The electronic properties of trans-4-Methoxycinnamic acid were analyzed using Density Functional Theory (DFT), with the key findings summarized in Table 2. The molecule exhibits a Highest Occupied Molecular Orbital (HOMO) energy of -5.9160 eV and a Lowest Unoccupied Molecular Orbital (LUMO) energy of -1.6275 eV, resulting in an energy gap (Eg) of 4.2885 eV. This moderate energy gap indicates good stability and suitability for optoelectronic applications, as it balances electronic excitation efficiency with chemical inertness.

Table2: Chemical global descriptor parameters of Trans-4-Methoxycinnamic molecule.

Chemical global descriptor	
HOMO (eV)	-5.9160
LUMO (eV)	-1.6275
E_g	4.2885
μ	-3.7718
η	2.1443
S	0.2332
ω	3.3173
ΔN_{max}	1.7590

Other electronic descriptors, such as the chemical potential (μ = -3.7718 eV) and hardness (η = 2.1443 eV), further confirm the molecule's stability and resistance to deformation under external perturbations. The softness (S = 0.2332 eV) and electrophilicity index (ω = 3.3173 eV) reflect the molecule's ability to interact with its environment, making it a promising candidate for non-linear optical (NLO) applications.

Vibrational Analysis

The vibrational properties of trans-4-Methoxycinnamic acid were studied using Density Functional Theory (DFT), and the results are illustrated in Figures 2 and 3, which depict the IR and Raman spectra, respectively. These spectra reveal the characteristic vibrational modes of the functional groups within the molecule, providing insights into its structural integrity and intramolecular interactions.

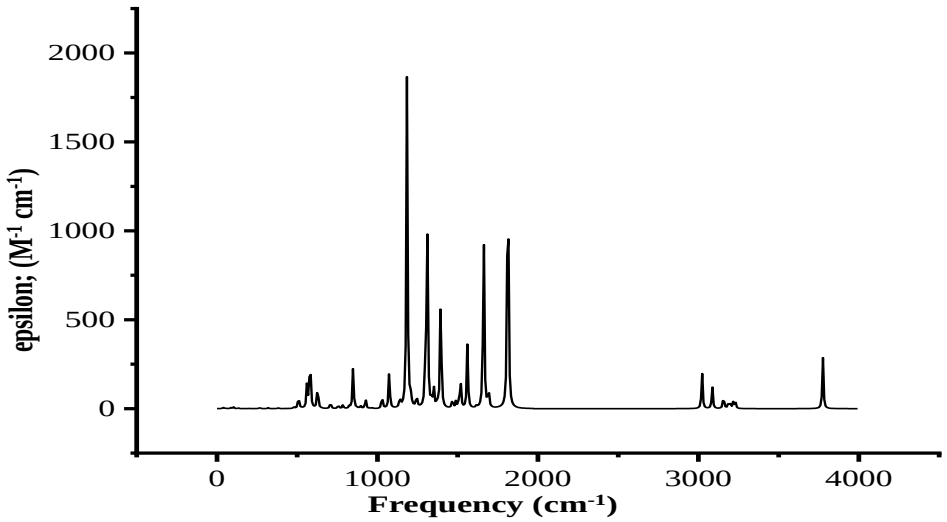

Figure 2: IR activity of Trans-4-Methoxycinnamic molecule.

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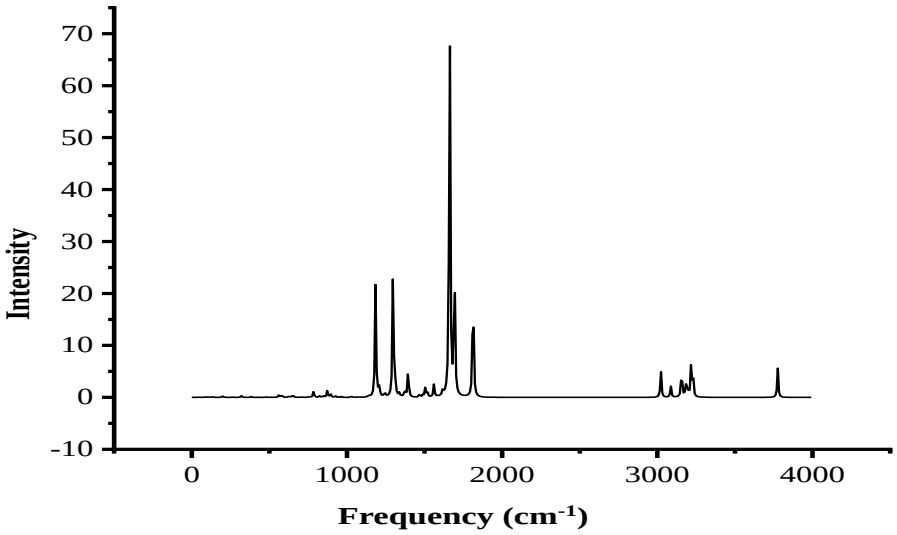

Figure 3: Raman spectra of Trans-4-Methoxycinnamic molecule.

The IR spectrum (Figure 2) shows prominent peaks corresponding to the stretching vibrations of the C=O group in the carboxylic acid, which appears in the range of 1700–1750 cm^{-1}, and the C=C bonds of the aromatic ring, observed between 1500–1600 cm^{-1}. The O-H stretching vibrations, indicative of the carboxylic acid group, are detected in the range of 3200–3400 cm^{-1}, confirming the presence of this functional group in the molecule.

The Raman spectrum (Figure 3) complements the IR analysis by highlighting the vibrations of the methoxy (-OCH_3) group and the aromatic C-H bonds. The symmetric and asymmetric stretching modes of the methoxy group are observed around 2800–3000 cm^{-1}. The Raman peaks also provide detailed information about the in-plane and out-of-plane bending modes of the aromatic system, confirming the molecule's planar structure.

Frontier Molecular Orbitals

The analysis of frontier molecular orbitals (FMOs) provides crucial insights into the electronic properties and reactivity of trans-4-Methoxycinnamic acid. The spatial distribution of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) is depicted in Figure 4, illustrating the molecule's electron density regions critical for electronic transitions.

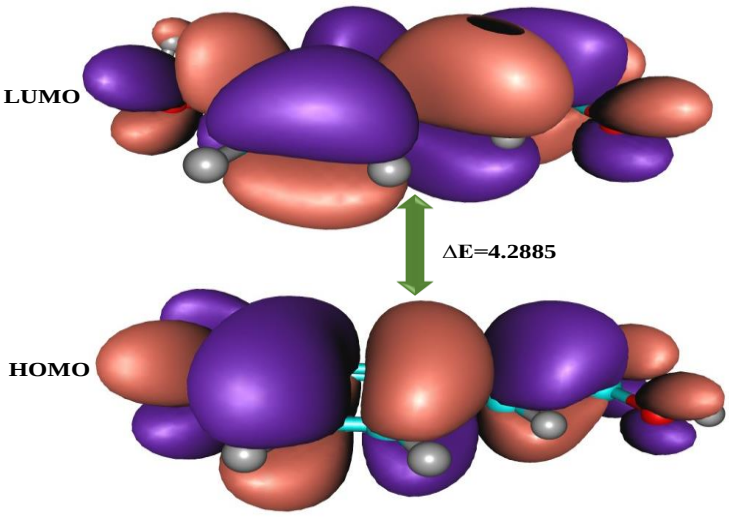

Figure 4: Frontier molecular orbital of Trans-4-Methoxycinnamic molecule.

The HOMO is primarily localized on the aromatic ring and the methoxy group, highlighting the delocalization of π-electrons in these regions. This distribution indicates that the methoxy substituent significantly contributes to the electron-donating capability of the molecule, enhancing its polarizability and dipole moment. In contrast,

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the LUMO is predominantly concentrated around the carboxylic acid group, reflecting its role as an electron-accepting site.

The calculated HOMO-LUMO energy gap (Eg = 4.2885 eV, as listed in Table 2) indicates moderate electronic reactivity, making the molecule suitable for optoelectronic applications. The separation of electron density between the HOMO and LUMO suggests a high degree of intramolecular charge transfer (ICT), a desirable property for UV absorption and non-linear optical (NLO) behavior.

Mulliken Atomic Charges

The Mulliken atomic charge distribution for trans-4-Methoxycinnamic acid, illustrated in Figure 5, provides a detailed view of the electron density across the molecule, shedding light on its reactivity and polarizability. The analysis shows significant electron density on the oxygen atoms in the carboxylic acid group and the methoxy group, which are the most electronegative regions of the molecule.

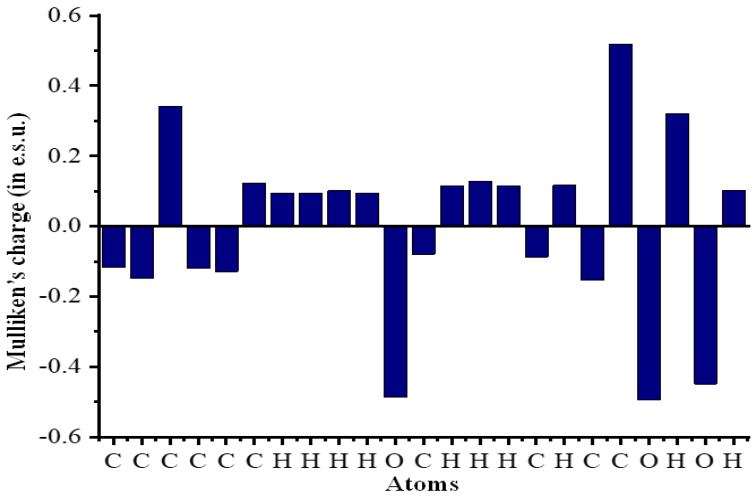

Figure 5: Mulliken's atomic charge on atom of Trans-4-Methoxycinnamic molecule.

The oxygen atoms of the carboxylic acid group carry a high negative charge, reflecting their role in stabilizing interactions and contributing to the molecule's dipole moment. Similarly, the oxygen in the methoxy group exhibits a notable negative charge, enhancing its electron-donating ability and reinforcing the conjugation within the molecule.

Conversely, the hydrogen atoms connected to the carboxylic acid group show a positive charge, indicating their potential as sites for hydrogen bonding. The carbon atoms in the aromatic ring display varying charge values, consistent with the delocalization of π-electrons throughout the conjugated system.

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