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Spectroscopic analysis of cinnamic acid using quantum chemical calculations

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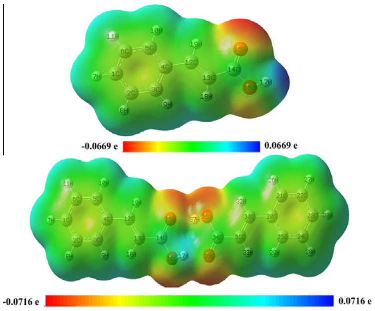
HIGHLIGHTS

- Monomer and dimer structures of cinnamic acid were examined.
- Spectroscopic analysis was characterized by FT-IR, FT-Raman and NMR techniques.
- MSP and Mulliken charge analysis of the compound were studied.
- HOMO and LUMO energies and UV of the molecule were calculated.

GRAPHICAL ABSTRACT



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ABSTRACT

In this present study, FT-IR, FT-Raman, ^{13}C NMR and ^{1}H NMR spectra for cinnamic acid have been recorded for the vibrational and spectroscopic analysis. The observed fundamental frequencies (IR and Raman) were assigned according to their distinctiveness region. The computed frequencies and optimized parameters have been calculated by using HF and DFT (B3LYP) methods and the corresponding results are tabulated. On the basis of the comparison between computed and experimental results assignments of the fundamental vibrational modes are examined. A study on the electronic and optical properties; absorption wavelengths, excitation energy, dipole moment and frontier molecular orbital energies, were performed by HF and DFT methods. The alternation of the vibration pattern of the pedestal molecule related to the substitutions was analyzed. The ^{13}C and ^{1}H NMR spectra have been recorded and the chemical shifts have been calculated using the gauge independent atomic orbital (GIAO) method. The Mulliken charges, UV spectral analysis and HOMO–LUMO analysis of have been calculated and reported. The molecular electrostatic potential (MEP) was constructed.

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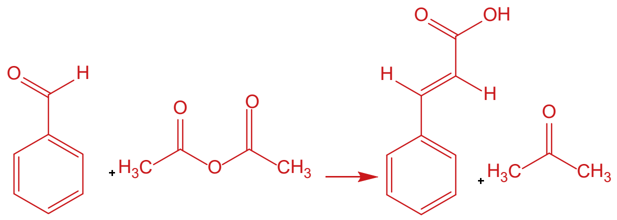
Introduction



Cinnamic acid is (CA) an organic compound with the formula $(C_6H_5CHCHCO_2H)$. It is a white crystalline compound that is slightly soluble in water. It occurs naturally in a number of plants and freely soluble in many organic solvents. CA is widely spread in the plants and possesses wide range of activities [1]. It is also used as precursor for the synthesis of commercially important cinnamic esters. Cinnamic esters are obtained from various plant sources and find application in perfumery, cosmetic industries and in pharmaceutics. This compound is mainly used in anti-tumor and antimicrobial activity [2]. Methoxy substituted cinnamate such as ethyl 3,4,5-trimethoxycinnamate plays an important role in controlling inflammatory diseases [3]. CA and its derivatives are secondary metabolites with antioxidant and antibacterial activities produced by plants in response to stressful conditions, such as infections or wounding [4]. Previous studies have shown the pharmacological properties of cinnamic acid and its derivatives in antioxidant and anti-diabetic activities [5–7]. Cinnamate can act as optical filters or deactivate substrate molecules that have been excited by light for the protection polymers and organic substances. In cosmetic grades, they are used as sunscreen agents to reduce skin damage by blocking UV.

Experimental details

The molecule CA was purchased from Sigma–Aldrich Chemicals, USA, which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The FT-IR spectrum of the compound was recorded in Bruker IFS 66V spectrometer in the range of 4000–400 cm^{-1}. The spectral resolution is ±2 cm^{-1}. The FT-Raman spectrum of the same was also recorded in the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 μm line widths with 200 mW power. The spectra are recorded in the range of 4000–100 cm^{-1} with scanning speed of 30 cm^{-1} min^{-1} of spectral width 2 cm^{-1}. The frequencies of all sharp bands are accurate to ±1 cm^{-1}. The ^{13}C & ^{1}H NMR spectrum was recorded by spin solve high resolution bench top FT-NMR spectrometer. The operating frequency: 42.5 MHz proton with resolution: 50% line width, <25 ppb (1 Hz) in sensitivity is greater than 10,000:1.

Computational methods

In the present work, the entire quantum chemical calculations have been performed at HF and DFT (B3LYP) methods using the Gaussian 03 W program [8]. B3LYP represents Becke's three parameter exact exchange-function (B3) [9] combined with gradient-corrected correlation functional of Lee, Yang and Parr (LYP) [10,11]. The optimized structural parameters are used in the vibrational frequency calculations at DFT (B3LYP) levels. The minimum energy of geometrical structure is obtained by using level 6-311+G(d, p) and 6-311++G(d, p) basis sets. At the optimized geometry for the title molecule no imaginary frequency modes are obtained, so there is a true minimum on the potential energy surface is found. The computed vibrational frequencies are scaled as 0.9067 for HF and the range of wavenumbers above 1700 cm^{-1} are scaled as 0.958 and below 1700 cm^{-1} scaled as 0.983 for B3LYP [12,13] to account for systematic errors caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity. After scaled with the scaling factor, the deviation from the experiments is less than 10 cm^{-1} with a few exceptions. The assignments of the calculated normal modes have been made on the basis of the corresponding PEDs. The PEDs are computed from quantum chemically calculated vibrational frequencies using VEDA program [13]. Gaussview program [14] has been considered to get visual animation and for the verification of the normal modes assignment. The electronic properties, such as HOMO–LUMO energies, absorption wavelengths and oscillator strengths are calculated using B3LYP method of the time-dependent DFT (TD-DFT) [14–15], based on the optimized structure in solvent (DMSO and methanol) and gas phase. The thermodynamic properties of the title compound at different temperatures have been calculated in gas phase using B3LYP/6-311++G(d, p) method.

Results and discussion

Geometric optimization and conformational analysis

The molecular structure of CA belongs to Cs point group symmetry. The optimized structures of CA monomer and dimer are shown in Fig. 1. CA has a substituent's of C_2H_2COOH attached to benzene ring. To determine the most energy conformation of the CA molecule, a conformation analysis was performed. The potential energy graph is obtained by the rotation of the CCOH group from 0° to 360° varied in steps of 10° with the dihedral angle C13—C14—O16—H17 of the molecule using AM1 method is depicted in Fig. 2. These result shows that CA molecule has one possible structure, depend on the positions of the hydroxyl group bonded to carbon atom. According to the DFT calculation of conformer with 6-311++G(d, p) basis set, the rotational conformer was predicted more stable from C_S symmetry group. The optimized geometrical parameters are calculated by different methods are listed in Table 1. The dimmer molecule is linked by strong intermolecular O—H···O hydrogen bond of 1.688 Å between oxygen atom and hydroxyl group of another molecule to give rise to a dimer. Then, in order to test the effect of intermolecular interactions, the CA dimer formed by O—H···O intermolecular hydrogen bonds is investigated by theoretical methods. The computed O—H, O—H···O, O···O bond distances are equal to 1.688, 1.694 and 2.243 Å, respectively. The optimized parameters are slightly overestimated with crystallographic literature values [16,17]. Researchers [18] have explained the changes in the frequency, bond length or bond angle. The computed optimized C—H bond lengths in the benzene ring fall in the range from 1.083 to 1.085 Å by B3LYP and 1.073 to 1.077 Å. The ring C—C bond distances of CA are found to have higher values in case of B3LYP with respect to HF. The bond length of C3—C4 elongated more due to substituent effect.

The aromatic C—C bond lengths are calculated in both methods are within range 1.380–1.400 Å. It is very close agreement with experimental values. The C—C—H bond angles are reported 119.5 and 119.6 [19]. For the title compound, the calculated bond angle of C1—C2—H7 is 120.0°. Similarly, the C6—C6—H7 bond angle is 120.2°. The hexagonal structure of the ring is mutilated by the substitutions and is proved by the bond angle order C3—C4—C5 < C1—C2—C6 < C1—C6—C5 < C2—C3—C4 < C1—C2—C3 < C4—C5—C6. The rest of the bond angles of the ring are comparatively less. Substitution with the C_2H_2COOH group leads to some changes of the bond angles in the benzene ring. The density

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