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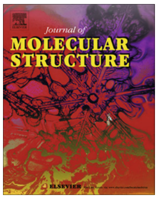

# Conformational, structural, vibrational, electronic and quantum chemical investigations of *cis*-2-methoxycinnamic acid

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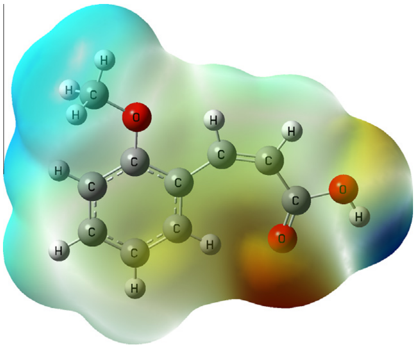
## HIGHLIGHTS

- Spectral properties of *cis*-2-methoxycinnamic acid have been studied.
- The more stable conformations of the molecule are determined.
- The stable structure has C=O and C=C bond in *s-cis* orientation.
- The barrier height between more and less stable conformer is 2.43 kcal $\text{mol}^{-1}$.
- The MEP has the range $+1.140e \times 10^{-2}$ to $-1.140e \times 10^{-2}$.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The Fourier transform infrared (FTIR) and FT-Raman spectra of *cis*-2-methoxycinnamic acid have been measured in the range 4000–400 and 4000–100 $\text{cm}^{-1}$, respectively. Complete vibrational assignment and analysis of the fundamental modes of the compound were carried out using the observed FTIR and FT-Raman data. The geometry was optimised without any symmetry constrains using the DFT/B3LYP method utilising 6-311++G** and cc-pVTZ basis sets. The thermodynamic stability and chemical reactivity descriptors of the molecule have been determined. The exact environment of C and H of the molecule has been analysed by NMR spectroscopies through $^{1}H$ and $^{13}C$ NMR chemical shifts of the molecule. The energies of the frontier molecular orbitals have also been determined. Complete NBO analysis was also carried out to find out the intramolecular electronic interactions and their stabilisation energy. The vibrational frequencies which were determined experimentally are compared with those obtained theoretically from density functional theory (DFT) gradient calculations employing the B3LYP/6-311++G** and cc-pVTZ methods.

## Introduction

Phenolic acid derivatives constitute a group of natural compounds present in human diet in significant amounts, which have long been known to display both antioxidant (through their radical scavenging activity) and prooxidant properties [1–3]. They are

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involved in numerous metabolic reactions and are naturally occurring in many plant-derived food products, largely responsible for the browning process [4–6]. Apart from being widely used as antioxidant food additives [7,8], some of them were lately found to behave as inhibitors of deleterious oxidative processes; e.g. in the prevention of cardiovascular diseases and inflammatory processes [9,10], or even in cancer [11–17].

Cinnamic acid (3-phenyl-2-propenoic acid), possesses antibacterial, antifungal and parasite fighting abilities [18,19]. The derivatives of cinnamic acid are important pharmaceutical agents for high blood pressure and stroke prevention and possess antitumour activities [20]. The biochemical properties of polyphenolic secondary plant metabolites such as esters of cinnamic acids (caffeic, ferulic, *p*- and *o*-coumaric, sinapic acid) attract much attention in biology and medicine. These compounds show antiviral, antibacterial, vasoactive, antiinflammatory and other properties. Cinnamic acids play vital role in the synthesis of other important compounds. It posses antitumour activity against Sarcoma 180 as well as antimicrobial activity [21]. Cinnamic acid is a fragrance ingredient used in many fragrance compounds. It may be found in fragrances used in decorative cosmetics, fine fragrances, shampoos, toilet soaps and other toiletries as well as in non-cosmetic products such as household cleaners and detergents.

The effect of alkali metals (Li → Na → K → Rb → Cs) on the electronic structure of cinnamic acid) was studied by FTIR, FT-Raman and NMR spectroscopic techniques [22]. The investigation of the polarised IR spectra of cinnamic acid and of its deuterium derivative crystals have been reported [23]. The IR and Raman spectra of the two polymorphic forms (58°- and 68°-forms) of *cis*-cinnamic acid were measured and the spectral differences discussed on the basis of the crystal structures of the two forms [24]. Hydrogen bonded networks of methoxy-substituted α-phenylcinnamic acids studied by spectroscopic and computational methods [25]. Infrared and Raman spectroscopies have been used to monitor the [2 + 2] photodimerisation reactions of α-trans-cinnamic acid and of a number of its derivatives [26]. Trimerisation of E- and Z-α-phenylcinnamic acid was investigated by semiempirical quantum chemical methods [27]. Various F-substituted E-2,3-diphenyl propenoic acid molecules were synthesised and their aggregation behaviour was studied by experimental (FT-IR spectroscopy) and computational (semiempirical and DFT) methods [28]. The molecular packing in *p*-hydroxycinnamic acid has been determined by single-crystal X-ray analysis in order to establish the role played by hydrogen bonding in inhibiting esophase formation [29]. Owing to the complexity of the molecule, the normal coordinate analysis is carried out to obtain complete informations of the molecular motions involved in the normal modes of 8H5NQ and also to calculate the potential energy distribution of the vibrational modes of the compound utilising Wilson's FG matrix method [30–32]. The normal coordinate calculations were performed with the program of Fuhrer et al. [33].

In the molecule of *cis*-2-methoxycinnamic acid the carboxylic group is separated from the aromatic ring by a double bond. It causes conjugation between the double bond and the π-electron system. In the present investigation owing to the biological significance and non-availability of the structural, electronic and spectral details of *cis*-2-methoxycinnamic acid (*cis*-2MCA) in the literature, we have undertaken the complete structural and spectroscopic investigations of the molecule.

## Experimental

The compound *cis*-2MCA is purchased from Aldrich chemicals, U.S.A., and is used as such to record the FTIR, FT-Raman and NMR spectra. The FTIR spectrum of the compound is recorded by KBr pellet method on a Bruker IFS 66V spectrometer equipped with a Globar source, Ge/KBr beam splitter and a TGS detector in the range of 4000–400 cm$^{-1}$. The spectral resolution is 2 cm$^{-1}$. The FT-Raman spectra of the compound are also recorded in the range 4000–100 cm$^{-1}$ using the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 μm with 200 mW powers. A liquid nitrogen cooled-Ge detector was used. The frequencies of all sharp bands are accurate to 2 cm$^{-1}$. The $^{1}$H (400 MHz; $CDCl_3$) and $^{13}$C (100 MHz; $CDCl_3$) nuclear magnetic resonance (NMR) spectra are recorded on a Bruker HC400 instrument. Chemical shifts for protons are reported in parts per million scales (δ scale) downfield from tetramethylsilane.

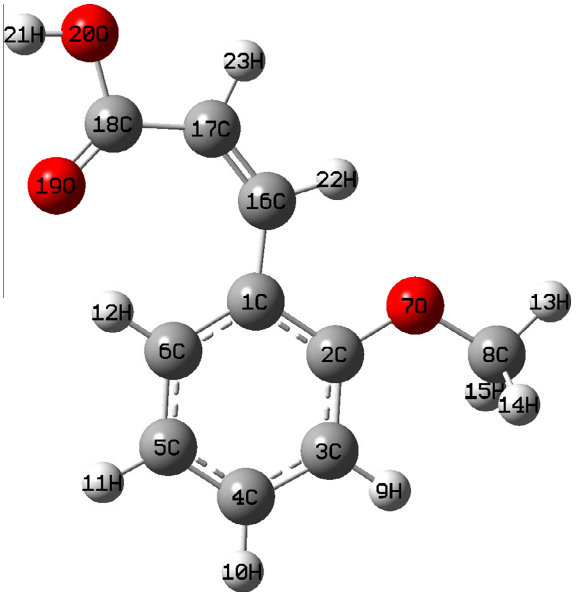

**Fig. 1.** The structure and atom numbering scheme of *cis*-2-methoxycinnamic acid.

## Computational details

The density functional theory (DFT) [34] with three parameter hybrid functional (B3) [35,36] for the exchange part and the Lee–Yang–Parr (LYP) correlation functional [37] have been utilised for the molecular geometry optimisation and then by computation of molecular structural parameters, vibrational frequencies, thermodynamic properties and energies of the optimised structure using the standard 6-311++G** and high level cc-pVTZ basis sets.

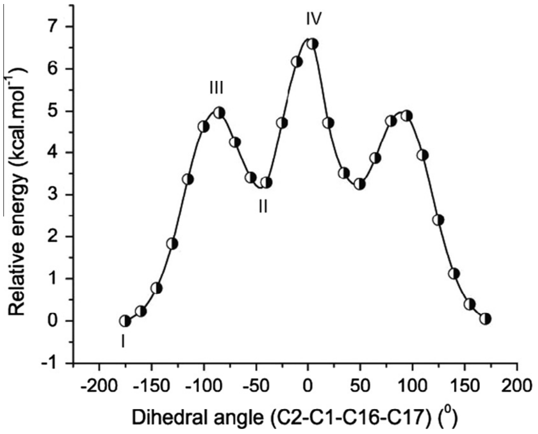

**Fig. 2.** Potential energy profile of *cis*-2-methoxycinnamic acid showing the orientation of the —CH═CH—COOH group.