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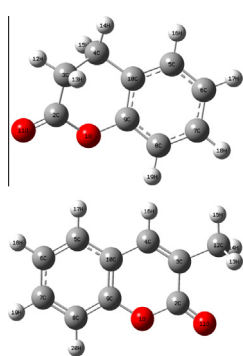
Spectroscopic and quantum chemical electronic structure investigations of 3,4-dihydrocoumarin and 3-methylcoumarin

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HIGHLIGHTS

- *Ab initio* and DFT calculation are compared.
- HOMO and LUMO analysis has been done.
- ¹H and ¹³C chemical shift calculations have been calculated.

GRAPHICAL ABSTRACT



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ABSTRACT

A complete vibrational analysis of 3,4-dihydrocoumarin and 3-methylcoumarin have been performed according to SQM force field method based on *ab initio* and DFT calculation 6-311++G(d,p) basis set and their frequencies are compared. The influences of carbon–oxygen bond and methyl group to the vibrational frequencies of the title compounds have been discussed. The pronounced decrease of the lone pair orbital occupancy and the molecular stabilization energy show the hyperconjugation interaction from the NBO analysis. Calculations of molecular orbital geometry show that the visible absorption maxima of DHC and 3MC correspond to the electron transition between frontier orbitals such as translation from HOMO to LUMO. Gauge-including atomic orbital (GIAO) ¹H and ¹³C chemical shift calculations have been calculated. Area of high, neutral and low electrostatic potential is determined for DHC and 3MC.

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Introduction

Coumarins are found in a large number of natural products. They occur widely as secondary plant metabolites and are known to exhibit numerous interesting biological properties. More than 1800 different natural coumarins have been discovered and

described to date. Most of these coumarins are mono- or deoxygenated on the aromatic ring [1]. Recently, more attention has been drawn towards the less common tri- and tetraoxygenated coumarins, which are shown to exhibit very interesting pharmacological properties such as antibacterial activity [2], antiplatelet aggregation [3] and antileukemia activity [4]. Many natural 5,6,7-trioxygenated coumarins have the capacity to induce cell differentiation in human leukemia U-937 cells, which make them potential lead compounds in the search for differentiation therapeutics [4].

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Ramoji et al. [5] have extensively studied the vibrational assignments and *ab initio* studies of 3-acetyl-6-bromocoumarin and 3-acetyl-6-methylcoumarin. Tonannavar et al. [6] have elucidated halogen effect and isotope effect of 6-chloro and 7-chloro-4-bromomethylcoumarin. DFT analysis has been made by Arivazhagan et al. [7] for 7-acetoxy-4-methylcoumarin. Literature survey reveals that to the best of our knowledge no *ab initio* HF/DFT with 6-311++G(d,p) basis set calculations of 3,4-dihydrocoumarin (DHC) and 3-methylcoumarin (3MC) have been reported so far. It is, therefore thought worthwhile to make a comprehensive vibrational analysis using both experimentally observed IR and Raman wavenumbers.

Experimental details

The pure sample of DHC and 3MC were obtained from Lancaster chemical company, UK and used as such without any further purification to record FT-IR and FT-Raman spectra. The room temperature Fourier Transform IR spectra of DHC and 3MC were measured in the 4000–400 cm^{-1} region at a resolution of $\pm \text{cm}^{-1}$ using BRUKER IFS-66V Fourier transform spectrometer equipped with an MCT detector, a KBr beam splitter and globar arc source.

The FT-Raman spectrum was recorded on a BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory. The FT-Raman spectrum was recorded in the 3500–50 cm^{-1} Stokes region using the 1064 nm line of Nd:YAG laser for the excitation operating at 200 mW power. The reported wave numbers were expected to be accurate within $\pm 1 \text{ cm}^{-1}$.

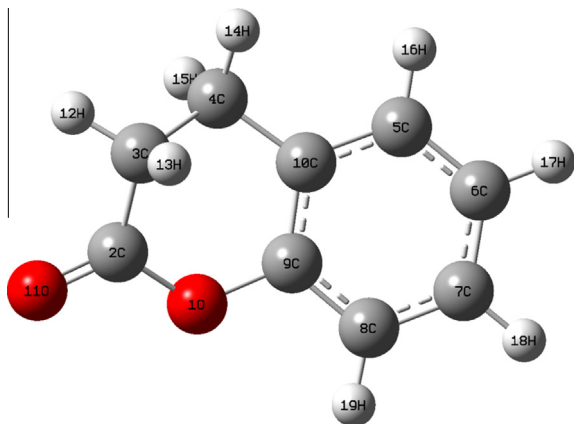


Fig. 1. Optimized molecular structure of 3,4-dihydrocoumarin.

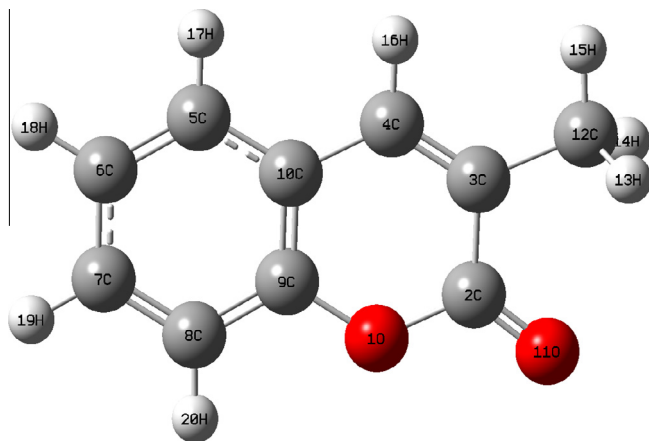


Fig. 2. Optimized molecular structure of 3-methylcoumarin.

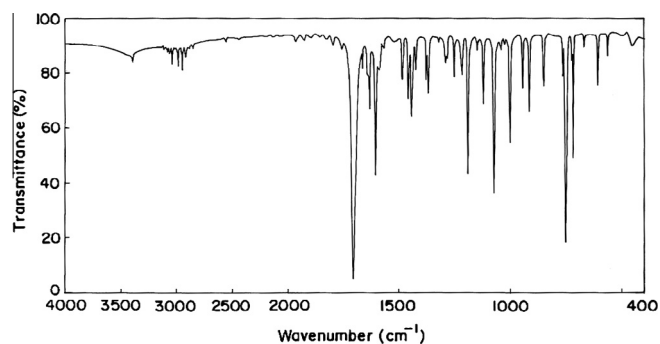


Fig. 3. FT-IR spectrum of 3,4-dihydrocoumarin.

Computational methods

The density functional (DFT/B3LYP) at the 6-311++G(d,p) basis set level is adopted to calculate the properties of the DHC and 3MC in this work. All the calculations are performed using GAUSSIAN 09W program package [8] with the default convergence criteria without any constraint on the geometry [9]. Multiple scaling of the force field has been performed by scaled quantum mechanical (SQM) procedure [10,11] the systematic error caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity [12]. Normal co-ordinate analysis has been performed to obtain full description of the molecular motion pertaining to the normal modes with MOLVIB program version 7.0 written by Sundius. The natural bonding orbitals (NBOs) calculations are performed using NBO 5.0 program as implemented in the Gaussian 09W [8] package at the DFT/B3LYP/6-311++G(d,p) level in order to understand various second order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the intermolecular delocalization or

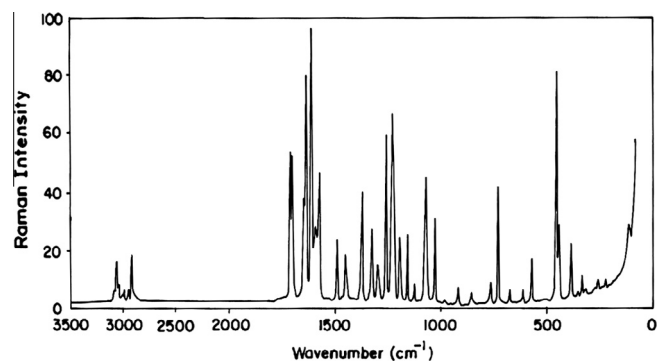


Fig. 4. FT-Raman spectrum of 3,4-dihydrocoumarin.

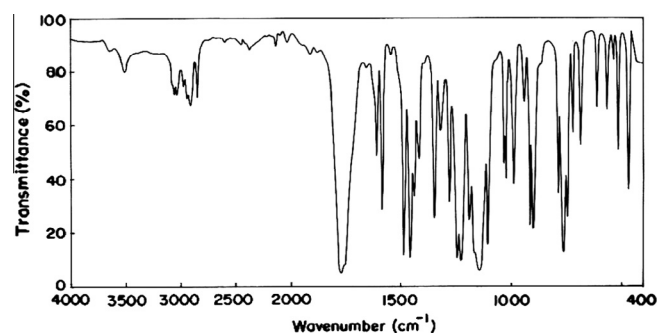


Fig. 5. FT-IR spectrum of 3-methylcoumarin.

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