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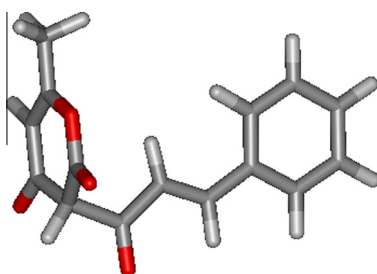
Vibrational spectroscopic study of dehydroacetic acid and its cinnamoyl pyrone derivatives

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HIGHLIGHTS

- DFT calculation for the optimized molecular structures of the discussed γ -pyrones.
- Evaluation of NBO atomic net charges.
- Measurement and simulation of their vibrational spectra.
- Assignment and evaluation of these spectra.

GRAPHICAL ABSTRACT



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ABSTRACT

The infrared and Raman spectra of dehydroacetic acid and some of its derivatives were measured. The assignments of the vibrational bands were based on quantum chemical calculations and normal coordinate analysis. The optimized structures, atomic net charges and dipole moments of the investigated molecules were also results of our quantum chemical calculations. The analysis of the last properties made possible a deeper insight into the structure and substituent effect on the investigated molecules. One of them is presented in the graphical abstract.

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Introduction

In this article we deal with some derivatives of dehydroacetic acid. The optimized structures of these molecules are shown in Fig. 1.

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Dehydroacetic acid (3-acetyl-6-methyl-3,4-dihydro-2H-pyran-2,4-dione) (marked as L1 in this article) is a very popular substance in organic chemistry. It exists in five tautomeric forms [1]. L1 was discovered by Geuther in 1866 [2]. Rassweiler and Adams described controversy relating its structure in. "The structure of dehydro-acetic acid", which was not firmly ascertained until 1924 [3].

A great amount of articles about synthesis of this substance is listed in literature [4]. Some patents of L1 preparation owned by companies are mentioned in literature [5–6]. This compound has a wide application as starting material in synthesis of various compounds [7–8]. L1 and its salts are used as stabilizers in cosmetic

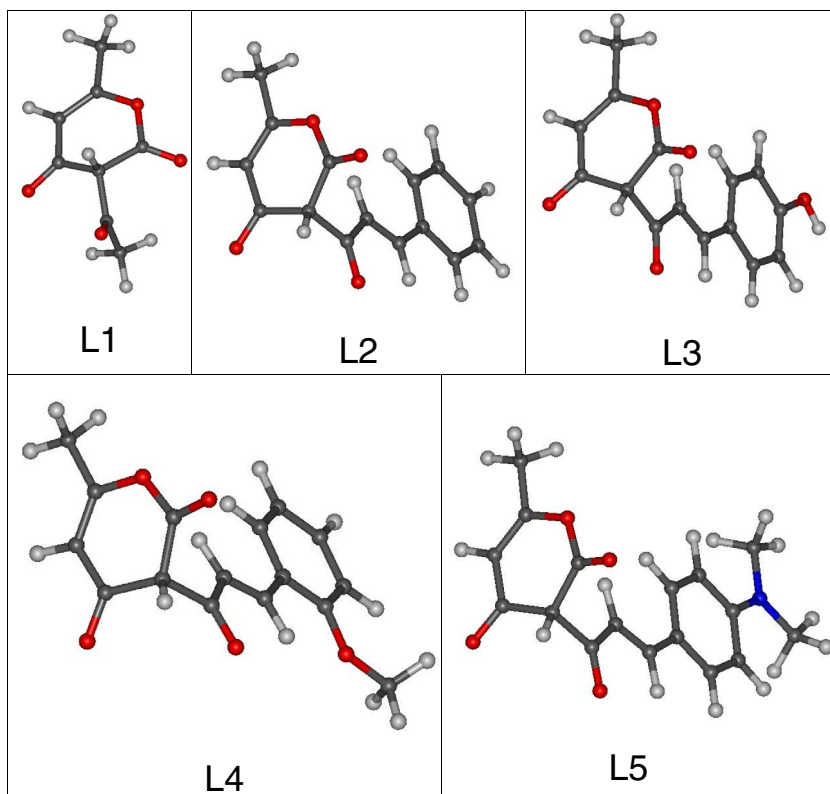


Fig. 1. Optimized molecular structures.

and pharmaceutical products [9–11] and as preservatives and additives in food [12–15] due to its fungicide and bactericide activity.

In this work L1 and its derivatives L2–L5 (Fig. 1) known as cinnamoyl pyrones [16–18] were studied. The compounds L3, L4 and L5 are substituted derivatives of L2. Willey et al. first synthesised compound L2 from L1 in 1955 [19]. Many compounds were synthesized from L2 e.g. thiazepines and diazepines as new ligands with affinity to GABA_A receptor [20–21]. Mohanty et al. synthesised L3 in 1977 [22]. Syntheses, spectral and thermal studies, antibacterial and antifungal activity of transition metal complexes with L3 were published by Patange and coworkers [23]. From this study results the ligand is bidentate and coordinates by the phenolic oxygen and the acetyl carbonyl group of dehydroacetic acid fragment. Ligand L3 showed weak antibacterial activity and moderate antifungal activity in comparison with metal complexes of L3. Metal complexes showed moderate antibacterial activity against the bacteria *Staphylococcus aureus* and *Escherichia coli* and significant antifungal activity against the fungi *Aspergillus flavus*, *Curvularia lunata* and *Penicillium notatum*. L3 was used in Patent “Method of screening compounds” by Zon et al. in 2005 oriented to a target-blind approach to drug discovery [24]. L4 was first synthesised as intermediate product for synthesis of 4-hydroxy-6-methyl-3- β -arylpropionyl-2-pyrones by Rachedi et al. in 1989 [25]. L5 was first synthesised from L1 by Rupe et al. in 1932 [26]. L5 was used in synthesis of substituted 1,4-thiazepine and its analogs, applied to induce potential cell death in a variety of clinical conditions of uncontrolled or abnormal growth of cells [27]. Ramkumar et al. used L1 and L5 to prepare the compounds that show a potential HIV-1 integrate inhibitory effect [28]. L1–L5 were also used for synthesis of 1,5-benzothiazepine derivatives [29–32]. Xi et al. synthesised and bioevaluated a series of α -pyrone derivatives also with aromatic derivatives as potential activators of Nrf2/

ARE pathway in 2013 [33]; these compounds are similar to our ligands L2–L5.

Recently, Tykhanov et al. also studied some spectral and structural properties of L2–L5 substances [16–18]; according to their results L2–L5 compounds exist in five tautomeric forms, like L1. The ¹H NMR and quantum chemical analysis of the stability of tautomers of some cinnamoyl derivatives and vinyls were studied [16]. The predominant tautomeric forms of these ligands are shown in Fig. 1. Mulliken charges on oxygen atoms of hydroxy group and carbonyl fragments, dissociation constants, molar fractions protolytic forms in ground and excited states and photophysical characteristics of fluorescent cinnamoyl pyrones in solution and polymer matrices were also studied by Tykhanov scientific group [17]. To the best of our knowledge, there have been no other publications dealing with the structure and spectra of the compounds studied in this work.

The aim of this work is the deeper analysis of the properties of compounds L1–L5 as promising ligands of metal complexes, for quantitative analytical determination of metal ions. Therefore we studied in addition to spectroscopic properties also the substituent effects, the atomic net charges and the dipole moments.

Our recent article [34] deals with an analytical application of one of the investigated compounds.

Experimental

Infrared spectra were recorded on a Nicole 6700 spectrometer in the 3400–400 cm⁻¹ region. The resolution was 4 cm⁻¹. 128 repetitions were added for increasing the signal-to-noise ratio.

Raman spectra were measured with a Horiba Jobin–Yvon Labram spectrometer, in the 2000–100 cm⁻¹ region. The spectra were excited with a diode laser at 785 nm wavelength. The

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