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# Esters of 1-coumarinylbenzylphosphonic acid—IR-spectroscopic and theoretical elucidation

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ABSTRACT

The IR-spectroscopic properties of three esters of 1-coumarinylbenzylphosphonic acid are elucidated both in solution and in solid-state. Linear-polarized IR-spectroscopy of oriented colloid suspensions in nematic host is used for experimental IR-characteristic band assignment in solid-state. Theoretical quantum chemical DFT calculations at B3LYP level of theory and 6-31++G** basis set are carried. Theoretical electronic structure and vibrational properties of compounds studied are discussed.



## 1. Introduction

Interest on coumarin derivatives is based on their wide biological activity. Spasmolytic effect, antiarrhythmic, cardiothonic, antiviral, and anticancer properties have been obtained [1–3]. Phosphorus-containing coumarins are a novel group of compounds with remarkable cytotoxicity of the selected tumor cell lines [1–3]. Derivatives containing a phosphorus atom at position 2 of a $\gamma$-pyrone ring are known as efficient antibacterial agents [4–7]. These data are in the basis of the series of systematic investigations about the synthetic routes for the preparation of different classes phosphorus-containing coumarins [8–12].

IR-spectroscopy and NMR are powerful methods for structural organic chemistry and numerous paper deal with $^{1}$H-, $^{13}$C- and $^{31}$P-NMR investigations. However, IR-spectroscopic investigations on phosphorus-containing coumarins are rare [13–15]. In this paper we are represented linear-polarized IR-spectroscopic and theoretical study of the esters of 1-coumarinylbenzylphosphonic acid, depicted in Scheme 1.

## 2. Experimental

### 2.1. Materials and methods

*Conventional and polarized IR-spectra* were measured on a Bomem Michelson 100 FTIR-spectrometer (4000–400 cm$^{-1}$, 2 cm$^{-1}$ resolution, 200 scans) equipped with a PerkinElmer wire-grid polarizer. Non-polarized solid-state IR spectra were recorded using the nujol mull technique. The oriented samples were obtained as a colloid suspension in a nematic liquid crystal ZLI 1695. The theoretical approach, experimental technique for preparing the samples, procedures for polarized IR-spectra interpretation and the validation of this new linear-dichroic infrared orientation solid-state method for accuracy and precision has been presented. The influence of the liquid crystal medium on peak positions and integral absorbances of the guest molecule bands, the reological model, the nature and balance of the forces in the nematic liquid crystal suspension system, and morphology of the suspended particles also been discussed [16–19]. IR-spectra in chlorophorm solution are recorded using 0.044 cm KBr cell.

*Quantum chemical calculations* are performed with the GAUSSIAN 98 and Dalton 2.0 program packages [20,21]. The output files are visualized by means of the ChemCraft program [22]. The geometries of (**1**)–(**3**) were optimized at density functional theory (DFT) using the 6-311++G** basis set. The DFT method employed is B3LYP, which combines Backe's three-parameter non-local exchange function with the correlation function of Lee, Yang and Parr. Molecular

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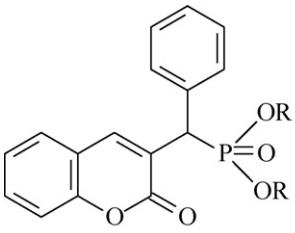



R = $CH_3$ (1)
R = $CH_2CH_3$ (2)
R = Ph (3)

**Scheme 1.** Chemical diagram of the esters of 1-coumarinylbenzylphosphonic acid.

geometries of the studied species were fully optimized by the force gradient method using Bernys' algorithm. For every structure, the stationary points found on the molecule potential energy hypersurfaces were characterized using standard analytical harmonic vibrational analysis. The absence of the imaginary frequencies, as well as of negative eigenvalues of the second-derivative matrix, confirmed that the stationary points correspond to minima of the potential energy hypersurfaces. The calculated vibrational frequencies and infrared intensities were checked to establish which kind of performed calculations agreed best with the experimental data. The DFT method provides accurate vibrational data, as far as the calculated standard deviations of less than 8 $cm^{-1}$ are concerned [23,24], which correspond to groups, not participating in significant intra- or intermolecular interactions. A modification of the results using the empirical scaling factor 0.9614 is done to achieve better correspondence between the experimental and theoretical values.

Compounds (**1**)–(**3**) are *synthesized* according [9]. A solution of the 3-(1-bromobenzyl)-2-oxo-2H-chromene (2 mmol) and the corresponding trialkyl phosphate (12 mmol) in dry toluene (3 ml) was refluxed for 5 h. The solvent and the excess of the phosphate were removed under reduced pressure. The residue was chromatographed on silica gel column (eluted with *n*-hexane/EtOAc mixtures of increasing polarity). The products are recrystallized from ether and melting points were in agreement with the proposed values (116–118 °C for methyl ester, 104–105 °C for ethyl ester and 112–113 °C for phenyl ester of 1-coumarinylbenzylphosphonic acid).

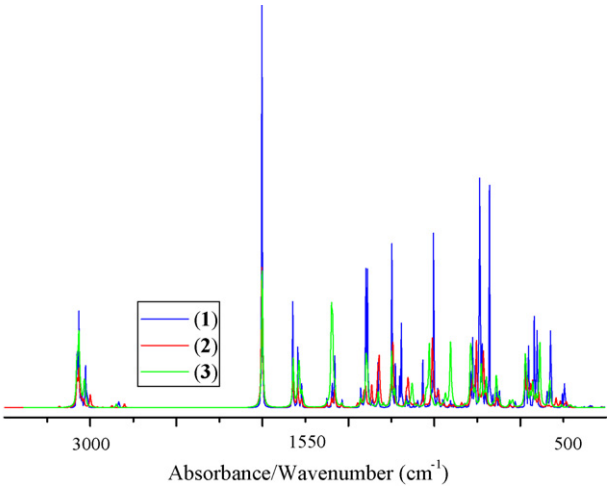
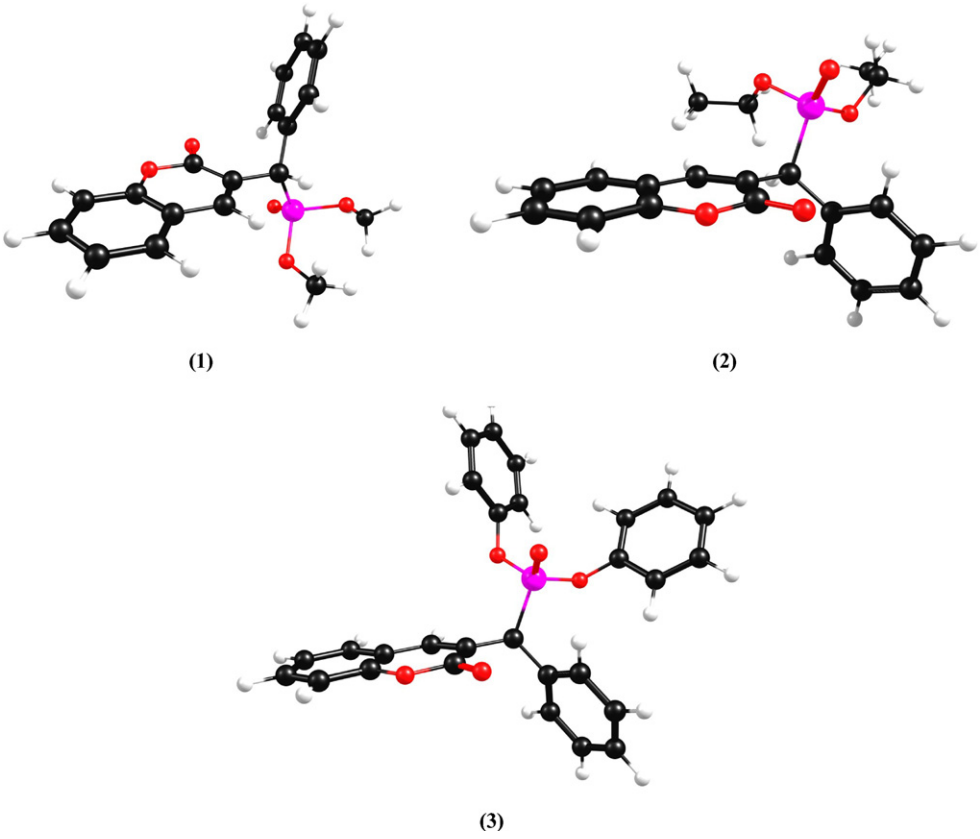



**Fig. 1.** Calculated IR-spectra of compounds (**1**)–(**3**).




**Scheme 2.** Most stable conformers of (**1**)–(**3**).