



Electronic states of emodin and its conjugate base. Synchrotron linear dichroism spectroscopy and quantum chemical calculations

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ABSTRACT

The electronic transitions of emodin (1,3,8-trihydroxy-6-methyl-9,10-anthraquinone, **E**) and its conjugate base (3-oxido-6-methyl-1,8-dihydroxy-9,10-anthraquinone, **Ecb**) were investigated by UV-Vis linear dichroism (LD) spectroscopy on molecular samples aligned in stretched poly(vinylalcohol). The experiments in the UV region were performed with synchrotron radiation, thereby obtaining significantly improved signal to noise ratio compared with traditional technology. The LD spectra provided information on the polarization directions of the observed transitions, thereby leading to resolution of otherwise overlapping, differently polarized transitions. The investigation was supported by PCM-TD-DFT calculations; a mixed discrete/continuum solvation model was applied in the case of the strongly solvated **Ecb** anion. The calculations led to excellent agreement with the observed transitions, resulting in the assignment of at least seven excited electronic states in the region 15,000–50,000 cm⁻¹ for each species. A recent assignment of the absorption spectrum of **E** to a superposition of contributions from 9,10- and 1,10-anthraquinoid tautomeric forms was not supported by the results of the present investigation.

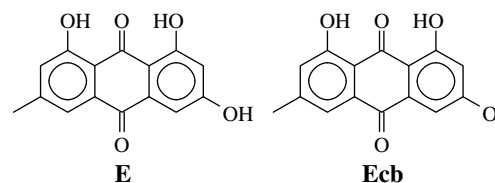
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1. Introduction

Emodin (1,3,8-trihydroxy-6-methyl-9,10-anthraquinone, **E**) is one of the most abundant anthraquinones found in nature [1]. From ancient times, **E** has been an active component in herbal extracts used in China for treatment of a wide variety of diseases [2], and the biological activity of the compound is a subject of current investigations [3]. UV-Vis spectroscopy is generally applied as an analytical tool in the investigation of the biochemical reactivity of **E** [4], but to our knowledge, no detailed experimental and theoretical investigations of the electronic transitions of the compound have been published. The aim of this investigation is to provide an understanding of the electronic transitions of **E** and its conjugate base **Ecb**.

E is an orange–yellow amorphous solid that is insoluble in water, but soluble in several organic solvents. It is readily soluble in alkaline aqueous solvents; the pK_{a1} value was estimated to be 7.2 in a water–methanol mixture [5] and 5.7 in acetonitrile [6]. **E** changes color in the presence of bases or various metal ions [5] and it is thus a useful spectrophotometric reagent. Pal and Jana [5] investigated the UV-Vis absorbance spectrum in water–meth-

anol mixtures as a function of pH and established a one-proton equilibrium in the range pH 2–10. They assigned the acidic proton to the hydroxyl group in the 3-position, corresponding to the conjugate base 3-oxido-6-methyl-1,8-dihydroxy-9,10-anthraquinone, **Ecb**. The interpretation of the prototropic equilibria of **E** by Pal and Jana has recently been challenged by Fain et al. [7]. Moreover, these authors assigned the absorption spectrum of **E** to a superposition of contributions from 9,10- and 1,10-anthraquinoid tautomers.



We have previously investigated the electronic structure and spectra of several hydroxyanthraquinones and related species [8–12], including the closely related compound chrysazin (1,8-dihydroxy-9,10-anthraquinone) [9] and its reduction product anthralin (1,8-dihydroxy-9(10H)-anthracenone) [11,12]. A preliminary account of a UV-Vis linear dichroism (LD) [13,14] investigation of **E** by using stretched polyethylene as an anisotropic solvent has been published on the Internet [15]. In the present communication, we

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report the results of an UV–Vis LD investigation of **E** and **Ecb** partially aligned in stretched poly(vinylalcohol) (PVA). LD spectroscopy yields information on molecular transition moment directions, thereby frequently leading to resolution of otherwise overlapping, differently polarized transitions, and to symmetry assignments of the observed molecular states [13,14]. Moreover, this information is of importance in the study of the biological reactivity [13,14].

The experiments in the UV spectral region were performed with linearly polarized synchrotron radiation (Institute for Storage Ring Facilities, University of Aarhus [16]), thereby obtaining substantially improved signal to noise ratio compared with traditional technology [16]. This is a great advantage when using a solvent medium like PVA which absorbs and scatters strongly in the UV region, leading to severe baseline problems particularly above $45,000\text{ cm}^{-1}$. Compared with a traditional source of linearly polarized UV radiation, such as a deuterium lamp equipped with a Glan prism polarizer, synchrotron radiation allows measurements at significantly increased wavenumbers and leads to generally improved precision of the orientation factors derived for the observed transitions (see below).

The measured absorption bands for **E** and **Ecb** are assigned to electronic transitions predicted with time-dependent density functional theory (TD-DFT) calculations. The influence of a polar and protic solvent like PVA was estimated by the polarized continuum model (PCM), and in the case of the **Ecb** anion, by a combined discrete/continuum model. The experimental and theoretical results lead to a detailed description of electronic transitions in **E** and **Ecb**.

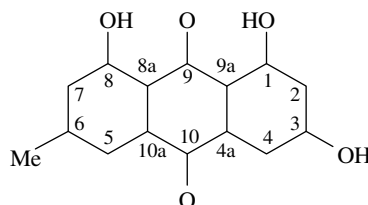
2. Calculations

All calculations were performed with the Gaussian03 software package [17]. The gas phase minimum energy equilibrium geometry of **E** was calculated with B3LYP [18] DFT and the 6-31G(d,p) basis set [17]. Two minima with an energy difference of 0.9 kJ mol^{-1} were localized, corresponding to different in-plane conformations of the OH group in position 3. The most stable molecular conformation is shown in Fig. 1 and the computed bond lengths are listed in Table 1. Transitions to the 35 lowest excited singlet electronic

states of **E** were computed by using the TD-B3LYP procedure [19] with the 6-31+G(d,p) basis set [17]. The influence of an alcoholic solvent on the electronic transitions was approximated by the polarized continuum model, PCM [20] (Gaussian03: `scrf(pcm,solvent = ethanol)`) [17]. This level of approximation is similar to that recommended by Perpète and coworkers for anthraquinone dyes (level “M–C”) [21], except for the inclusion of diffuse basis functions in the present TD calculation. Essentially similar electronic transitions and moment directions were predicted for the two conformations mentioned above. The computed electronic transitions for the most stable conformation (Fig. 1) are given in Table 2.

Corresponding calculations on the **Ecb** anion tend to underestimate the observed wavenumber of its visible absorption band by $2000\text{--}3000\text{ cm}^{-1}$. Evidently, specific solvation of the exposed, negatively charged oxygen center in position 3 by an alcoholic solvent is likely to be significant. This effect was approximated by considering a hydrogen bonded complex with a single ethanol molecule. The distance between the oxygen nucleus in position 3 and the hydroxyl proton of the ethanol molecule was fixed at 1.50 Å ; the remaining geometrical parameters were optimized with B3LYP/6-31G(d,p). The geometries of four complexes with different in-plane orientations of the ethanol species were optimized, followed by single-point B3LYP/6-31+G(d,p) energy calculations with

Table 1
B3LYP/6-31G(d,p) equilibrium bond lengths in Å for emodin (**E**) and its conjugate base (**Ecb**), see text



	E	Ecb
C1–C2	1.400	1.383
C1–C9a	1.425	1.441
C2–C3	1.392	1.432
C3–C4	1.407	1.454
C4–C4a	1.385	1.372
C4a–C9a	1.416	1.438
C4a–C10	1.495	1.490
C5–C6	1.410	1.403
C5–C10a	1.386	1.392
C6–C7	1.389	1.393
C6–C(Me)	1.508	1.511
C7–C8	1.408	1.405
C8–C8a	1.417	1.417
C8a–C9	1.460	1.476
C8a–C10a	1.418	1.412
C9–C9a	1.454	1.417
C10–C10a	1.491	1.498
C1–O1	1.337	1.349
C3–O3	1.356	1.269
C8–O8	1.338	1.344
C9–O9	1.268	1.289
C10–O10	1.226	1.230
C2–H	1.083	1.085
C4–H	1.086	1.084
C5–H	1.085	1.085
C7–H	1.085	1.086
C–H(Me) ip	1.092	1.094
C–H(Me) oop	1.096	1.096
O1–H	0.991	0.992
O3–H	0.967	–
O8–H	0.990	1.005
O1...O9	2.571	2.571
O8...O9	2.571	2.523

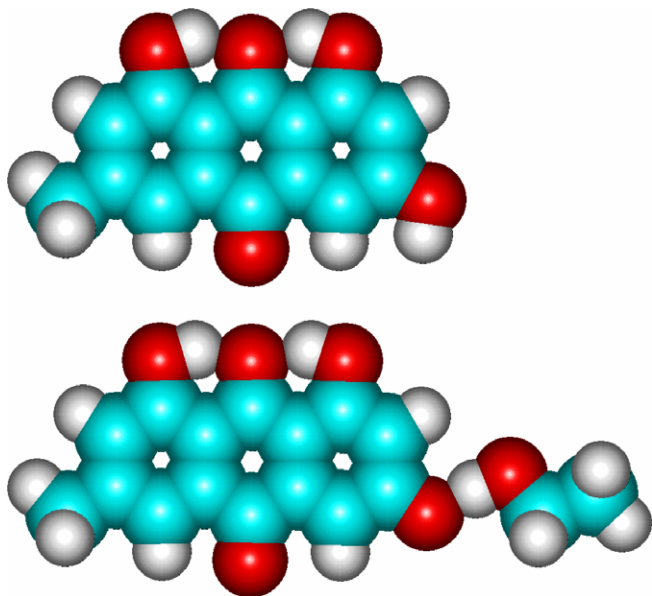


Fig. 1. Predicted molecular conformations. Top: Emodin (**E**). Bottom: Hydrogen-bonded molecular complex between deprotonated emodin (**Ecb**) and ethanol (see text).

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