Electronic Absorption Spectra of Substituted Anthraquinones and Their Simulation Using ZINDO/S Method

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Abstract

Electronic absorption spectra of chrysophanol (1,8-dihydroxy-3-methylanthracene-9,10-dione), physcion (1,8-dihydroxy-3-methoxy-6-methylanthracene-9,10-dione) and emodin (1,3,8-trihydroxy-6-methylanthracene-9,10-dione) were investigated. Molecular geometries of the substituted anthraquinones in the ground state were optimized using semiempirical AM1 method without imposing any symmetry constrains. The ground state geometries of all the molecular systems were found to be planar. For interpretation of the spectra, ZINDO/S-CI investigation employing singly excited configuration using the completely optimized geometries was carried out. Such calculations on the electronic spectra of chrysophanol, physcion, and emodin were carried out for the first time. On the basis of these investigations, the assignments of the spectra were successfully predicted.

Key words: anthraquinones, ZINDO/S, electron absorption spectra

1. Introduction

The anthraquinones and their hydroxy and amino derivatives posses a wide ranging potential for application in pharmaceutical, food and dye industries Fain (1970), Tomson (1971), Patai (1974). Due to the wide usefulness of derivatives of anthraqinones, several investigations have been carried out in order to understand the characteristics of electronic states of these molecules. However, theoretical considerations of the electronic properties of these systems are lacking as very few theoretical studies have been carried out on their electronic spectroscopy. Therefore, as part of our investigations on the spectroscopy of substituted anthraquinones, we carried out the detailed theoretical and experimental studies on the electronic absorption spectra of 1,8-dihydroxy-3-metoxy-6-methyl-9,10-anthraquinone (physcion), 1,3,8-tri-hydroxy-6-methyl-9,10-anthraquinone (emodin), and 1,8-dihydroxy-3-methyl-9,10-anthraquinone (chrysophanol) (Fig. 1).
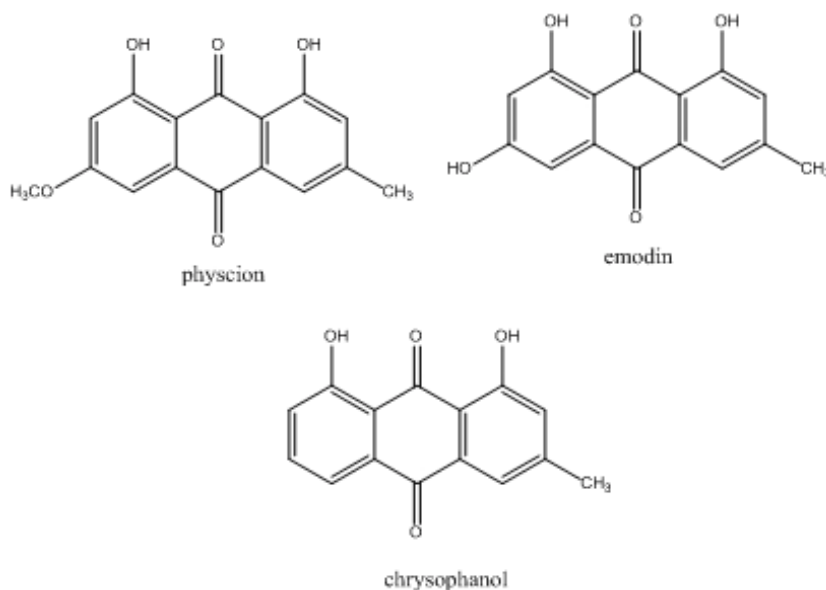
Fig. 1. Molecular structure of anthraquinones under investigation.

The experimental data on the geometries of the anthraquinones under investigation are not available. It is well known that the ZINDO/1 and AM1 methods reproduce successfully structural/geometrical parameters of the parent molecules 1,4-dihydroxy-9,10-anthraquinone, 1,5-dihydroxy-9,10-anthraquinone, and 1,8-dihydroxy-9,10-anthraquinone (Khan et al. 2003). Bearing this in mind, we performed the calculations of the electronic transition energy intensities of these substituted anthraquinones using the Zerner's Intermediates Neglect of Differential Overlap/Spectroscopy (ZINDO/S) Lipkowitz (1990) semiempirical method. This method has been successfully tested for the calculations of the ground and excited state properties for a wide rang of organic compounds (Kubo at al. 1991).

2. Material and methods

Physcion, emodin, and chrysophanol are not commercially available in pure form, and were isolated from the lichens *Xanthoria* and *Caloplaca* (Manojlovic et al. 1998), (Manojlovic et al. 2002), (Manojlovic et al. 2005). These anthraquinones were separated and purified by column chromatography using benzene and benzene-acetone mixtures (20:1, 10:1, 5:1 and 1:1), as eluents. These compounds were identified by elemental analysis and spectroscopic studies (UV, IR and 1H NMR) and compared with literature data. The electronic absorption spectra were measured in the UV-visible region using a computer-controlled JASCO UV/VIS/NIR spectrophotometer. All the measurements were carried out at room temperature.

Molecular orbital calculations for emodin, physcion and chrysophanol were performed using the CaChe 6.01 software. The equilibrium geometries were located using the search procedure contained within this program. The ground state geometries of the molecular systems under consideration were optimized employing the AM1 method (Dewar at al. 1985), (Dewar at al. 1986), Stewart (1990). The computation of the optimized geometries of the individual molecular systems was performed with the standard parameters as implemented in the software. Our investigation showed that the planar structures had the deepest local minima in all

molecules considered (Figure 1). It is in agreement with the results obtained for amino substituted anthraquinones (Khan et al. 2003).

Electronic transition energies and oscillator strengths of the molecules were calculated employing the all-valence electron ZINDO/S method (Head et al. 1985), (Head et al. 1986). The SCF-CI calculations were carried out using the Hartree-Fock (HF) method, employing singly-excited configurations only. Such a treatment generally provides a satisfactory description of the lower excited states, as the contributions of the higher order excitations are usually insignificant. The ZINDO/S calculations were made employing the standard parameters as in the original paper (Anderson et al. 1991).

3. Results and discussion. Electronic absorption spectra and their assignments

This section deals with our experimental and theoretical studies of the electronic absorption spectra of the substituted anthraquinonens physcion, emodin, and chrysophanol. The interpretation of the spectra was based on the ZINDO/S calculations performed on the AM1 geometries.

Physcion. We studied the electronic spectrum of this molecule in methanol (Fig. 2). In the ultraviolet region, we observed four strong absorptions at 225, 253, 265 and 286 nm. The UV band at 225 nm was accompanied with two shoulders at 219 and 217 nm. In the visible region, a broad absorption band was observed at 433 nm. The results of the computational investigation showed very good matching with these bands: 225, 246, 280, 302 and 430 nm. With the methyl and methoxy groups in the positions 3 and 6, the physcion molecule belongs to the C_1 point group. The first observed band at 430.0 nm arises from the HOMO$\rightarrow$ LUMO transition and is assigned as $\pi\rightarrow\pi^*$ transitions in this molecule. The calculation predicts a $\pi\rightarrow\sigma^*$ transition at 280 nm with moderate oscillator strength, but it underestimates the oscillator strength of the $\pi\rightarrow\pi^*$ transition at 302 nm. The band at 246 nm implies that the $\pi\rightarrow\pi^*$ transitions in this molecule are allowed by the spatial symmetry.
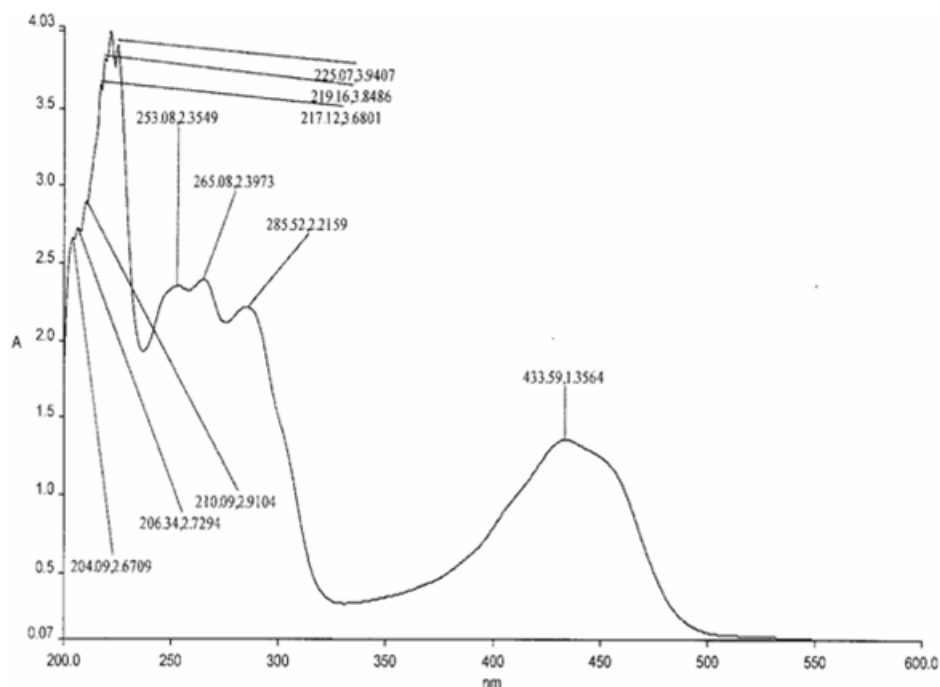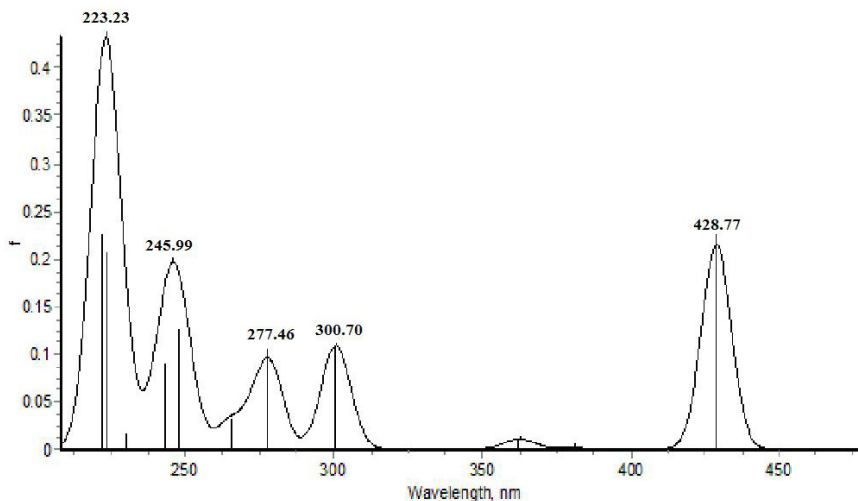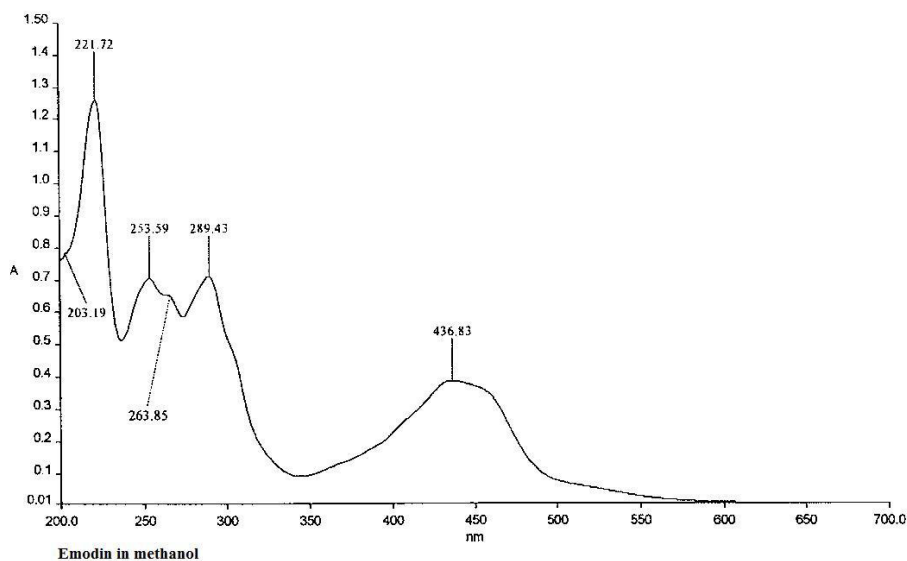
Physcion in methanol
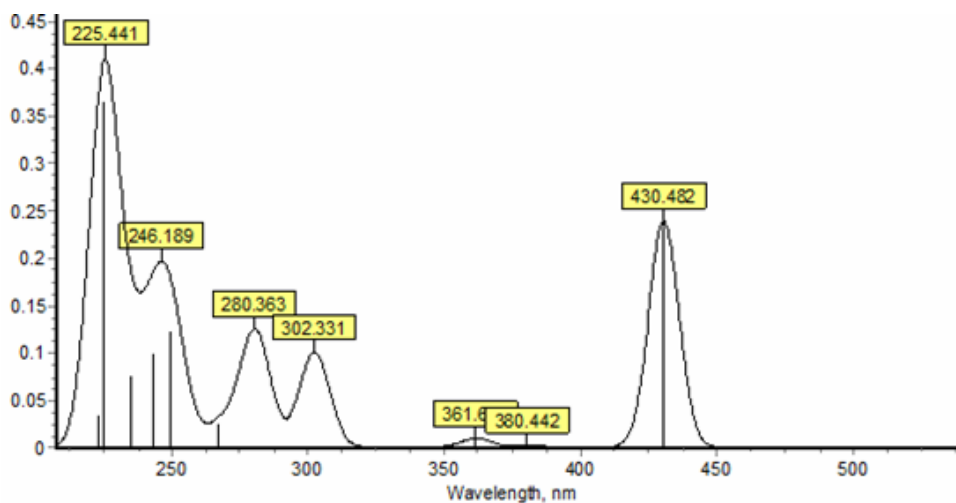
Fig. 2. Electronic absorption spectrum of physcion measured in methanol and calculated by means of the ZINDO/S method.
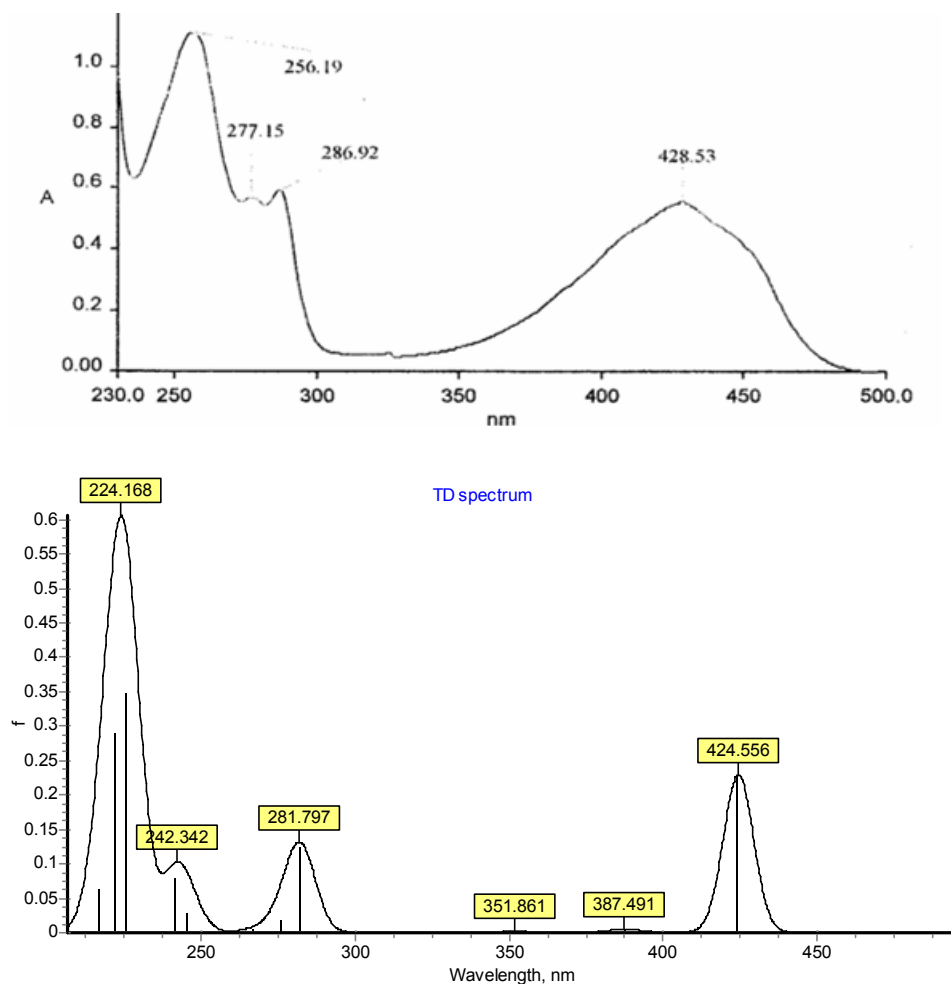
Emodin. The electronic absorption spectrum of emodin was measured in methanol at 298 K in the wavelength region of 250-500 nm (Fig. 3). The five prominent bands are identified with the maxima at 436, 289, 264, 254, and 222 nm. The broad band at ~430 nm was found to have a dominant charge transfer character. To get a more comprehensive picture about this molecule we studied its electronic spectrum theoretically. The geometry optimization predicted

that the most stable ground state structure of the molecule allowed the formation of the intramolecular hydrogen bond. Emodin belongs to the C_1 point group, which means that all the $\pi \rightarrow \pi^*$ transitions in this molecule are allowed by the spatial symmetry. For calculating the electronic transition energies and their oscillatory strengths, the ZINDO/S calculation was carried out. The calculation predicted four bands with the maxima at 429, 301, 277, 245, and 223 nm. The ZINDO/S results are in good agreement with experimental results.

Fig. 3. Electronic absorption spectrum of emodin measured in methanol and calculated by means of the ZINDO/S method.

Chrysophanol. The UV-visible spectrum of chrysophanol measured in methanol at 298 K is depicted in Fig. 4. This experiment revealed three bands located at 287, 277 and 256 nm in the UV region. The broad band at 428 nm was found to have a dominant charge transfer character. The ZINDO/S calculations predict a large number of symmetry-allowed transitions in the UV-visible spectral region. In the ultraviolet region, we observed two strong absorptions at 256 and 277 nm. The results of the ZINDO/S calculations underestimate the experimentally obtained wave lengths. The absorption at 287 nm matches well with the calculated results for transition at 282 nm. In the visible region, a broad absorption band of medium intensity is observed at 428 nm. This is identified as the CT band, which is characteristic for anthraquinone derivatives. The ZINDO/S method estimates its position at 424 nm. The present assignments of the $\pi \rightarrow \pi^*$ transitions of chrysophanol molecule are in perfect agreement with those of the previous two anthraquinone derivatives.

Fig. 4. Electronic absorption spectrum of chrysophanol measured in methanol and calculated by means of the ZINDO/S method.

4. Conclusions

The electronic absorption spectra of physcion, emodin, and chrysophanol were measured. The geometries of the molecular systems were optimized using the AM1 method. Calculations of their electronic transition energies and oscillator strengths are carried out for the first time using the ZINDO/S method. The overall agreement between the calculated and the experimental results is quite satisfactory. These results clearly show that this method can be very successful in investigations of biological activities of these compounds.

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