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Induced Circular Dichroism Spectra of 2-(2,4,6-Cycloheptatrien-1-ylidene)-4-cyclopentene-1,3-dione Included in β-Cyclodextrin

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Abstract. The assignment of the absorption spectra of 2-(2,4,6-cycloheptatrien-1-ylidene)-4-cyclopentene-1,3-dione (**1**) is reported by measuring the induced circular dichroism spectra of the β-cyclodextrin complex with **1**. It is concluded from the signs of the induced circular dichroism bands that the first absorption band (17.1×10^3–34.3×10^3 cm^{-1}) is composed of three electronic transitions having perpendicular, parallel and perpendicular polarizations with respect to the long axis (z) of **1**. The second absorption band (34.3×10^3–42.8×10^3 cm^{-1}) is composed of two electronic transitions having parallel polarizations with respect to the long axis of **1** and the third absorption band (42.8×10^3–47.1×10^3 cm^{-1}) has the transition dipole moment perpendicular to the long axis of **1**. Our experimental assignments are supported by CNDO/S CI calculations.

Key words: β-Cyclodextrin, inclusion complexes, induced circular dichroism spectra.

1. Introduction

A great number of quinones occur in nature which are of importance in biological systems [1]. Much experimental and theoretical work concerning the electronic spectra of quinones with $4n\pi$-electrons has been published [2–6]. The electronic spectra of quinones with $(4n + 2)\pi$-electrons have not been investigated.

Harata and Uedaira [7] have measured the induced circular dichroism (ICD) spectra of the β-cyclodextrin (β-CD) complexes with naphthalene derivatives and indicated theoretically that from the signs of the ICD spectra it is possible to determine the polarization directions of the absorption bands of the guest molecule in the cavity of β-CD.

The purpose of this paper is to assign the electronic spectra of quinone with $(4n + 2)\pi$-electrons such as 2-(2,4,6-cycloheptatrien-1-ylidene)-4-cyclopentene-1,3-dione (**1**) by measuring the ICD spectra and by comparing the experimental results with those obtained theoretically by the CNDO/S CI method [8, 9]. The structure of **1** is shown in Figure 1.

2. Experimental

2-(2,4,6-Cycloheptatrien-1-ylidene)-4-cyclopentene-1,3-dione (**1**) was synthesized by one of the present authors (M.O.) [10]. It was recrystallized three times from cyclohexane.

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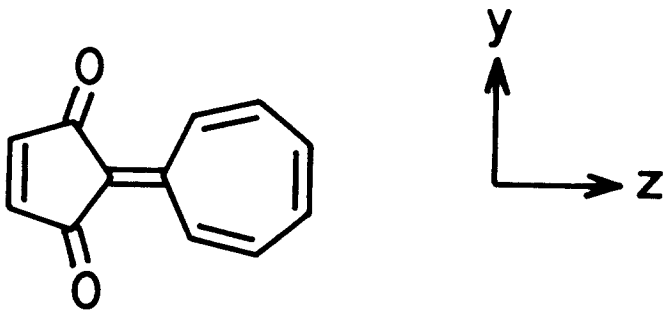

Fig. 1. Structure of 2-(2,4,6-cycloheptatrien-1-ylidene)-4-cyclopentene-1,3-dione (**1**).

β-Cyclodextrin (β-CD) was a commercial product and was recrystallized three times from water. The absorption spectra were recorded on a Hitachi U-3200 recording spectrophotometer. The ICD spectra were measured using a Jasco J-40 circular dichrograph of the Instrument Center, Institute for Molecular Science, Okazaki. The concentration of β-CD was adjusted to 0.01M throughout the measurements. All measurements were made at room temperature.

3. M.O. Calculations

As the experimental geometries of **1** are unknown, the geometries of **1** were optimized using the MNDO method [11]. The transition energies and oscillator strengths were computed using the CNDO/SCI method [8, 9]. Sixty singly-excited configurations with an energy below $80.7 \times 10^3\ cm^{-1}$ and 50 doubly-excited configurations having an energy below $78.6 \times 10^3\ cm^{-1}$ were considered in the configuration interaction treatment.

4. Results and Discussion

The absorption spectra are shown in Figure 2, where the ICD spectra of the β-CD complex with **1** are also shown. The transition energies (ΔE) and oscillator strengths (f) calculated by the CNDO/S CI method are listed in Table I along with the experimental results. The observed ICD spectrum shows negative, positive, negative, positive and negative peaks at 19.9×10^3, 23.9×10^3, 31.3×10^3, 38.0×10^3 and $45.6 \times 10^3\ cm^{-1}$, respectively. The ICD spectrum indicates a positive shoulder at $41.4 \times 10^3\ cm^{-1}$. The geometrical structure of β-CD excludes the formation of an equatorial inclusion complex for **1** [12]. Thus the ICD spectrum of the β-CD complex with **1** is attributed to the structure of an axial inclusion complex. Harata and Uedaira [7] have shown theoretically that the transition of the guest molecule in the cavity of β-CD with a transition dipole moment perpendicular to the molecular axis of β-CD gives a negative ICD value and that the transition with a transition dipole moment parallel to the axis gives a positive ICD value. Thus according to the theoretical conclusions of Harata and Uedaira [7] it can be concluded that the first absorption band (17.1×10^3–$34.3 \times 10^3\ cm^{-1}$) consists of three electronic transitions having perpendicular, parallel and perpendicular polarizations with respect to the long axis of **1**. The second absorption band (34.3×10^3–$42.8 \times 10^3\ cm^{-1}$) consists of two electronic transitions

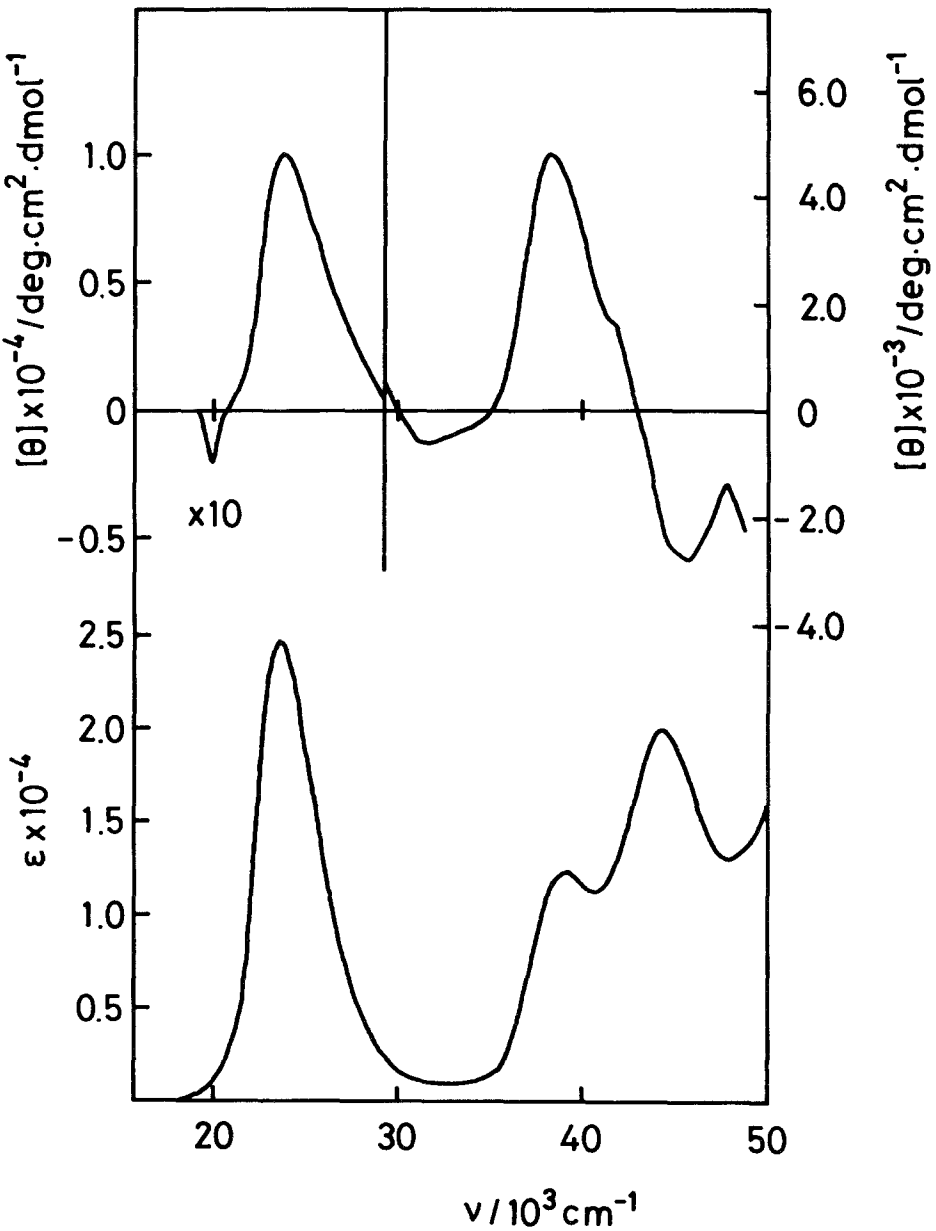

Fig. 2. Induced circular dichroism (top) and absorption (bottom) spectra of the β-cyclodextrin complex with **1** in aqueous solution at room temperature. The concentrations of β-cyclodextrin and **1** were 1.00×10^{-2}M and 4.32×10^{-5}M, respectively.

with polarization parallel to the axis of **1** and the third absorption band (42.8×10^3–47.1×10^3 cm^{-1}) has a perpendicular polarization with respect to the axis of **1**. Table I predicts that there are three electronic transitions (two perpendicular polarizations and a parallel polarization) in the first absorption band. The CNDO/S CI calculations (Table I) indicate that the second absorption band consists of two electronic transitions with polarizations parallel to the long axis of **1**. Table I confirms that the third absorption band

Table I. Transition energies (ΔE), oscillator strengths (f) and polarizations of 2-(2,4,6-cycloheptatrien-1-ylidene)-4-cyclopentene-1,3-dione

Theoretical[a]			Experimental[b]	
$\Delta E/10^3$ cm^{-1}	f (dimensionless)	pol.	$\Delta E/10^3$ cm^{-1}	pol.
24.2	0.0172	y	19.9	y
29.2	0.3808	z	23.9	z
32.9	0.0096	y	31.3	y
42.6	0.0583	z	38.0	z
46.3	0.0889	z	41.4	z
46.5	0.0289	y	45.6	y
47.1	0.0013	y		

[a] As all $n \rightarrow \pi^*$ transitions are forbidden or have negligible intensity, they have been omitted.
[b] Determined from the ICD spectrum.

consists of a transition polarized perpendicular to the long axis of **1**. The ICD spectrum suggests that there is an electronic transition polarized perpendicular to the long axis of **1** above 47.7×10^3 cm^{-1}. Table I strongly supports this.

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