

Induced Circular Dichroism Spectra of Benz[*b*]anthracene Included in β -Cyclodextrin

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Abstract. The assignment of the absorption spectra of benz[*b*]anthracene (**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 ($20.4\text{--}30.9 \times 10^3 \text{ cm}^{-1}$) has the transition dipole moment perpendicular to the long axis and the second absorption band ($30.9\text{--}37.2 \times 10^2 \text{ cm}^{-1}$) has the transition dipole moment parallel to the long axis of **1**. Our assignments are in complete agreement with earlier assignments. The induced circular dichroism spectra exhibit Cotton splittings at 19.1×10^3 and $42.8 \times 10^3 \text{ cm}^{-1}$. It can be concluded from Cotton splittings of the induced circular dichroism spectra that the association of two 1 : 1 inclusion complexes forms a ground-state dimer.

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

1. Introduction

Many authors [1–3] have investigated the polarization directions of the electronic absorption bands of benz[*b*]anthracene (**1**). The polarization of the first and second absorption bands has been determined from single crystal spectra as being parallel to the short and long axes, respectively [1, 2].

Harata and Uedaira [4] have measured the induced circular dichroism (ICD) spectra of the β -cyclodextrin (β -CD) complexes with naphthalene derivatives and indicated from the rotational strength calculated by using the method of Kirkwood [5] and Tinoco [6] that it is possible to make the band assignment of the guest molecule in the cavity of β -CD.

The aim of the present paper is to re-examine the assignment of the absorption bands of **1**.

2. Experimental

2.1. MATERIALS

The β -cyclodextrin (β -CD) and benz[*b*]anthracene (**1**) were obtained from the Sigma Chemical Co. (St. Louis, MO, U.S.A.). β -CD was recrystallized three times from an aqueous solution. Compound **1** was recrystallized three times from cyclohexane.

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2.2. INSTRUMENTS

The electronic absorption spectra were recorded at room temperature on a Hitachi U-3200 recording spectrophotometer. The ICD spectra were measured at room temperature on a Jasco J-40A circular dichrograph. In order to obtain an adequate signal-to-noise ratio, multiple scanning and averaging were accomplished using a J-DP 501N data processor.

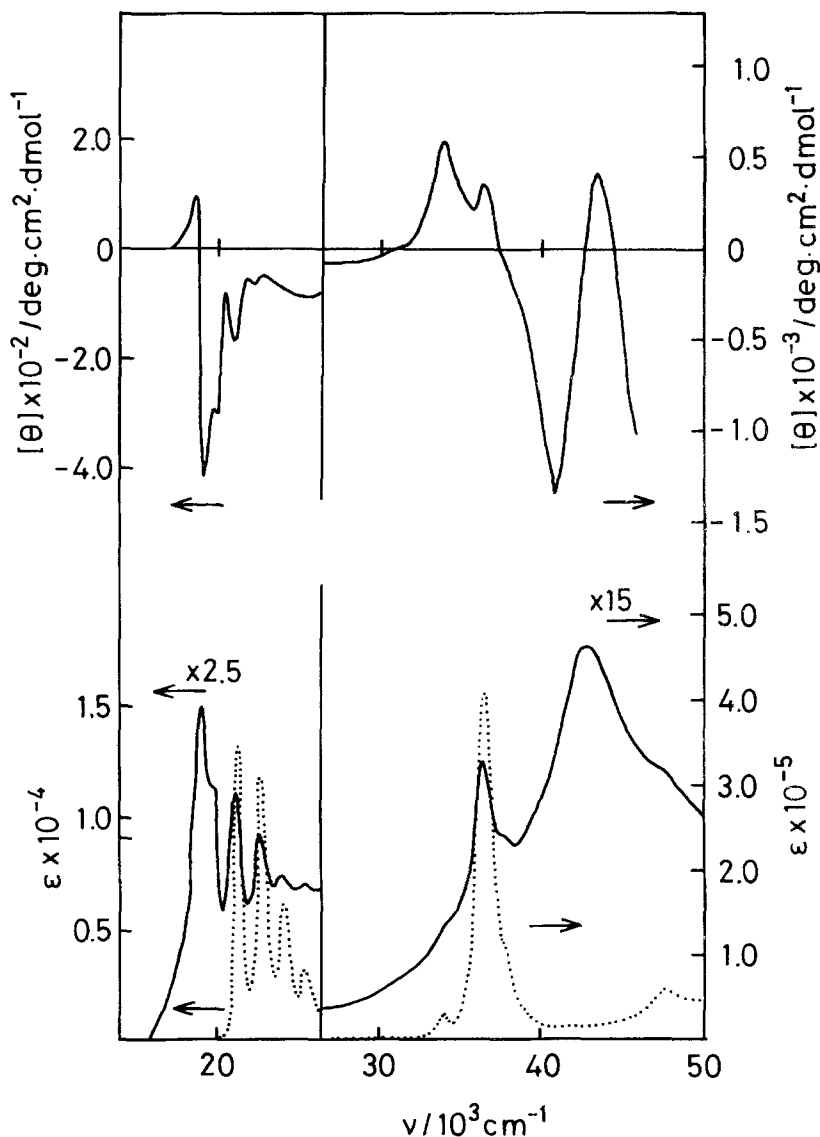


Fig. 1. Induced circular dichroism (top) and absorption (bottom) spectra of the β -cyclodextrin complex with benz[*b*]anthracene in 20% ethanol-water solution. The concentration of β -cyclodextrin was 1.00×10^{-2} M. The ICD measurements were made on deaerated solution in which the concentration of benz[*b*]anthracene ranged from 1.34×10^{-4} to 2.68×10^{-5} M. The dotted line represents the absorption spectrum of benz[*b*]anthracene in ethanol. All measurements were made at room temperature.

3. Results and Discussion

The observed ICD spectra of the β -CD complex with **1** are shown in Figure 1, where the absorption spectra are also shown. There is a negative ICD curve in the first absorption band ($20.4 - 30.9 \times 10^3 \text{ cm}^{-1}$) of the β -CD complex with **1**. In the region of the second absorption band ($30.9 - 37.2 \times 10^3 \text{ cm}^{-1}$), the β -CD complex with **1** shows a positive ICD curve. The geometrical structure of β -CD excluded the formation of an equatorial inclusion complex for **1** [7, 8]. Thus the ICD spectrum of the β -CD complex with **1** is attributed to the structure of an axial inclusion complex. Harata and Uedaira [4] 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 [4] it can be concluded that the first absorption band has perpendicular polarization with respect to the long axis of **1** and the second absorption band has parallel polarization with respect to the long axis. Our assignment for the first and second bands is in complete accord with the

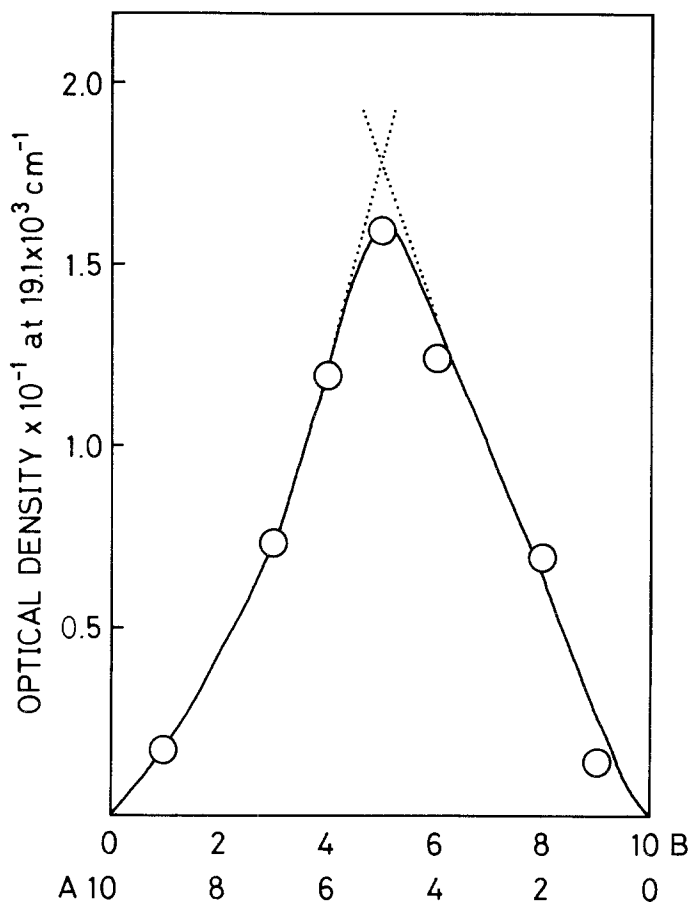


Fig. 2. The continuous variation plots for β -cyclodextrin (A) and benz[*b*]anthracene (B).

assignment given by measuring the dichroic spectra in the crystalline state [1, 2].

The ICD spectra exhibit Cotton splittings at 19.1×10^3 and $42.8 \times 10^3 \text{ cm}^{-1}$. The Cotton splittings mean that the absorption bands at 19.1×10^3 and $42.8 \times 10^3 \text{ cm}^{-1}$ are due to a dimer. The continuous variation curve of optical density at $19.1 \times 10^3 \text{ cm}^{-1}$ is shown in Figure 2. Figure 2 indicates a distinct maximum for equal concentration of a 1:1 complex. These facts imply that the association of two 1:1 inclusion complexes (a 2:2 inclusion complex) leads to the formation of the ground-state dimer. The 2:2 inclusion complex of β -CD may be formed by head-to-head association of two β -CD molecules to include the benz[*b*]anthracene molecule in the cylindrical cavity.

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