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Induced Circular Dichroism Spectra of the Cyclodextrin Complexes with 2-Thioxo-1,3-benzodithiole and 2-Selenoxo-1,3-benzodithiole

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Abstract. The induced circular dichroism (ICD) spectra of β-cyclodextrin (β-CD) complexes with 2-thioxo-1,3-benzodithiole and 2-selenoxo-1,3-benzodithiole have been measured. From the signs of the ICD spectra of both complexes, the polarization directions for the excited states have been investigated.

Key words. β-Cyclodextrin, induced circular dichroism spectra.

1. Introduction

2-Thioxo-1,3-benzodithiole (**1**) and 2-selenoxo-1,3-benzodithiole (**2**) have led to recent considerable interest in the chemistry of dibenzotetrathiafulvalene [1] since they are important precursors of this compound [2]. The structures of compounds **1** and **2** are shown in Figure 1.

Harata and Uedaira [3] 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.

As polarization investigations have proved to be powerful in determining the symmetries of excited state wavefunctions and in studying electronic interactions such as vibronic and spin-orbit coupling [4–6], we have investigated the polarizations of the electronic absorption bands of **1** and **2** by using the experimentally very simple β-CD complex method [3, 8].

2. Experimental

2-Thioxo-1,3-benzodithiole (**1**) and 2-selenoxo-1,3-benzodithiole (**2**) were prepared by the authors (J.N. and M.H.) [2], and recrystallized three times from cyclohexane. 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

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Fig. 1. The structures of 2-thioxo-1,3-benzodithiole (**1**) and 2-selenoxo-1,3-benzodithiole (**2**).

circular dichrograph at the Instrument Center, Institute for Molecular Science, Okazaki. Stoppered silica cells of 1 and 10 cm path-lengths were used. The concentration of β-CD was adjusted to 0.01 M throughout the measurements. All measurements were made at room temperature.

3. Results and Discussion

The geometrical structure of β-CD [8, 9] means that it is impossible for **1** and **2** to form equatorial inclusion complexes. Therefore the ICD spectra of the β-CD complexes with both compounds will be attributed to the structure with an axial inclusion. Harata and Uedaira [3] 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 the transition having a transition dipole moment parallel to the axis gives a positive ICD value. On the basis of the theoretical conclusions of Harata and Uedaira [3], the polarization directions of the electronic absorption bands of **1** and **2** are discussed herein.

3.1. 2-THIOXO-1,3-BENZODITHIOLE

The observed ICD spectra of the β-CD complex with 2-thioxo-1,3-benzodithiole (**1**) are shown in Figure 2, where the absorption spectra are also shown. The ICD spectra show negative, positive, negative, negative, positive and positive peaks at 25.8×10^3, 28.6×10^3, 33.0×10^3, 38.3×10^3, 42.1×10^3 and $44.5 \times 10^3\ \text{cm}^{-1}$, respectively. According to the theoretical conclusion of Harata and Uedaira [3], it can be concluded that the first (24.5×10^3–$31.8 \times 10^3\ \text{cm}^{-1}$) absorption band consists of two electronic transitions with a transition moment perpendicular to the long axis and with a transition moment parallel to the long axis of **1**, the second (31.8×10^3–$36.3 \times 10^3\ \text{cm}^{-1}$) absorption band consists of an electronic transition having perpendicular polarization with respect to the long axis of **1**, the third (36.3×10^3–$40.0 \times 10^3\ \text{cm}^{-1}$) absorption band consists of an electronic transition having perpendicular polarization with respect to the long axis of **1**, the fourth (40.0×10^3–$43.8 \times 10^3\ \text{cm}^{-1}$) absorption band is composed of an electronic transition with a transition moment parallel to the long axis, and the fifth (43.8×10^3–$47.5 \times 10^3\ \text{cm}^{-1}$) absorption band is also composed of an electronic transition having parallel polarization with respect to the long axis of **1**.

There is a weak absorption band at $23.8 \times 10^3\ \text{cm}^{-1}$. The absorption spectra were measured in cyclohexane and in various polar solvents (butyl ether, trichloroethylene and ethanol). With increasing polarity of the solvent, the peak at

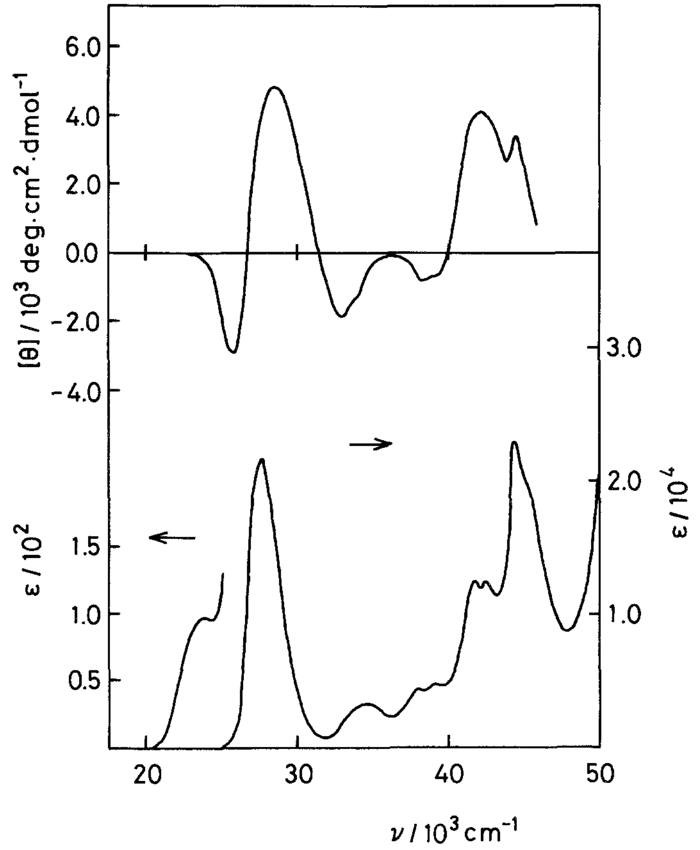

Fig. 2. Induced circular dichroism (upper) spectra of the β-CD complex with **1** in 20% ethanol–aqueous solution. Absorption (lower) spectra of **1** in ethanol.

23.8×10^3 cm^{-1} shifted to the blue. On the basis of the usual concept that the $n \rightarrow \pi^*$ electronic transition is blue-shifted in polar solvents [10, 11], it is concluded that the absorption band at 23.8×10^3 cm^{-1} is composed of an $n \rightarrow \pi^*$ transition.

3.2. 2-SELENOXO-1,3-BENZODITHIOLE

The absorption and ICD spectra of the β-CD complex with 2-selenoxo-1,3-benzodithiole (**2**) are shown in Figure 3. The ICD spectra show negative, positive, negative, positive and positive peaks at 22.0×10^3, 24.7×10^3, 32.3×10^3, 39.5×10^3 and 43.3×10^3 cm^{-1}, respectively. On the basis of the theoretical conclusion of Harata and Uedaira [3], it can be concluded that the first (21.3×10^3–30.0×10^3 cm^{-1}) absorption band consists of two electronic transitions with a transition moment perpendicular to the long axis and with a transition moment parallel to the long axis of **2**, the second (30.0×10^3–35.0×10^3 cm^{-1}) absorption band consists of an electronic transition having perpendicular polarization with respect to the long axis of **2**, the third (35.0×10^3–41.3×10^3 cm^{-1}) absorption band is composed of an electronic transition with a transition moment parallel to

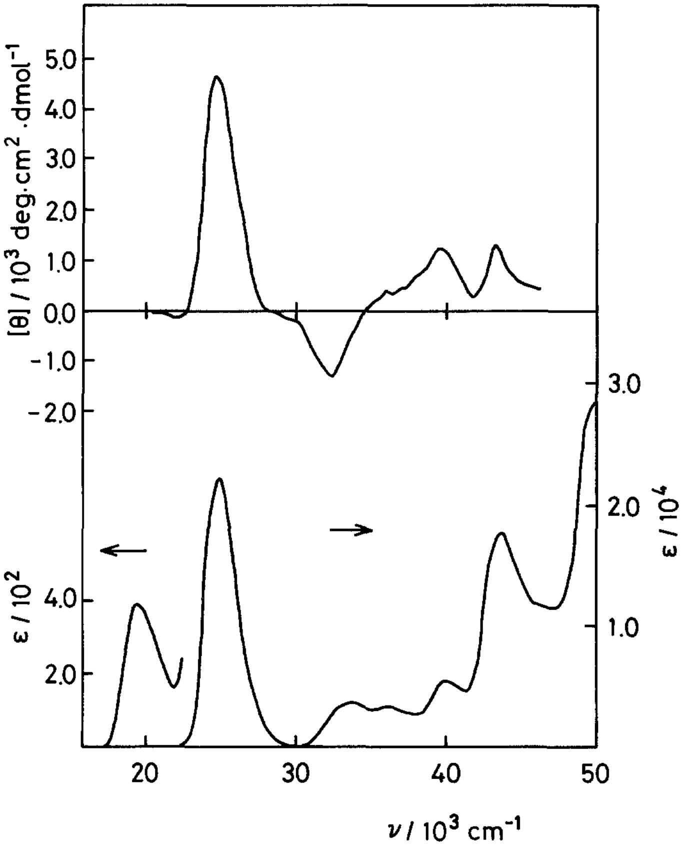

Fig. 3. Induced circular dichroism (upper) spectra of the β-CD complex with **2** in 20% ethanol–aqueous solution and absorption (lower) spectra of **2** in ethanol.

the long axis and the fourth (41.3×10^3–46.3×10^3 cm^{-1}) is also composed of an electronic transition having parallel polarization with respect to the long axis of **2**.

A weak absorption band appears at 19.5×10^3 cm^{-1}. The absorption spectra were measured in cyclohexane and in polar solvents (butyl ether, trichloroethylene and ethanol). With increasing polarity of the solvent, the peak at 19.5×10^3 cm^{-1} shifted to shorter wavelength. According to the results of solvent effects [10, 11], it can be concluded that the absorption band at 19.5×10^3 cm^{-1} is composed of an $n \rightarrow \pi^*$ transition.

References

1. H. Kobayashi and J. Nakayama: *Bull. Chem. Soc. Jpn.* **54**, 2408 (1981).
2. J. Nakayama, H. Sugiura, and M. Hoshino: *Tetrahedron Lett.* **24**, 2585 (1983).
3. K. Harata and H. Uedaira: *Bull. Chem. Soc. Jpn.* **48**, 375 (1975).
4. A. Bree, A. R. Lacey, I. G. Ross, and R. Zwarich: *Chem. Phys. Lett.* **26**, 329 (1974).
5. J. J. Dekkers, G. Ph. Hoornweg, W. P. Cofino, C. MacLean, and N. H. Velthorst: *Chem. Phys. Lett.* **67**, 24 (1979).

6. T. Terada, M. Koyanagi, and Y. Kanda: *Bull. Chem. Soc. Jpn.* **53**, 352 (1980).
7. N. Ikeda and H. Yamaguchi: *Chem. Phys. Lett.* **56**, 167 (1978).
8. J. A. Hamilton, M. N. Sabesan, L. K. Steinrauf, and A. Geddes: *Biochem. Biophys. Res. Commun.* **73**, 659 (1976).
9. M. M. Harding, J. M. Maclennan, and R. M. Paton, *Nature* **274**, 621 (1978).
10. M. Kasha: *Discuss. Faraday Soc.* **9**, 14 (1950).
11. H. McConnell: *J. Chem. Phys.* **20**, 700 (1952).