

## Induced Circular Dichroism and Magnetic Circular Dichroism Spectra of Maleimide and Related Molecules

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The induced circular dichroism (ICD) spectra of the inclusion complexes of maleimide, phthalimide, and naphthalene-2,3-dicarboximide with  $\beta$ - or  $\gamma$ -cyclodextrin (CDx) have been measured. The structure of the CDx inclusion complexes are interpreted by the signs and shapes of ICD spectra compared with the results of PPP calculations. In maleimide and naphthalene-2,3-dicarboximide, the ICD spectra of the  $\beta$ -CDx inclusion complex are very similar to those of the  $\gamma$ -CDx inclusion complex in spite of the differences in dimensions between the cavity of  $\beta$ -CDx and that of  $\gamma$ -CDx. In phthalimide, the ICD spectra of the  $\beta$ -CDx inclusion complex are very different from those of the  $\gamma$ -CDx inclusion complex. The split-type ICD bands at 220–235 nm show that the dimer of phthalimide is formed in the presence of  $\beta$ -CDx.

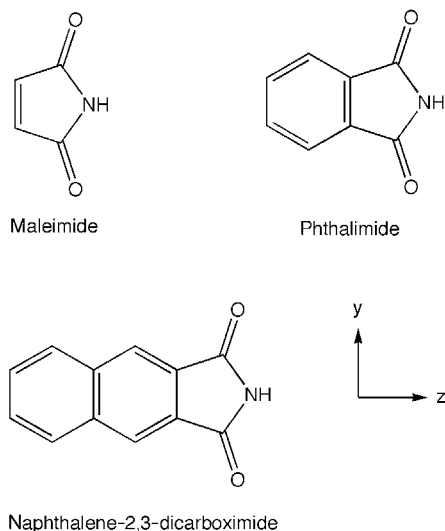
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**1. Introduction.** – Cyclodextrins are torus-shaped cyclic oligosaccharides that have been studied as a supramolecular host because they have an internal hydrophobic cavity that provides a nonpolar environment for the guest molecules in aqueous solution [1][2]. The  $\beta$ -cyclodextrin (CDx) and the  $\gamma$ -CDx are composed of seven and eight D-glucopyranose units, respectively. The guest molecule of an appropriate size can be accommodated into the cavity of CDx to form the inclusion complex. The shape and sign of induced circular dichroism (ICD) spectra of the CDx inclusion complex provide precise structural information. *Harata* and *Uedaira* have measured the ICD spectra of the  $\beta$ -CDx inclusion complexes with naphthalene derivatives and studied the orientation of the guest molecule within the cavity of the  $\beta$ -CDx [3]. Some authors have extended further detailed studies concerning the shape and sign of the ICD spectra of the  $\beta$ -CDx and  $\gamma$ -CDx inclusion complexes [4–7]. In the ICD spectra of the inclusion complex of the guest molecule with CDx, the signs of ICD bands are correlated with directions of the transition moments of the guest molecule in the cavity of the CDx. If the direction of the electric dipole moment in the guest molecule is parallel to the long axis of the CDx cavity, then the rotational strength gives a positive ICD value, and the transition with the electric dipole moment perpendicular to the long axis of CDx gives a negative ICD value. Thus, ICD spectra are a very useful tool to estimate an orientation of the guest molecule within the cavity of CDx if the direction of the electric dipole moment in the guest molecule is known.

For CDx inclusion complexes, strong split-type ICD spectra like an exciton-coupling effect have been observed [8–10]. Exciton splitting of excited states in the molecular aggregates may appear as split ICD spectral pattern if spatial interactions such as stacking between two guest molecules are present. The split-type ICD spectra

are attributed to the formation of a 2 : 2 CDx/guest molecule inclusion complex. It is suggested that the dimer of the guest molecules is trapped within the CDx cavities.

The magnetic circular dichroism (MCD) spectra of some quinones have been measured and assigned by semi-empirical calculations [11–13]. Since the sign of MCD bands is negative or positive, the MCD spectra are a very effective tool for assignment of absorption spectra. In this work, we have considered the structures of the inclusion complexes of 1*H*-pyrrole-2,5-dione (maleimide), 1*H*-isoindole-1,3(2*H*)-dione (phthalimide), and 1*H*-benz[*f*]isoindole-1,3(2*H*)-dione (naphthalene-2,3-dicarboximide) with  $\beta$ - or  $\gamma$ -CDx by means of the corresponding ICD and MCD spectra.



**2. Results and Discussion.** – The absorption and MCD spectra of maleimide together with the ICD spectra of the CDx inclusion complex are shown in *Fig. 1*. The MCD and ICD spectra below 205 nm cannot be observed due to the absorption of solvents. The *Faraday B* value (**B**) is given by

$$\mathbf{B} = -(33.53)^{-1} \int_{\text{band}} ([\theta]_{\text{M}}/\nu) d\nu$$

where  $\nu$  is the frequency and  $[\theta]_{\text{M}}$  is the molar ellipticity [14]. The calculated  $(-1) \times$  (*Faraday B* values), transition energies, and oscillator strengths are listed in the *Table*, the *Faraday B* values being correlated with the opposite sign of the molar ellipticity.

The PPP calculations of maleimide show that the negative (250–350 nm), negative (220–250 nm), and positive (210–220 nm) bands in the MCD spectra are assigned to the  ${}^1\text{B}_2$  ( $\text{S}_1$ ),  ${}^1\text{B}_2$  ( $\text{S}_2$ ), and  ${}^1\text{A}_1$  ( $\text{S}_3$ )  $\pi \rightarrow \pi^*$  transitions, respectively. In the ICD spectra of the  $\beta$ - and  $\gamma$ -CDx inclusion complexes, there are negative (250–350 nm), negative (220–250 nm), and positive (210–220 nm) bands. The ICD spectra of maleimide show that a transition with a transition dipole moment parallel to the *y* axis ( ${}^1\text{B}_2$ ) gives a negative ICD value, and that with a transition dipole moment parallel to the *z* axis ( ${}^1\text{A}_1$ )

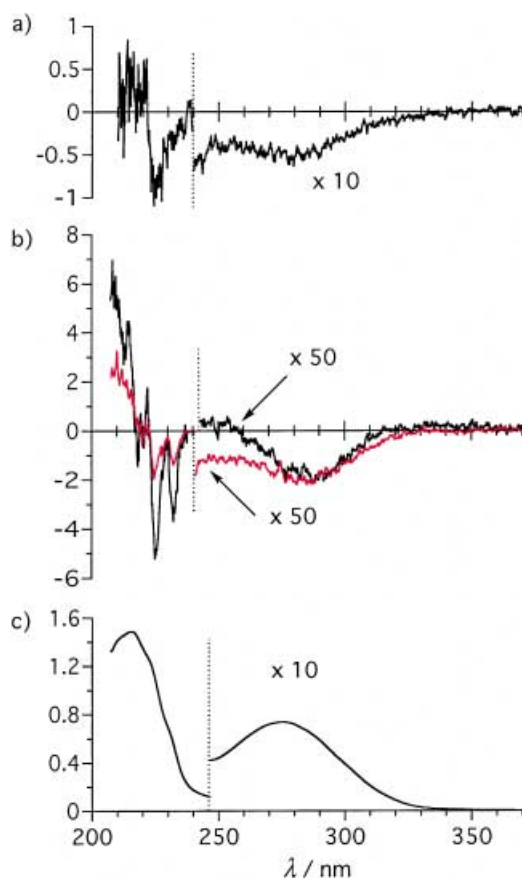


Fig. 1. a) MCD Spectra, c) absorption spectra of maleimide in EtOH. b) ICD Spectra of  $\beta$ -CD (in black) and  $\gamma$ -CD (in red) complexes with maleimide in 10% aqueous EtOH solution.

gives a positive ICD value. Thus, it is thought that the molecular  $z$  axis of maleimide is parallel to the molecular axis of  $\beta$ - or  $\gamma$ -CDx in the inclusion complexes. The signs and shape of ICD spectra of the  $\beta$ -CDx inclusion complex are very similar to those of the  $\gamma$ -CDx inclusion complex, in spite of the different sizes of CDx cavities. The size of CDx cavity may have no influence on the structure of the inclusion complex because the size of maleimide is very small compared with the size of CDx cavity.

In the MCD spectra of phthalimide and ICD spectra of the  $\gamma$ -CDx inclusion complex (Fig. 2), there are a negative band (220–245 nm) and a positive band (210–220 nm). From the PPP calculations, it is concluded that the negative and positive bands are assigned to the  ${}^1B_2$  ( $S_3$ ) and  ${}^1A_1$  ( $S_4$ )  $\pi \rightarrow \pi^*$  transitions, respectively. The ICD spectra of the  $\gamma$ -CDx inclusion complex show that a transition with a transition dipole moment parallel to the  $y$  axis ( ${}^1B_2$ ) gives a negative ICD value, and that a transition dipole moment parallel to the  $z$  axis ( ${}^1A_1$ ) gives positive ICD value. Therefore, the long molecular axis ( $z$  axis) of phthalimide may be parallel to the

Table 1. Calculated Transition Energies ( $\lambda_{\max}/\text{nm}$ ), Oscillator Strengths ( $f$ ) and  $(-1) \times (\text{Faraday } \mathbf{B} \text{ values})$  by the PPP method

State	$\lambda_{\max}$	$f$	$-\mathbf{B}/10^{-4}$	Assignment
Maleimide				
S <sub>1</sub>	283	0.397	-1.49	<sup>1</sup> B <sub>2</sub>
S <sub>2</sub>	242	0.061	-0.847	<sup>1</sup> B <sub>2</sub>
S <sub>3</sub>	225	0.011	1.30	<sup>1</sup> A <sub>1</sub>
Phthalimide				
S <sub>1</sub>	303	0.076	-25.2	<sup>1</sup> A <sub>1</sub>
S <sub>2</sub>	290	0.226	15.1	<sup>1</sup> B <sub>2</sub>
S <sub>3</sub>	240	0.148	-7.18	<sup>1</sup> B <sub>2</sub>
S <sub>4</sub>	233	0.383	25.6	<sup>1</sup> A <sub>1</sub>
S <sub>5</sub>	209	0.016	7.51	<sup>1</sup> B <sub>2</sub>
Naphthalene-2,3-dicarboximide				
S <sub>1</sub>	338	0.114	2.27	<sup>1</sup> A <sub>1</sub>
S <sub>2</sub>	292	0.081	-17.5	<sup>1</sup> B <sub>2</sub>
S <sub>3</sub>	265	0.559	14.8	<sup>1</sup> A <sub>1</sub>
S <sub>4</sub>	263	0.242	-24.1	<sup>1</sup> B <sub>2</sub>
S <sub>5</sub>	237	0.061	1.70	<sup>1</sup> A <sub>1</sub>
S <sub>6</sub>	233	0.061	1.26	<sup>1</sup> B <sub>2</sub>

molecular axis of  $\beta$ - or  $\gamma$ -CDx. In the wavelength region 247–330 nm, a very weak and broad band is observed in the MCD spectra and ICD spectra of the  $\gamma$ -CDx inclusion complex. On the other hand, in the ICD spectra of the  $\beta$ -CDx inclusion complex, there are a negative band (295–330 nm) and a positive band (247–295 nm). From the PPP calculations, the negative and positive bands are assigned to the <sup>1</sup>A<sub>1</sub> (S<sub>1</sub>) and <sup>1</sup>B<sub>2</sub> (S<sub>2</sub>)  $\pi \rightarrow \pi^*$  transitions, respectively. However, the signs of the ICD bands are not consistent with signs of ICD values estimated from the directions of transition moments. In the wavelength region 220–247 nm, there are a negative MCD band and a negative ICD band for the  $\gamma$ -CDx inclusion complex. The sign and shape of ICD spectra of the  $\gamma$ -CDx inclusion complex is analogous to those of the MCD spectra. However, for the  $\beta$ -CDx inclusion complex, there are a positive (220–227 nm) and a negative (227–235 nm) ICD band, which are resolved by a curve-fitting procedure using Gaussian functions. The  $+/-$  signal alternation in ICD or split-type ICD spectra shows that the dimer of phthalimide is formed only in the presence of  $\beta$ -CDx.

In the ICD spectra of naphthalene-2,3-dicarboximide with  $\beta$ - or  $\gamma$ -CDx (Fig. 3), a negative and a positive band are in the wavelength region 305–380 nm. The PPP calculations show that the positive (315–380 nm) and negative (305–315 nm) bands are assigned to the <sup>1</sup>A<sub>1</sub> (S<sub>1</sub>) and <sup>1</sup>B<sub>2</sub> (S<sub>2</sub>)  $\pi \rightarrow \pi^*$  transitions, respectively. From signs of ICD spectra and directions of transition moments, it is concluded that the long molecular axis ( $z$  axis) of naphthalene-2,3-dicarboximide is parallel to the molecular axis of CDx. On the other hand, a negative band (305–380 nm) was observed in the MCD spectra. The *Faraday*  $\mathbf{B}$  value of the first transition (<sup>1</sup>A<sub>1</sub>, S<sub>1</sub>) may be hidden by the next strong *Faraday*  $\mathbf{B}$  value (<sup>1</sup>B<sub>2</sub>, S<sub>2</sub>). In the wavelength region 220–305 nm, the positive and negative bands in the ICD and MCD spectra are assigned to the <sup>1</sup>A<sub>1</sub> (S<sub>3</sub>) and <sup>1</sup>B<sub>2</sub> (S<sub>4</sub>)  $\pi \rightarrow \pi^*$  transitions, respectively. The shape of the ICD spectra for the  $\beta$ -CDx inclusion complex is very similar to that for the  $\gamma$ -CDx inclusion complex, and the

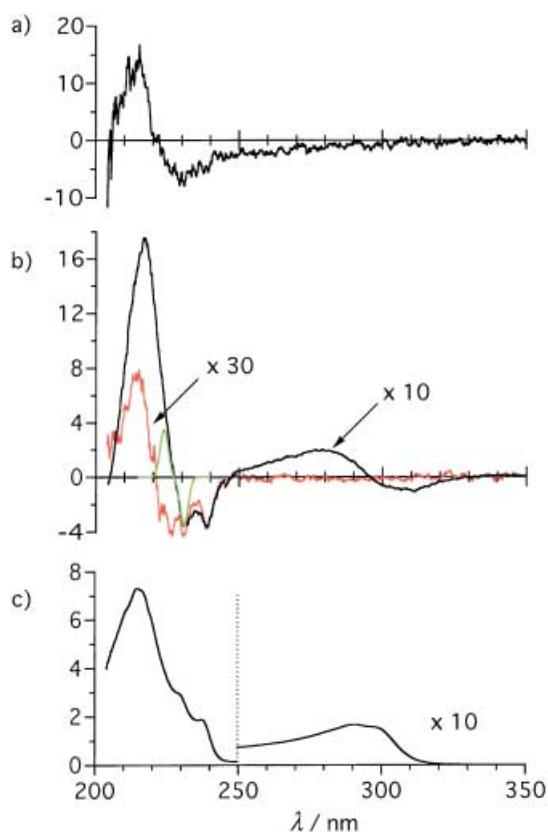


Fig. 2. a) MCD Spectra, c) absorption spectra of phthalimide in EtOH. b) ICD Spectra of  $\beta$ -CD (in black) and  $\gamma$ -CD (in red) complexes with phthalimide in 10% aqueous EtOH solution. The green line is obtained by curve fitting procedure.

intensity of the ICD bands for the  $\beta$ -CDx inclusion complex is strong compared to that for the  $\gamma$ -CDx inclusion complex. Thus, it is considered that the guest molecule (naphthalene-2,3-dicarboximide) may be bound in the cavity of  $\beta$ -CDx, which is smaller than that of  $\gamma$ -CDx. In analogy to naphthalene-2,3-dicarboximide, phthalimide may be similarly bound in the  $\beta$ -CDx cavity as in the  $\gamma$ -CDx. Thus, the dimer of phthalimide is present only in the  $\beta$ -CDx aqueous solution.

#### Experimental Part

*General.* The compounds (maleimide, phthalimide, and naphthalene-2,3-dicarboximide, *Sigma-Aldrich Co.*) were recrystallized twice from ethanol.  $\beta$ - and  $\gamma$ -CDx (*Kanto Chemical Co.*) were purified by repeated recrystallizations from dist. H<sub>2</sub>O. Spectral-grade solvents (EtOH) were used as received. The absorption spectra were recorded on a *Jasco U-Best35* spectrophotometer. The ICD spectra were measured with a *Jasco J-600C* spectropolarimeter. Stopped silica cells of 1- and 5-cm path-lengths were used. The concentrations of CDx were maintained in all experiments at  $9.00 \times 10^{-3}$  M. The MCD spectra were recorded on a *Jasco J-600C* spectropolarimeter with a 1.32-T electromagnet. All measurements were carried out at r.t.

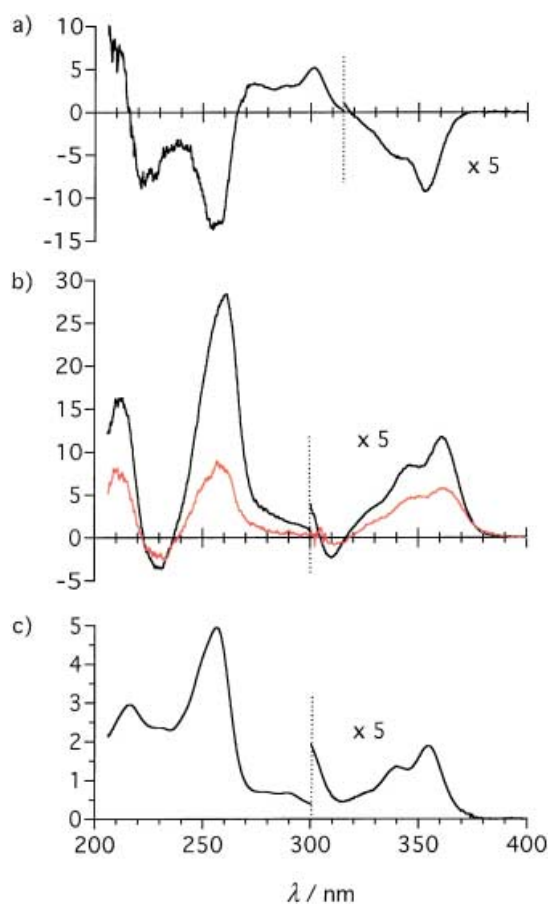


Fig. 3. a) MCD Spectra, c) absorption spectra of naphthalene-2,3-dicarboximide in EtOH. b) ICD Spectra of  $\beta$ -CD (in black) and  $\gamma$ -CD (in red) complexes with naphthalene-2,3-dicarboximide in 10% aqueous EtOH solution.

*Calculations.* The molecular structure of phthalimide was taken from X-ray diffraction data [15]. In the absence of relevant experimental structural data of maleimide and naphthalene-2,3-dicarboximide, the geometries were optimized by using the PM3 method in MOPAC [16] in  $C_{2v}$  symmetry. With these geometries, we calculated the electronic transition energies, transition moments, and *Faraday B* values by using the PPP method [17]. The ionization potentials and one-center repulsion integrals for the heteroatoms were those given in [18]. The resonance integrals were calculated by the *Wolfsberg–Helmholtz* method [19] with a parameter  $k = 0.86$ . The two-center repulsion integrals were obtained by the *Mataga–Nishimoto* formula [20].

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