Induced Circular Dichroism and Molecular Orientations of β-Cyclodextrin Inclusion Complexes with 9,10-Anthraquinone and 9,10-Phenanthrenequinone

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Synopsis. The induced circular dichroism (ICD) spectra of β-cyclodextrin inclusion complexes with 9,10-anthraquinone and 9,10-phenanthrenequinone have been measured, and the electronic structures and molecular orientations of the guests are discussed in terms of the ICD signs and theoretical results.

Cyclodextrins (CDxs) are known as typical hosts in inclusion chemistry. One of the most important spectroscopic benefits brought about by inclusion-complex formation is induced circular dichroism (ICD); since a CDx is composed of several D(+)-glucopyranose units, the Cotton effect is induced on the electronic absorption bands of an achiral guest molecule. On the basis of the coupled oscillator theory, it has been shown that the guest electronic transition polarized perpendicular to the CDx cavity axis exhibits a negative ICD, whereas that polarized parallel exhibits a positive ICD.[1,2] The ICD measurement of CDx-inclusion complexes has been shown to be a very simple and useful tool in the assignment of electronic absorption bands both for neutral molecules[1-5] and for radical ions.[6] In other words, information on the molecular orientation can be gathered from knowledge of the directions of the transition dipole moments in the guest molecule.[4,5] In this report, we will discuss the inclusion orientations and assignment of the electronic absorption spectra of 9,10-anthraquinone (9,10-AQ) and 9,10-phenanthrenequinone (9,10-PhQ) on the basis of the observed ICD signs and the results of the published molecular orbital calculations.[7-9]

Results and Discussion

Figures 1 and 2 show the electronic absorption and ICD spectra of the β-CDx inclusion complexes with 9,10-AQ and 9,10-PhQ respectively in an aqueous solution as observed at room temperature, while Table 1 compares the experimental and theoretical spectral data.[8] Since the nπ* transitions overlap with the ππ* transitions, the precise discussion is restricted to the ππ* transitions; accordingly, the theoretical spectral data cited in Table 1 are concerned solely with the ππ* transitions.

Referring to the molecular orientation of the β-CDx inclusion complex with 1,4-naphthoquinone,[5] the two oxygen atoms of 9,10-AQ are seemingly not fully included in the β-CDx cavity, while one of the benzene moieties can be included. Namely, as is illustrated in Fig. 3, 9,10-AQ is partially included to take an axial orientation with β-CDx; hence, the electronic transitions polarized along the long and short molecular axes should be positive and negative respectively in

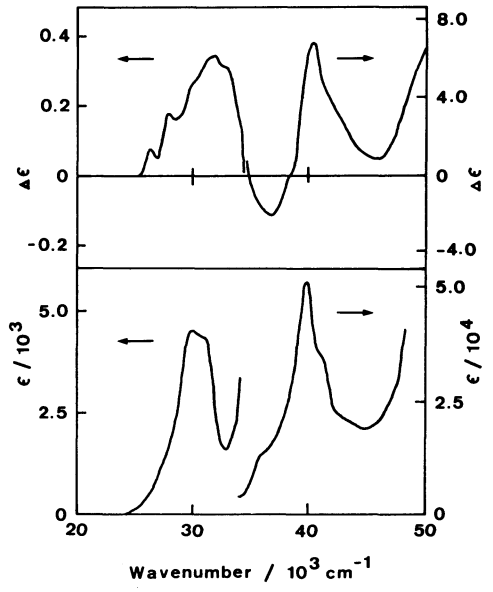

Fig. 1. ICD (upper) and electronic absorption (lower) spectra of β-CDx inclusion complex with 9,10-AQ in aqueous solution observed at room temperature.

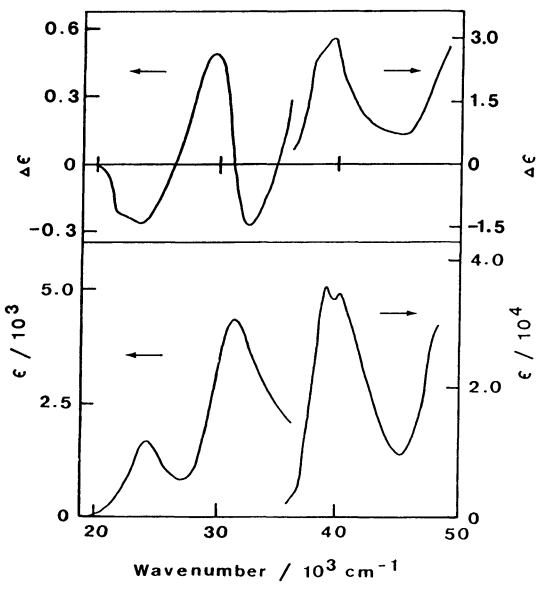

Fig. 2. ICD (upper) and electronic absorption (lower) spectra of β-CDx inclusion complex with 9,10-PhQ in aqueous solution observed at room temperature.

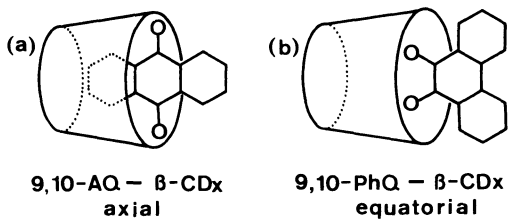

Fig. 3. Probable partial inclusion and molecular orientations in the β-CDx inclusion complexes with 9,10-AQ (a) and 9,10-PhQ (b).

ICD sign. Thus, the absorption bands at 29750 and 39630 cm^{-1} are found to be polarized along the long molecular axis, while the shoulder band at 35900 cm^{-1} is polarized along the short molecular axis. When the axial inclusion is assumed, the theoretical prediction based on the PPP method[8] is in good agreement with the ICD spectrum, as is shown in Table 1, as far as the ππ* transtions are concerned. The absorption bands appearing at 29750, 35900, and 39630 cm^{-1} can be correlated to the ^1L_a, ^1L_b, and ^1B_b bands of anthracene respectively. The structure around 27000 cm^{-1} in the ICD spectrum is due to either the ππ* vibronic or nπ* transition;[7-9] no definite conclusion can be deduced, since the nπ* band overlaps with the ππ* band.[10,11]

Now, let us turn to the β-CDx inclusion complex with 9,10-PhQ. In what follows, we assume that the above-mentioned ICD-sign rule for the guest electronic transitions[1,2] can also be applied when, as is illustrated in Fig. 3(b), a substantial portion of the guest is located outside the CDx cavity. According to the theoretical data in Table 1 obtained on the basis of the PPP method,[8] the first ππ* transition is polarized along the long molecular axis. The second and third transitions are predicted to be polarized differently from each other and to appear around 33000 cm^{-1}; actually, the ICD spectrum in Fig. 2 exhibits two differently polarized transitions in the 28000—35000 cm^{-1} region. The fourth transition is predicted to be short-axis polarized and to be located at 39040 cm^{-1}. If 9,10-PhQ is axially included in β-CDx, the ICD signs should be plus, minus, plus, and minus in order from the low- to the high-energy region; this is in disagreement with the ICD signs shown in Fig. 2. From the correlation between the theoretical and experimental results, the ICD spectrum can be ascribed to such an equatorial inclusion complex as is illustrated in Fig. 3. The minimum and maximum molecular dimensions of a 9,10-PhQ molecule are estimated to be 8.0 and 11.6 Å respectively, inclusive of the van der Waals radii of the hydrogen and oxygen atoms. Thus, in view of the cavity size of β-CDx, 9,10-PhQ is included in β-CDx, not completely but partially, as well as equatorially, with the *o*-benzoquinone moiety located in the cavity; the major binding force between 9,10-PhQ and β-CDx seems to be brought about by intermolecular hydrogen bonding between the carbonyl groups of 9,10-PhQ and the hydroxyl groups of β-CDx. An nπ* transition with out-of-plane polarization must be negative in ICD sign, irrespective of whether the inclusion is axial or

Table 1. ππ* Transition Energies (ΔE), Oscillator Strengths (f), and Polarization (Pol.) of 9,10-AQ and 9,10-PhQ

No.	Theoretical[a]			Experimental	
	$\Delta E/10^3$ cm^{-1}	f	Pol.[b]	$\Delta E/10^3$ cm^{-1}	log ε
		(1) 9,10-AQ			
1	32.83	0.191	L	29.75	3.66
2	33.24	0	Forb.		
3	33.72	0	Forb.		
4	37.59	0.569	S	35.90	4.09
5	42.11	0.935	L	39.63	4.71
6	42.75	0	Forb.		
7	47.03	0	Forb.		
8	47.29	0.192	S		
		(2) 9,10-PhQ			
1	27.67	0.157	L	24.09	3.20
2	32.83	0.054	S	29.85[c]	
3	33.47	0.008	L	32.89[c]	
4	39.04	0.560	S	39.25	5.56
5	40.56	0.660	L		
6	42.51	0.003	S		
7	44.12	0.004	L		
8	48.24	0.001	S		

a) Taken from Ref. 8. b) L, S, and Forb. denote the long-axis polarized, short-axis polarized, and forbidden transitions respectively. c) Determined from the ICD spectrum shown in Fig. 2.

equatorial. The negative shoulder at 21250 cm^{-1} in the ICD spectrum is possibly due to the nπ* transition,[9] but no definite conclustion can be deduced since, just as in the case of 9,10-AQ, the nπ* band overlaps with the ππ* band.[10,11] The theoretical fifth intense transition cannot be identified in the ICD spectrum, probably because it falls outside the spectral range studied.

In conclusion, the ICD spectra of 9,10-AQ and 9,10-PhQ can be ascribed to the axial and equatorial inclusion complexes with β-CDx respectively, as is illustrated in Fig. 3. The respective molecular orientations of the two quinones studied can be interpreted as natural consequences of the intermolecular hydrogen bonding between the quinones and the host.

Experimental

The 9,10-AQ and 9,10-PhQ (Tokyo Kasei, GR) were recrystallized from ethanol (Wako, SSG). The β-CDx (Tokyo Kasei, GR) was recrystallized five times from water and then dried under a vacuum at 80 °C. The deinoized and distilled water was used as a solvent. The electronic absorption and ICD spectra of the β-CDx inclusion complexes were recorded at room temperature, about a day after the sample-preparation, on a Shimadzu MPS 50-L spectrophotometer and on a JASCO J-500C circular dichrograph respectively. A JASCO J-501N data processor was used for the accumulation of the ICD spectra. The concentration of β-CDx was set at 1.5×10^{-2} mol dm^{-3}, while those of the quinones were adjusted so that the maximum absorbances fell in the range of 1.2—1.5.

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