Application of a General Rule to Induced Circular Dichroism of Naphthalene Derivatives Complexed with Cyclodextrins

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A general rule, previously derived for a complex between an achiral guest compound and a chiral macrocyclic host compound, can explain the inversion of circular dichroism (CD) signs observed in the complexation of 2-substituted naphthalenes (2-naphthol, 2-methylnaphthalene, 2-chloronaphthalene, 6-bromo-2-naphthol) with α- and β-cyclodextrins, where the substrates are included deeply in the cavity of β-cyclodextrin but only partly included in the cavity of α-cyclodextrin. The present success of the general rule supports its validity and usefulness.

Induced circular dichroism (ICD) caused by the complex formation between a chiral host molecule and an achiral guest molecule is a useful tool for the structural analysis of host−guest complexes. In a previous paper,[1] I derived a general rule for ICD that was based on the coupled-oscillator theory.[2−8] This rule is quite simple and can be easily applied to actual systems. Recently the sign of ICD of naphthalene derivatives (2-naphthol, 2-methylnaphthalene, 2-chloronaphthalene, 6-bromo-2-naphthol) has been reported to depend entirely on the type of cyclodextrins, that is, α- and β-cyclodextrins (CDx).[9−12] The inversion of the ICD sign must therefore be due to the structural difference of the two types of complexes. Namely, although β-CDx can include the naphthalene derivatives completely inside its cavity, α-CDx can entrap them only partially because of its smaller cavity size. In this paper the reason for the inversion of the ICD sign is explained by using the general rule mentioned above.

Equations 1 and 2, obtained as described previously,[1] represent the dependency of rotational strength (R_{0a}) on the position of a guest chromophore with parallel-polarized and perpendicular-polarized transition moments against the symmetric axis of a host macrocycle.

$$R_{0a} = DF(z) \qquad \text{parallel-polarized} \qquad (1)$$

$$R_{0a} = -DF(z)/2 \qquad \text{perpendicular-polarized} \qquad (2)$$

where z is the position of a chromophore shown in Figure 1, D is an intrinsic quantity determined by the electronic properties and structures of a host macrocycle and by the electronic properties of a guest molecule, and $F(z)$ represents the dependency on the position of a guest molecule. A more general form, eq 3, can be derived in a similar manner when the transition moment of a guest chromophore has an arbitrary direction (ϕ).

$$R_{0a} = DF(z)(3\cos^2\phi - 1)/2 \qquad (3)$$

Equation 3 indicates that the sign of ICD depends on the position (z) and direction (ϕ) of a transition moment of a guest molecule. This leads to the following important properties, most of which were presented in the previous paper:[1]

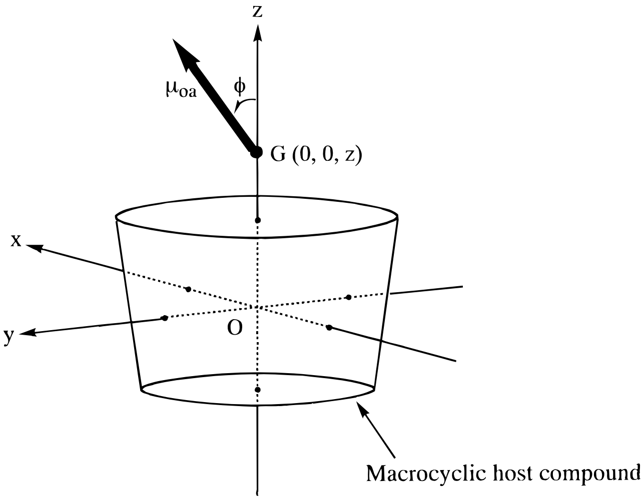

Figure 1. Truncated cone model; G and μ_{0a} represent the position and the transition moment of a guest molecule.

(1) The sign of ICD is inverted when the position of a guest molecule is moved from the inside of the cavity to the outside and the direction of the transition moment is fixed.

(2) The magnitude of ICD is greater when a guest molecule exists in the narrower-rim outside than in the wider-rim outside.

(3) In a transition polarized perpendicularly to the axis of a macrocycle, the ICD value should be −1/2 that of a parallel-polarized one. The sign of ICD changes at $\phi = 54.7°$.

The absorption wavelengths and the directions and oscillator strength of the transition moments of the naphthalene derivatives were obtained by INDO/1 calculation in ZINDO (ver. 3.6) of CAChe system (SONY Tektronix). In the configuration interaction calculation, 82 configurations were considered. The structures were optimized by AM1 before INDO/1 calculation. Calculated directions and magnitude of the transition moments are illustrated in Figure 2. These naphthalene derivatives have strong absorption bands at around 220∼230 nm, the transition moments are nearly parallel to the longitudinal axes (x-axis) (not illustrated for 6-bromo-2-naphthol), which are assigned to the ^1B_b band according to Platt's nomenclature.[13] The calculated angles between the ^1B_b transition moments and the x-axis are

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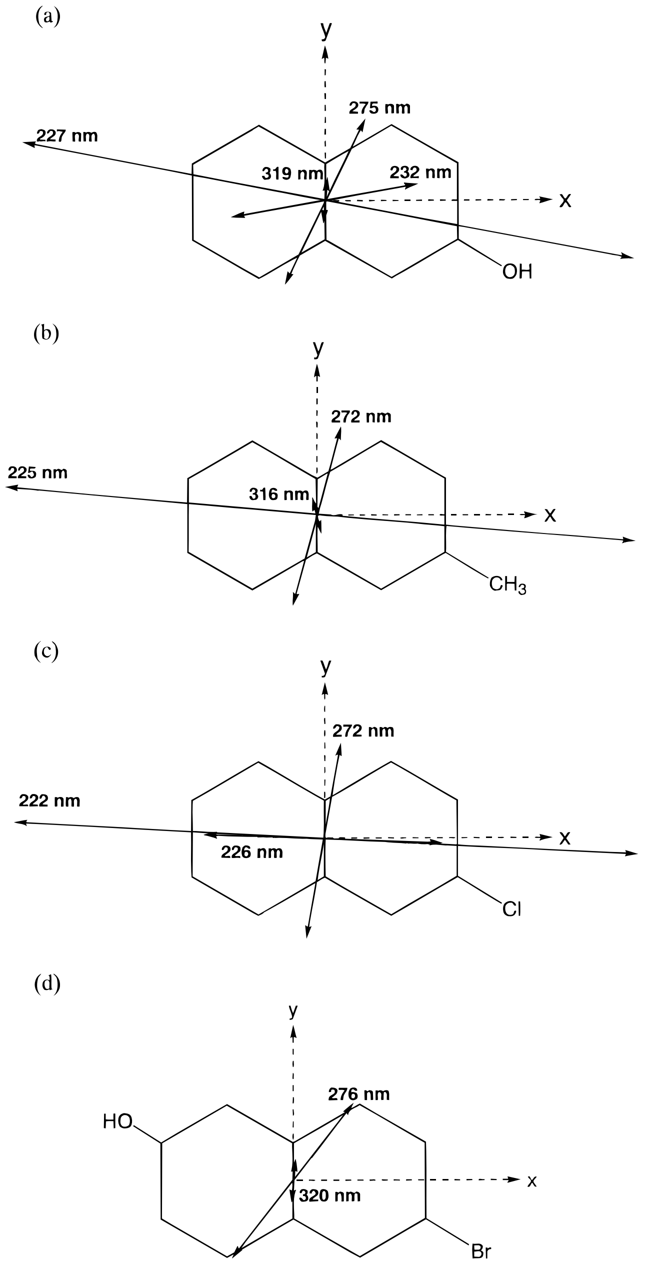

Figure 2. Calculated direction and magnitude of the transition dipole moments of (a) 2-naphthol, (b) 2-methylnaphthalene, (c) 2-chloronaphthalene, (d) 6-bromo-2-naphthol. Some of the weak transition moments are not illustrated here.

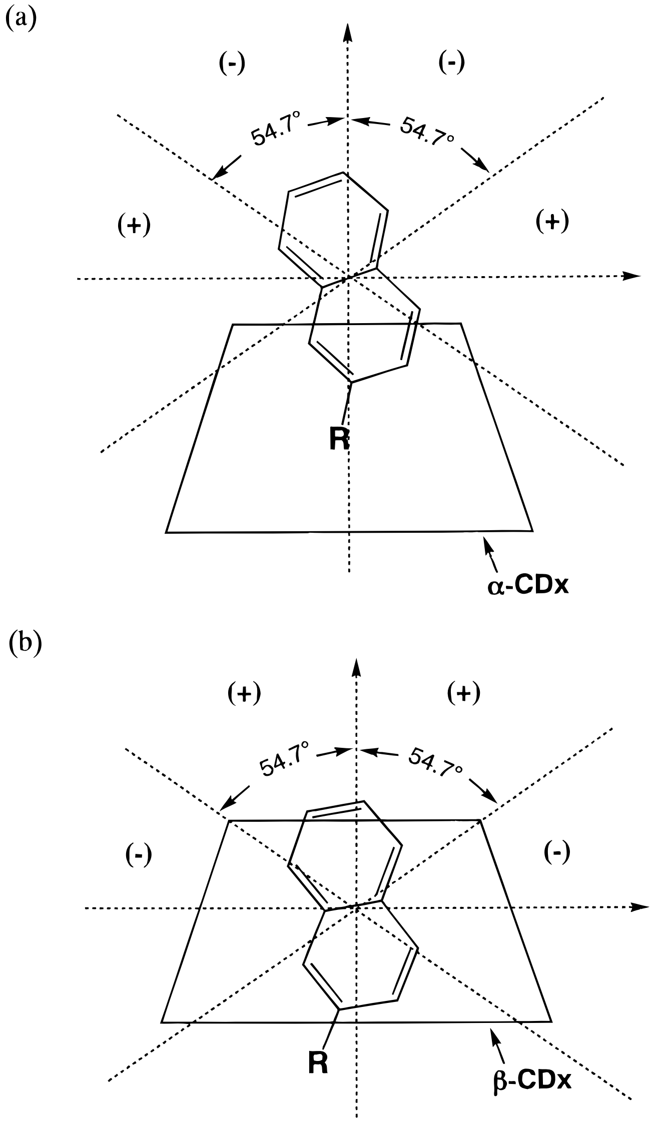

Figure 3. Schematic structures of complexes between a 2-substituted naphthalene and α-CDx (a) or β-CDx (b), showing theoretically possible ICD signs.

−10.8° for 2-naphthol (227 nm), −5.0° for 2-methylnaphthalene (225 nm), and −3.6° for 2-chloronaphthalene (222 nm).[14] The smaller absorption bands near 320 nm are assigned to the ^1L_b band, and those at around 270∼280 nm are assigned to the ^1L_a band. As a whole, these transitions tend to be polarized along

TABLE 1: Comparison of Theoretical and Observed ICD

	theoretical					observed				
				ICD	ICD	α-CDx		β-CDx		
substituted naphthalene	λ (nm)^a	f^a	assignment	(α-CDx)^b	(β-CDx)^b	λ (nm)^c	ICD^c	λ (nm)^c	ICD^c	assignment
2-naphthol	319	0.0072	^1L_b	+	−	330	+	320	−	^1L_b
	275	0.1494	^1L_a	+	−	275	+	275	−	^1L_a
	232	0.1500		−	+					
	227	1.6416	^1B_b	−	+	220	−	225	+	^1B_b
2-methylnaphthalene	316	0.0041	^1L_b	∼0	∼0					
	272	0.1466	^1L_a	+	−	290	+	280	−	^1L_a
	225	1.8045	^1B_b	−	+	<245	−	<250	+	^1B_b
2-chloronaphthalene	272	0.1571	^1L_a	+	−	285	+	285	−	^1L_a
	226	0.2401		−	+					
	222	1.6520	^1B_b	−	+	<245	−	<250	+	^1B_b
6-bromo-2-naphthol	320	0.0064	^1L_b	+	−	320−350	+	340	−	^1L_b
	276	0.1657	^1L_a	+	−	<290	+	<290	−	^1L_a

[a] λ (wavelength) and f (oscillator strength) values were calculated by INDO/1. Some of the weak absorption bands are not shown. [b] Theoretical ICD signs were determined in view of the directions of the transition moments (Figure 2) and the regions of ICD signs (Figure 3). [c] Observed wavelengths and ICD signs are cited from the following references: 2-naphthol,[9] 2-methylnaphthalene,[12] 2-chloronaphthalene,[10] 6-bromo-2-naphthol.[11]

the short axes (y-axis). The calculated angles between the ^1L_a transition moments and the x-axis are 64.0° for 2-naphthol (275 nm), 74.9° for 2-methylnaphthalene (272 nm), 80.3° for 2-chloronaphthalene (272 nm), and 52.6° for 6-bromo-2-naphthol (276 nm).

A molecular modeling consideration suggests that the substituted naphthalenes can be included axially and completely in β-CDx but only partially in α-CDx. The above properties (1) and (2) qualitatively predict that if a nearly long-axis polarized transition of a guest molecule gives positive ICD on complexation with β-CDx it should give negative ICD when partly included in α-CDx on the narrower rim side. In view of property 3, that is, that the sign of ICD varies at $\phi = 54.7°$, the possible regions for positive and negative ICD signs are illustrated in Figure 3. From the directions of the transition moments (Figure 2) and the regions of ICD signs (Figure 3), the theoretically predicted ICD signs can be obtained as summarized in Table 1. The calculated wavelengths are well compatible with the observed ones. For 2-methylnaphthalene, 2-chloronaphthalene, and 6-bromo-2-naphthol, Hamai tried to explain the inversion of the ICD sign by assuming deviation of the directions of transition moments from those of 2-naphthol.[10−12] However, the assumed angles of the transition moments, 95.3∼125.3° (angles described according to the definition in the present study) for the ^1L_a transition and 24.7∼54.7° for the ^1B_b transition, are in conflict with the values determined by the INDO/1 calculation, which gave angles of 52.6∼80.3 deg for the ^1L_a transition and −3.6 through −10.8° for the ^1B_b transition. A semiempirical linear combination of atomic orbitals−self-consistent field−molecular orbital−configuration interaction calculation based on the Pariser−Parr−Pople method gave 77.9° and −9.1° for the ^1L_a and ^1B_b transitions of 2-naphthol, respectively.[13] These latter values are close to the corresponding angles (64.0° and −10.8°) calculated by INDO/1 and support the reliability of the results calculated for the other naphthalene derivatives.

The present success in the interpretation of the ICD inversion phenomena proves the validity and usefulness of the general rule.

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(14) Defined such that counterclockwise rotation from the x-axis gives a positive angle.