Cotton Effect Induced in Optically Inactive Molecules and Molecular Complexes by Optically Active Environment. II. Acridine and Phenazine in Cellulose Diacetate Film

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Ultraviolet absorption spectra and induced circular dichroism (ICD) of acridine and phenazine were measured in cellulose diacetate film. The induced Cotton effect corresponding to each absorption maxima of these systems appeared. From the correspondence between the maxima of ICD and the peaks of the resolved absorption spectra, it was found that the sign of ICD is negative in the region where the molecular long-axis polarized transition plays a part in the CD induction and it is positive in the region where short-axis polarized transition does. A mechanism of CD induction tentatively proposed is that a dye molecule is imprisoned in a cage formed by an assembly of the folded chains of cellulose diacetate and the Cotton effect is induced by an electrostatic interaction between electronic transition dipole moments of the dye and of the chromophores involved in the cellulose diacetate cage.

The origin of the ICD (induced circular dichroism) spectra of optically inactive molecules dissolved in optically active medium is still controversial. The oldest explanation was a complex formation including hydrogen bonding between an achiral molecule and chiral solvent molecules,[1] but later on there have been discovered a variety of cases where the mechanism of ICD is not explained systematically. Among others, those which are worth notice are (a) due to the stereoregular arrangement of chiral host molecules such as cholesteric solvents[2] and helical biopolymers[3] along which achiral molecules are forced to line up in a regular way and (b) due to a formation of clathrates in which achiral species are imprisoned in an optically active cage.[4]

Part I of this series[5] has demonstrated that aromatic hydrocarbons and their molecular complexes embedded in acetylcellulose films exhibit the induced Cotton effect in their π-π^* absorption region and charge-transfer absorption region, respectively. The advantage of the experiment is that even very weak and/or closely overlapped vibrational bands and charge-transfer bands unresolved by the usual solution spectroscopy may be observed in such ICD spectra. We then tried to resolve vibrational bands in ICD spectra of several dye molecules in a film state and correlate them to the corresponding broad absorption spectra taken in solution. However, even when we used a high resolution spectropolarimeter together with a data processing computer, we found it difficult to resolve unambiguously each vibrational band in ICD spectra for filmed molecules which show rather broad absorption spectra in solution. Instead, we found an interesting correlation between the signs of ICD spectra and the direction of electronic transition moments of guest molecules. In the following, we report the ICD spectral feature of acridine and phenazine embedded in cellulose diacetate matrices, with specific emphasis on the correlation mentioned above.

Experimental

Acridine and phenazine, all commercial reagent grade, were purified by sublimation. Cellulose diacetate (Eastman Chemical, E-398-3, degree of polymerization 171) was used without further purification. An acetone solution of each dye was added to an acetone solution of cellulose diacetate, then the viscous solution was drawn onto a fused quartz plate and baked slowly in an oven to remove acetone. Original concentrations of the dyes and cellulose diacetate were held in the range $1—3\times10^{-4}$ mol dm^{-3}. The arrangement of the matrix, cellulose diacetate, was examined by the observation under a polarizing microscope. Films which were not opaque and showed no birefringence were selected. They were 5—15 μm in thickness with excellent transparency. The film thickness was roughly estimated from birefringence and retardation using a polarizing microscope. It was estimated that the dyes were doped at the ratio of 1:20—1:40 against the number of the sugar residues of cellulose diacetate.

Absorption spectra were taken on a JASCO UVIDEC-505 digital double-beam spectrophotometer. A JASCO model J-40S spectropolarimeter was used for the measurement of CD spectra of the sample films. In each measurement, the CD spectrum was calibrated with reference to the base line of the pure cellulose diacetate film whose thickness was identical with that of the sample film. An S/N ratio in a CD spectrum was improved by using a JASCO data processing machine DP-500 through repeated runs.

Results and Discussion

The UV and CD spectra of acridine embedded in a cellulose diacetate film are shown in Figs. 1 and 2 and those of phenazine in Figs. 3 and 4. The thickness of the sample film was 8 μm for acridine and 15 μm for phenazine when the spectra were taken in the longer wavelength region (280—500 nm), and it was 7 μm for acridine and 5 μm for phenazine when the spectra were taken in the shorter wavelength region (200—300 nm). The scales of the ordinate are the ellipticity (θ) for CD and the optical density (*O.D.*) for UV spectra. These quantities were not converted into the corresponding molecular characteristics, *i.e.*, molecular extinction coefficient and molecular ellipticity, since the thickness and concentration of each sample film could not be determined accurately. Incidentally, the same dyes dissolved in an acetone solution of cellulose diacetate did not show any induced Cotton effect.

The overall UV spectra of acridine and phenazine

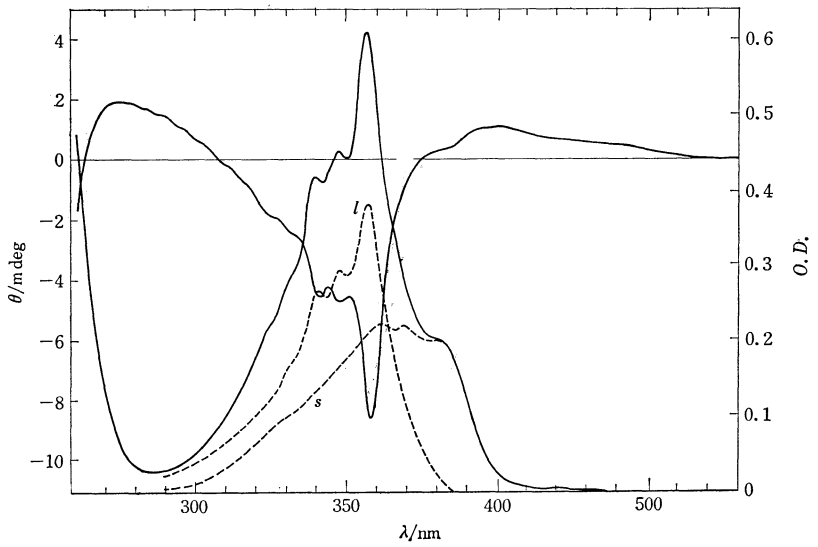

Fig. 1. UV and CD spectra of acridine in cellulose diacetate film in longer wavelength region. Film thickness: 8 μm. Dotted curves show the resolution of UV spectrum into the components of molecular long-axis polarized (*l*) and short-axis polarized (*s*) transitions.

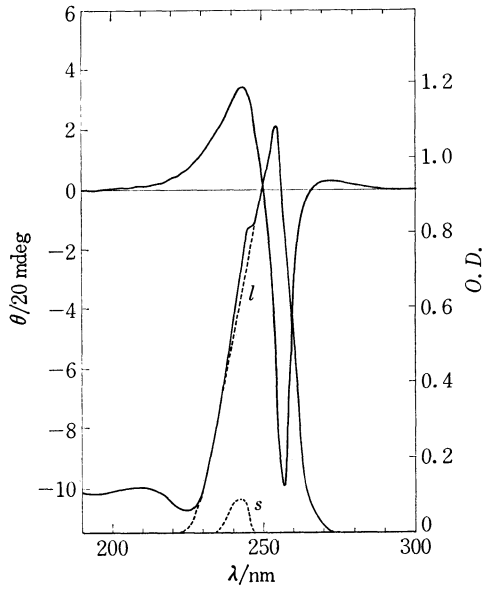

Fig. 2. UV and CD spectra of acridine in cellulose diacetate film in shorter wavelength region. Film thickness: 7 μm. Dotted curves are the same as in Fig. 1.

in film states shown in Figs. 1—4 are not very much different from those observed in CCl_4 and ethanol solutions; the overall spectral shifts to the red are 200 cm^{-1} at most. We also measured the infrared spectra of the sample films, which were not very much different (1—3 cm^{-1}) from those of the corresponding dyes in solution and in powder states. These suggest that the dye molecules embedded in cellulose diacetate films are the same and/or the like surroundings as those in solution. The calibration of CD curves with reference to the base line of the pure cellulose diacetate film is important, since cellulose diacetate itself has optical activity. The UV absorption and CD spectra of a typical cellulose diacetate film (thickness 10 μm) are shown in Fig. 5.

As seen in Figs. 1 and 2, the ICD spectrum of acridine is divided into five bands; a weak and trailing positive band peaked at around 400 nm (band I), an intense negative band whose vertex lies at 358 nm, being spread over 6000 cm^{-1} and rich in vibrational structures (band II), a weak positive band at 265—310 nm (band III), an intense and sharp negative band at 257 nm (band IV), and a positive band centered at 243 nm (band V). From Figs. 3 and 4, the ICD spectrum of phenazine is analyzed into the following; a weak and trailing positive band whose peak lies at around 405 nm (band I), an intense and broad negative band centered at 366 nm (band II), a medium positive band at 276 nm (band III), an intense and sharp negative band peaked at 255 nm (band IV), and a rather strong positive band whose maximum lies at 242 nm (band V).

It is well known that in these dye molecules the relatively weak ^1L_b bands (molecular long-axis polarized) overlap with the intense ^1L_a bands (short-axis polarized) in the wavelength region 300—400 nm, and the very weak ^1B_a bands (short-axis polarized) are hidden in the very intense ^1B_b bands (long-axis polarized) in the wavelength region 200—300 nm.[6] Furthermore, the longer wavelength region of these bands might be overlapped with very weak $n\rightarrow\pi^*$ bands. Since there has been made no accurate experimental analysis so far, we tentatively try to resolve the overlapped bands into their components, consulting the dichroic spectral analyses of these dyes embedded in stretched poly (vinyl alcohol) sheets made by Inoue *et al.*[7] The divided spectra of acridine and phenazine are shown by the dotted lines in Figs. 1—4, where we have paid no regard for $n\rightarrow\pi^*$ transitions.

From these band resolutions, we can safely say that in acridine and phenazine bands II and IV (negative) correspond to the long-axis polarized ^1L_b and ^1B_b bands, respectively. Band II of acridine has a detailed

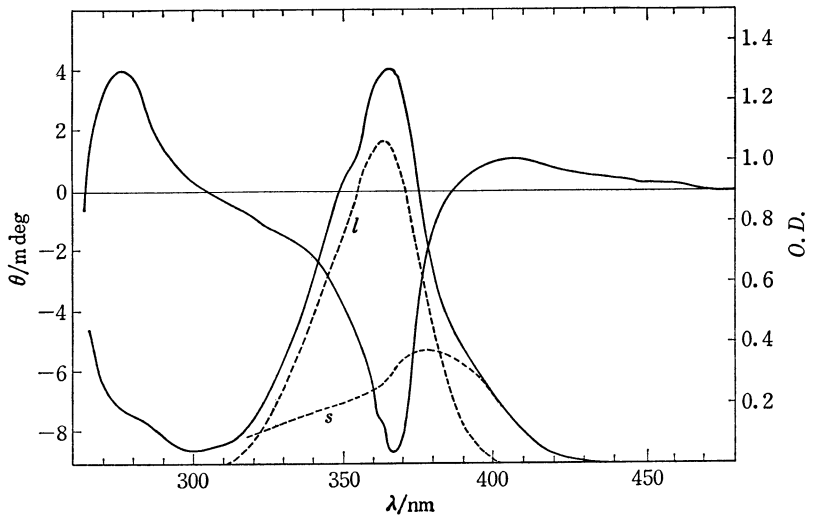

Fig. 3. UV and CD spectra of phenazine in cellulose diacetate film in longer wavelength region. Film thichness: 15 μm. Dotted curves are the same as in Fig. 1.

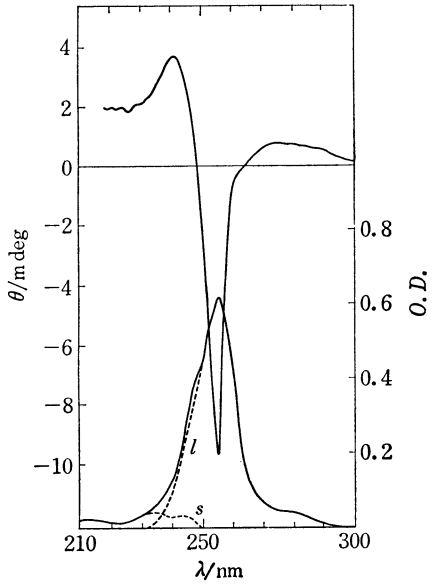

Fig. 4. UV and CD spectra of phenazine in cellulose diacetate film in shorter wavelength region. Film thickness: 5 μm. Dotted curves are the same as in Fig. 1.

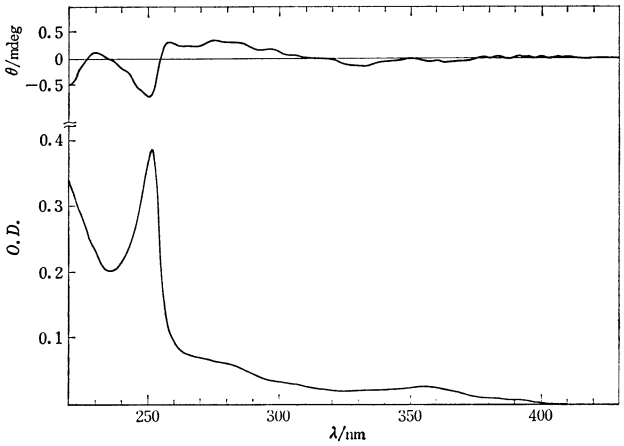

Fig. 5. UV and CD spectra of pure cellulose diacetate film.

structure, the ellipticity of each minimum being roughly proportional to the intensity of the corresponding vibrational absorption maximum in the UV spectrum. The peak of band I in the acridine film keeps at a distance from the maximum of the short-axis polarized ^1L_a transition, though the separation is not very large (*ca.* 2000 cm^{-1}), and its magnitude of ellipticity is too small if the origin of band I is assigned to be ^1L_a. This is probably because the originally rather intense positive band due to ^1L_a, which might be assumed to have a peak at around 370 nm, is partly cancelled out by very intense band II and then the resultant overlapped bandshape of Fig. 1 is observed. The same explanation applies to band I of the phenazine film (Fig. 3).

Band V of both acridine and phenazine is tentatively assigned to have an origin in the short-axis polarized ^1B_a transition. The question why the ellipticity of band V is so large while the resolved ^1B_a is very weak remains untouched. More inexplicable situation is the case of band IV. In the phenazine film, there appears a shoulder at about 280 nm in the absorption spectrum which roughly corresponds to the positive maximum of band III. Incidentally, such a shoulder is not observed in the solution spectrum of pure phenazine and phenazine+cellulose diacetate. On the contrary, even a shoulder does not appear in the 260—290 nm region of the absorption spectrum of the acridine film.

The whole spectral features mentioned above are summarized in Table 1. An obvious fact is that the long-axis polarized transition induces a *minus* CD and the short-axis polarized transition a *plus* CD. Furthermore, it may be safely said that the intensities of ICD bands I, II, and IV are proportional to those of the corresponding absorption spectra which have origins of CD induction.

We now discuss about a mechanism of the ICD in the present systems. A possibility of forming a charge-transfer complex between cellulose diacetate and the dye molecules is scarce, since we have not

Table 1. Correlation between the sign of induced circular dichroism (ICD) and the direction of polarization of allowed transitions

Band	$\frac{CD_{max}}{nm}$	CD sign	$\frac{\lambda_{max}}{nm}$	Direction of polarization	Tentative assignment
Acridine					
I	≈400 (w) [a]	+	370 (s)	short-axis	B_1
II	358 (s)	−	358 (s)	long-	A_1
III	275	+			
IV	257 (vs)	−	254 (vs)	long-	A_1
V	243 (s)	+	243 (vw)	short-	B_1
Phenazine					
I	≈405 (w)	+	380 (m)	short-	B_{2u}
II	366 (s)	−	365 (s)	long-	B_{1u}
III	265 (m)	+	(280) [b]		
IV	255 (vs)	−	255 (vs)	long-	B_{1u}
V	242 (m)	+	242 (vw)	short-	B_{2u}

a) Letters in parentheses are abbreviations for spectral intensities. b) A weak shoulder.

observed any absorption and CD spectra that are expected to be caused by a charge-transfer mechanism. Next, it is possible that the matrix partially forms a spatially regular helical structure along which the dye molecules are lined up just as mentioned in item (a) of the early paragraph. The entire cellulose diacetate matrix may be composed of a part where the cellulose chains line up regularly, probably in a helical structure in a certain spot, and a part where such chains are folded for some reason.[8] However, there were not enough dye molecules in our sample to induce CD through the dipole-dipole interaction between the helically stacked and/or intercalated dye molecules. Of course, it is still possible that the sparsely embedded dye monomer exhibits an ICD, being involved in a complicated interaction with the asymmetric environment of the matrix.[9] It will be mentioned later that even this will not be the case.

The remaining possibility is item (b) mentioned in the early paragraph. Our tentative model structure is that the dye molecule is imprisoned in a cage of a suitable spatial extent formed by an assembly of the folded chains of cellulose diacetate, and the Cotton effect is induced in the allowed transition region of the dye molecule due to the asymmetric perturbation of cellulose diacetate. It is hard to make proof of this model, but the following consideration might be of service to credit that the model is not an offhand one. First, the CD spectral shapes look closely like those induced in the β-cyclodextrin cage in which case we have succeeded in predicting the signs and magnitudes of ICD by making use of an approximate polarizability theory.[10] If a geometrical conformation of the cellulose diacetate cage were known, the very similar method could be applied to the present system in order to guess the ICD signs and intensities. Second, the relationship between the signs and intensities of the ICD spectra and the UV absorption spectral intensities in the present system can be compared with that observed for the DNA–dye and the RNA–dye systems.[9] In the latter systems we found two types of induced Cotton effect; one appearing at low P/D ratios (DNA phosphate residue/dye concentration) results from an interaction between dye dimers aggregated along the nucleic acid helices, which shows a quite different CD spectral feature from that of the present system, and the other appearing at high P/D ratios is probably due to an interaction between a dye monomer and an asymmetric perturber in DNA, which yields a CD spectral shape that closely resembles the present case. In the present study, we tried to find out whether the shape, sign, and intensity of the ICD are dependent on concentration, but we could not succeeded in getting a transparent film when the concentration of the dyes was increased. There is an evidence from polarized infrared measurements of a cellulose triacetate film that the folding of the cellulose chain occurs at a certain temperature in the vicinity of room temperature;[11] this fact suggests the existence of a spatial cavity in a cellulose film, either a perfect cage or mere vacant space.

At this stage of discussion, we must mention about our experimental detail, because there has often been asked the difficult problem of whether a strain effect remaning even in an unstretched film produces a spurious CD spectrum due to the linear dichroism of the sample;[12] the usual spectropolarimeter is unable to exclude a considerable amount of the linearly polarized beam passing through a sample. Strictly speaking, every film tested had an anisotropic portion which showed somewhat different absorption spectra when a linearly polarized light was illuminated and the film was rotated perpendicularly to the incident light. However, about two third of the whole surface of a good film selected under the inspection of a polarizing microscope were isotropic with regard to a linearly polarized light, and UV and CD spectra were obtained with reproducibility of 2%. These spectral data were not dependent on the film thickness (3—20 μm) and the dye and cellulose diacetate concentrations (1—8 $\times$ 10^{-4} mol dm^{-3} in acetone). We did not investigate the rate of vaporization of acetone, though it was considered to be important in order to prepare a film which is most suited for the study of this type. In-

cidentally, a sample made by immersion of the pure cellulose diacetate film in an acetone solution of the dyes did not show any CD spectrum. This way of preparing films are usally used in a linear dichroism observation for dyes embedded in stretched polymer films.[7,13] Therefore, the phenomenon demonstrated in the present article is not ascribable to a regular arrangement of the dye adhered to a distorted matrix as mentioned before.

Looking at a problem of CD induction in the present system from all angles just as mentioned hitherto, it admits of no doubt to believe that the circular dichroism to be induced in optically inactive molecules by optically active matrices is due to a complex formation between one molecule and one certain segment of the matrix. If this segment forms a cage in which the optically inactive molecule is imprisoned, the situation will be more favarable, though this is not a necessary condition. A direct mechanism of appearance of the ICD spectrum then is attributable to an electrostatic interaction between electronic transition dipole moments of the included molecule and of the chromophores involved in the segment cage. Unfortunately, a quantitative comparison between the signs and intensities of the observed ICD bands and those to be predicted along this line of theoretical consideration cannot be made unless a definite atomic arrangement of the cage in a film state is known. On the other hand, we will be able to do this with a clathrate compound whose three dimensional structure has been determined accurately and/or can be guessed without ambiguity. One of such systems is the clathrate between β-cyclodextrin and aromatic compounds, an analytical result of which will be presented soon.[10]

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