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Cotton Effect Induced in Optically Inactive Molecules and Molecular Complexes by Optically Active Environment. I. Pyrene, TCNNQ, and Their Molecular Complex in Acetylcellulose Film

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Ultraviolet absorption spectra, induced optical rotatory dispersion and circular dichroism of pyrene, TCNNQ, and their molecular complex were measured in acetylcellulose film and solution. The Cotton effect corresponding to each absorption maximum of these systems appeared. A perturbation of excited states of these molecules and their complex due to an asymmetric environment of acetylcellulose might be of paramount importance in producing a non-zero rotational strength in the corresponding molecular absorption region. The second charge-transfer band was clearly detected in the differential optical rotatory dispersion spectrum of the TCNNQ-pyrene molecular complex embedded in an acetylcellulose film. The method was shown to be promising in detecting very weak and closely overlapped transitions in various molecules.

Several works have appeared demonstrating the Cotton effect induced in various optically inactive molecules by optically active solvents.[1–5] Racemic or symmetric metal complexes were found to exhibit pronounced circlular dichroism (CD) sepctra in the region of their *d-d* absorptions when they were dissolved in optically active alcohols, usually diols.[1,2] In similar solvents, ketones, both aliphatic and aromatic, were also investigated in detail and confirmed to have a single (sometimes a double or more) CD spectrum induced around their $n\to\pi^*$ transition region.[3–5]

The precise mechanism of the phenomenon is still unkown but certain inferences have been made. One is that CD may be induced by a dissymmetric potential due to a solvent. Originally, hydrogen bonding was supposed to be the main origin,[1–3] but later it was found that such associative forces including hydrogen bonding are not a prerequisite since induced CD is observed also in the $n\to\pi^*$ absorption region of some nitrite or nitrate dissolved in optically active solvents.[4,5] The other explanation was that molecules like ketones are probably solvated into some dissymmetric configurations making themselves optically active.[3]

In this paper, we show that aromatic hydrocarbons in acetylcellulose film and solution also exhibit induced Cotton effect in their $\pi\to\pi^*$ absorption region. To the best of our knowledge no work has been reported on the induced optical activity for $\pi\to\pi^*$ transitions of aromatic molecules. Furthermore, we show that similar effects can be observed for a donor-acceptor type molecular complex in their charge-transfer absorption region.

Experimental

Pyrene, commercial reagent grade, was purified by recrystallization and sublimation. TCNNQ (11,11,12,12-tetracyano-1,4-naphthaquinodimethane) was synthesized by the method reported by Chantterjee[6] and purified by repeated recrystallization from methanol and methylenechloride, followed by vacuum sublimation. The pyrene-TCNNQ molecular complex was prepared from the purified pyrene and TCNNQ by simultaneous sublimation onto a heated glass plate.

The materials were first added to an acetone solution of acetylcellulose of commercial grade used as a matrix without further purification. The viscous solution was then drawn onto a fused quartz plate and baked in an oven to remove actone. Films approximately 5—15 μ in thickness with excellent transparency were obtained. The sample concentration in a film state was estimated from the measured density of acetylcellulose and was held in the range 10^{-2}–10^{-3} M. The film thickness was roughly estimated from birefringence and retardation using a polarizing microscope.

A Jasco ORD/UV/CD-5 spectrophotometer was used for the measurement of electronic absorption, ORD, and CD spectra of the samples. In each measurement, the ORD datum was calibrated with reference to the base line of the pure acetylcellulose film whose thickness was identical with that of the sample film. This was because acetylcellulose itself has a large negative rotatory dispersion. Similar measurements were carried out for the samples dissolved in an acetone solution of acetylcellulose.

Results and Discussion

The ultraviolet absorption (UV), ORD, and CD spectra of pyrene in an acetylcellylose film are shown in Fig. 1. The sample film used was 5μ in thickness and estimated to contain 5.3×10^{-2} M pyrene. The scales of the ordinate are the optical density(a vertical bar shown in the figure), the angle of rotation in degree (ϕ) and the circular dichroic optical density (ΔD), respectively, for the UV, ORD, and CD spectra. These quantities were not converted into the corresponding molecular characteristics, *i. e.*, molecular extinction coefficient, molecular rotation, and molecular ellipticity, since the concentration and thickness of each sample film could not be determined accurately.

The over-all UV spectrum shown in Fig. 1 is displaced to the red approximately by 300 cm^{-1}, compared to that observed in an ethanol solution. This suggests that the pyrene molecule embedded in an acetylcellulose film is in the same and/or the like surroundings as that in solution. Corresponding to each absorption maximum, namely to each vibrational

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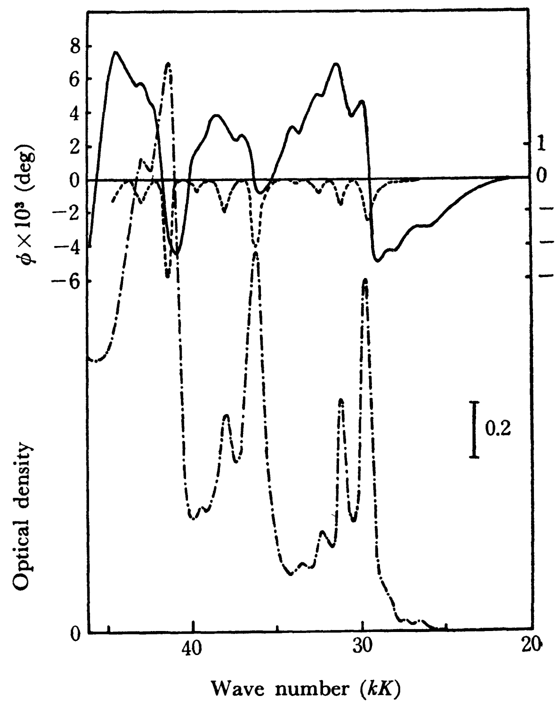

Fig. 1. UV (—·—·), ORD (——), and CD (······) spectra of pyrene in acetylcellulose film. Film thickness: 5 μ; concentration of pyrene: 5.3×10^{-2} M. A vertical bar indicates the scale of optical density.

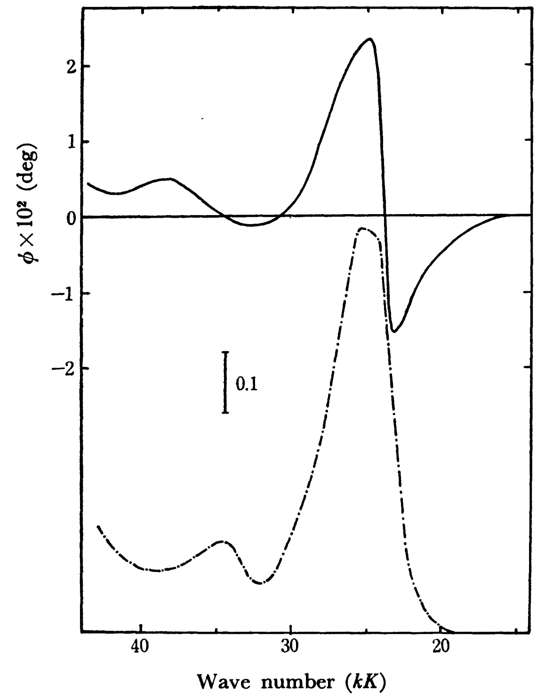

Fig. 2. UV (—·—·) and ORD (——) spectra of TCNNQ in acetylcellulose film. Film thickness: 14μ; concentration of TCNNQ: 1.5×10^{-2} M. A vertical bar indicates the scale of optical density.

spectrum of the ^1L_b, ^1L_a, ^1B_b, and ^1B_a bands of pyrene, a negative CD Cotton effect appears, the circular dichroic optical density of each minimum being roughly proportional to the intensity of the corresponding vibrational absorption maximum.

We have confirmed that the experimental ORD spectrum, though appearing somewhat complicated, can be well reproduced from the experimental CD spectrum, or *vice versa*, by the use of the Kronig-Kramers transform.[7] Only exception for this is the frequency region 26—29 kK where no CD spectral detail was detected as seen in Fig. 1. However, if more concentrated film of pyrene could be obtained, the respective vibrational transitions in this spectral region would show single negative CD absorptions.[8]

Fig. 2 shows the UV and ORD spectra of TCNNQ embedded in the acetylcellulose film of 14 μ thickness. The sample film contains approximatley 1.5×10^{-2} M TCNNQ. The UV absorption spectrum in this frequency region is in line with that observed in methylenechloride solution.[9] We have shown that the 25.3 kK absorption band corresponds to the lowest $\pi\rightarrow\pi^*$ B_2 transition polarized along the molecular longer axis (axis joining the carbon atoms of the 1- and 4-positions) and the weak 34.7 kK band to the next to the lowest $\pi\rightarrow\pi^*$ A_1 transition polarized along the molecular short axis.[9] As can be seen in Fig. 2, the respective $\pi\rightarrow\pi^*$ transitions show a sinlge negative Cotton effect, its rotational strength being roughly proportional to the corresponding dipole strength. A negative CD spectrum for each transition, which was originally expected to appear, was not detected under the present experimental conditions due to the low TCNNQ concentration. When the concentration of TCNNQ was increased, an induced CD spectrum, not a single negative but a double, was observed corresponding to each transition. It is thus found that the shape and intensity of the induced Cotton effect is markedly dependent on concentration. The situation is quite similar to that produced, for example, by nucleic acid-dye interactions in solution.[10,11] A monomer-dimer equilibrium of TCNNQ in sample films seems to play an important part.

The UV and ORD spectra of the pyrene-TCNNQ molecular complex in an acetylcellulose film are shown in Fig. 3. The thickness of the film was 10μ. In the lower frequency region beyond the strong 25.3 kK band of TCNNQ, the UV spectrum has one weak and broad band whose maximum is located at 15.3 kK and can be assigned to a charge-transfer band.[12] The ORD spectrum demonstrates the existence of some other bands at around 20 kK.

If we subtract the component ORD spectra of pyerne and TCNNQ from the ORD spectrum of the pyrene-TCNNQ complex, we obtain the plot in Fig. 4 (*differential* ORD spectrum), in which there remain two negative and one strong positive Cotton effect. This suggests that the first charge-transfer band is located at 15.5 kK, the second at around 23 kK, and the other strong band whose maximum is approximately at 27 kK is ascribed to an interaction between the component molecules.

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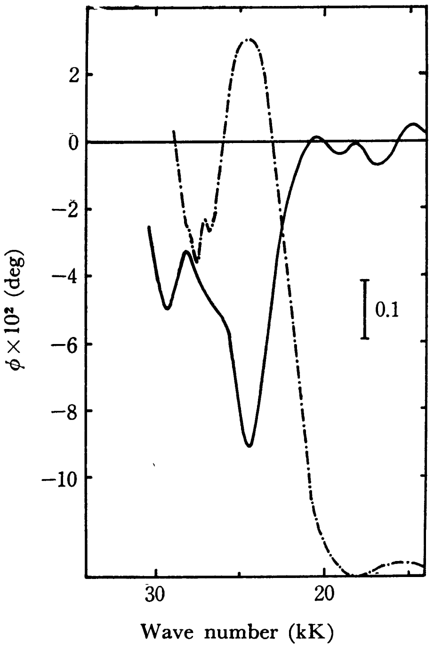

Fig. 3. UV (—·—·) and ORD spectra of the TCNNQ-pyrene molecular complex in acetylcellulose film. Film thickness: 10μ. A vertical bar indicates the scale of optical density.

According to our recent work on the polarized absorption spectrum of a pyrene-TCNNQ molecular complex crystal, the first charge-transfer band is found at 14.6 kK and the second charge-transfer band at 21.9 kK at room temperature.[13] The agreement is thus fairly good as to the location of the two charge-transfer bands, considering possible band shifts in solution and crystal. Though the 27 kK band can be seen as a tiny peak in Fig. 3, its origin is hard to guess. Even supposing that the peak is directly connected with the higher frequency side large Cotton component (negative and the absorption center is 27 kK) of the differential ORD spectrum (Fig. 4) and that this is induced from an inter-molecular interaction, it is inexplicable why such a large Cotton component is revealed.

The ORD and CD spectra of pyrene measured in an acetone solution of acetylcellulose were almost exactly the same as those in film, though whole spectral features were extremely obscure. It was confirmed that such optical activity is not induced for pyrene embedded in films of optically inactive polymers such as polyethylene and polystyrene. The situation is the same for the ORD spectra of TCNNQ and of the pyrene-TCNNQ molecular complex. These facts suggest that the induced optical activity is acribed *not* to distortion of molecular frames of the sample molecule and/or arrangement of the molecule in a crystalline state, but to dissymmetric potentials exerted by an optically active matrix.

Besides the fact that not only the intensity but also the shape of these induced ORD and CD spectra are strongly dependent on concentration, all their features remind us of the nucleic acid-dye interactions in solution.[10,11] If the induced Cotton effect in both cases is a general phenomenon caused by the same origin, the following interpretation might be right. A perturbation of molecular excited states (and possibly a ground state) due to an asymmetric environment of a matrix material may be of paramount imoprtance in producing non-zero matrix elements of electric and magnetic transition dipole moments for the molecule. The non-zero matrix elements yield a non-zero rotational strength at the molecular vibrational absorption region. Such an interaction more or less occurs whenever dissymmetric potentials exist, regardless of molecular species and molecular arrangement in matrix materials.[14] However, such problems as why the signs of all the CD bands of pyrene are negative, or why there is a sign reversal in the CD spectrum of TCNNQ, cannot be understood without consideration of the relative orientation of interacting units.[10]

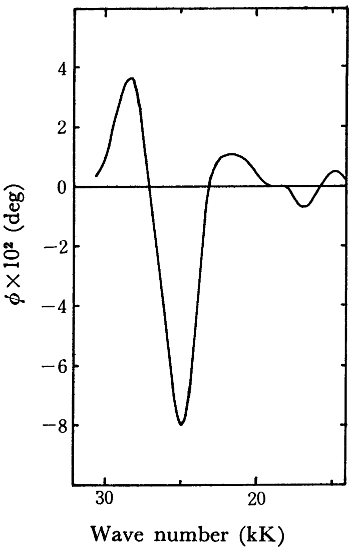

Fig. 4. The differential ORD curve for the TCNNQ-pyrene molecular complex.

The advantage of the present method is that many absorption bands in large molecules, even very weak and/or closely overlapped vibrational bands unresolved by the usual solution spectroscopy, may be observed in the corresponding induced CD and ORD spectra. In particular, very weak charge-transfer bands in donor-acceptor type charge-transfer complexes are detected with high probability and accuracy. A good example is the second charge-transfer band of the TCNNQ-pyrene molecular complex mentioned above, which was observed with difficulty in the single crystalline state of the complex.[12,13] The present method is thus considered superior to the usual microspectrophotometry, the technique for which is troublesome and a clear-cut spectrum rarely obtained.

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