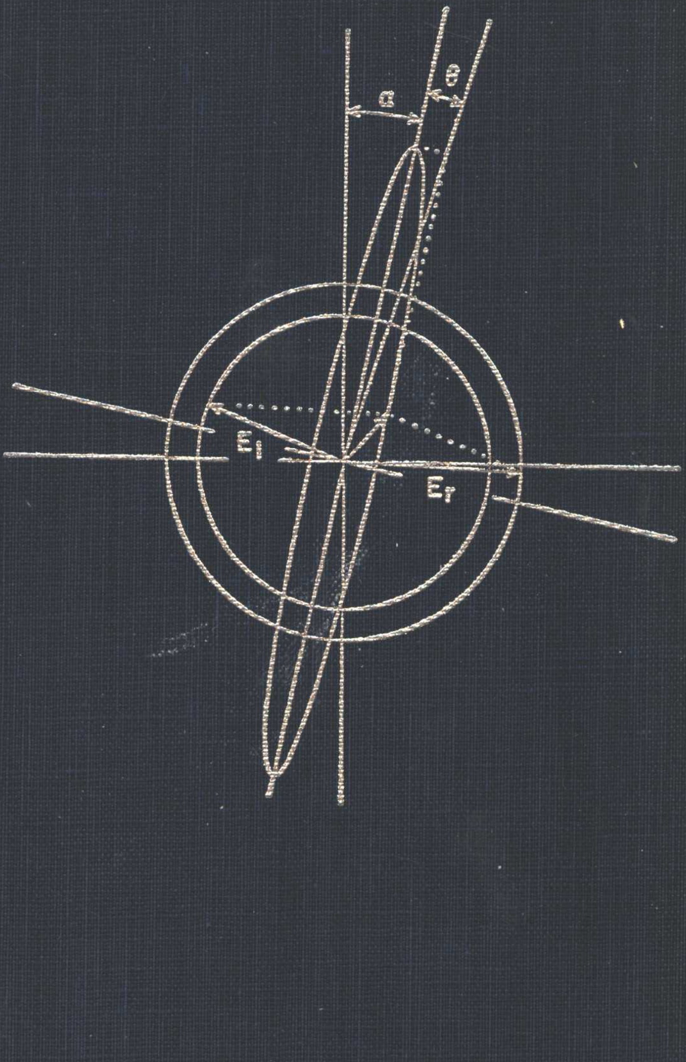
CIRCULAR DICHROIC SPECTROSCOPY
EXCITON COUPLING IN ORGANIC STEREOCHEMISTRY



CIRCULAR DICHROIC SPECTROSCOPY

— EXCITON COUPLING IN ORGANIC STEREOCHEMISTRY —

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PREFACE

Although optical rotational data, recorded in the familiar form of $[\alpha]_D$, is one of the oldest of the physical constants, chiroptical properties were not used as a modern structural tool until the 1950's when the methods of optical rotatory dispersion and circular dichroism were revived by C. Djerassi and L. Velluz/ M. Legrand, respectively. However, relative to other physical data, there exists a large psychological barrier in the daily use of chiroptical properties. One reason for this may be the large element of empiricism, or the unfilled gap between practical data and theory.

The chiral through-space interaction between two or more chromophores, the thesis of this monograph, is based on the coupled oscillator method, and together with the X-ray Bijvoet method, enables one to determine the absolute configurations of organic compounds without reference to authentic cases. The theory was developed in the 1930's by W. Kuhn (coupled oscillator theory) and J. G. Kirkwood (group polarizability theory), and subsequently extended by W. Moffitt, I. Tinoco, Jr., J. A. Schellman (biopolymers), S. F. Mason (dimeric alkaloid), B. Bosnich (inorganic complex) and others.

The application of the coupled oscillator method to various natural products, which we have termed "the exciton chirality method", is in most cases straightforward; it can also be used for a variety of other purposes besides absolute configurational studies. We have attempted to *illustrate* the application of this versatile method by quoting in many cases figures from our own measurements; many of the data are unpublished. In the last three chapters, the coupled oscillator theory is described in a language more understandable to organic chemists; however, an understanding of the theory is not necessary for the actual usage of the method.

Naturally, we would more than welcome any criticism regarding the handling and interpretation of data.

We acknowledge the following for permission to adapt published Figures.

Bulletin of the Chemical Society of Japan	Figure 2-4, 2-5
Journal of the American Chemical Society,	Figure 2-6, 3-29
Journal of the Chemical Society, Perkin Transaction 1,	Figure 3-35
The Chemical Society of Japan/Maruzen, Tokyo, 1965: Jikken Kagaku Koza, Zoku, vol. 11, "Electronic Spectroscopy,"	Figure 2-3
American Medical Association, Chicago, 1970: D. W. Urry, "Spectroscopic Approaches to Biomolecular Conformation,"	Figure 8-1
Benjamin, New York, 1965: N. J. Turro, "Molecular Photochemistry,"	Figure 11-11

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I. CHIRAL EXCITON COUPLING AND CIRCULAR DICHROIC SPECTRA

1-1. Introduction

Organic molecules with π-electron systems interact with the electromagnetic field of ultraviolet or visible light to absorb the resonance energy corresponding to the energy gap between the ground and excited states. The UV and visible absorption spectra[1] of a variety of π-electron chromophores have been extensively studied and utilized for the acquisition of chemical information; conjugated or isolated double or triple bonds, hetero-double bonds such as C=O or C=N-, and aromatics are familiar chromophores in organic chemistry.

Similarly, circular dichroic spectroscopy (CD spectra)[2] of optically active compounds is a powerful method for studying three-dimensional structures of organic molecules. Namely, the method provides information on the absolute configuration, conformation, reaction mechanism, etc.

The electronic absorption and circular dichroic spectra are mostly determined in the solution state, but occasionally in the gas phase as well. These spectra result from the interaction of the individual chromophore of each molecule with the electromagnetic field of light, the interaction with neighbouring molecules being negligible. For example, in the case of a solution of 10^{-4} mol/L concentration, which is suitable for UV determination of compounds having $\varepsilon = 10^4$, the average intermolecular distance is longer than 100 Å; i.e., greater than the size of common organic molecules so that solute-solute interactions can be neglected. Moreover, since molecules in solution are tumbling and randomly oriented, the mutual interaction between two molecules which is approximated by dipole-dipole interaction is negligible.

On the other hand, let us consider the changes in UV and CD spectra that may be anticipated by chromophore-chromophore interaction when aggregate systems, i.e., dimer, trimer, ..., oligomer, polymer, and molecular crystals interact with light. For example, in the case of a molecule having two identical chromophores (i and j) connected by σ-bonds in some orientation (Figure 1-1), the two chromophores are brought to an excited state by the same probability. Namely, the probability of the state of excited chromophore i is exactly equal to that of the state of excited chromophore j; therefore mixing of the two state gives the excited state of the whole system. In other words, the excited state (exciton)[3] delocalizes between the two chromophores i and j, just as in the case of electron delocalization in an ethylene double bond.

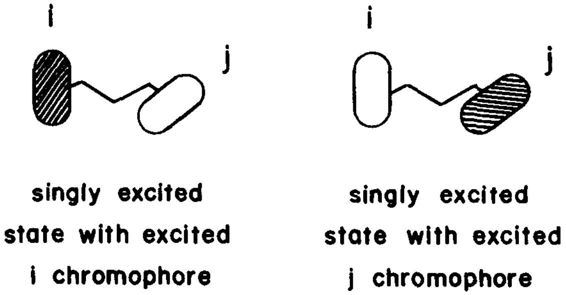

Figure 1-1. The excited state (exciton) delocalizes between two chromophores i and j.

The present interaction between excited states of chromophores — i.e., exciton coupling — was first studied in the field of electronic spectra of ionic or molecular crystals, and the theory of exciton coupling[4] was successfully applied to explain the so-called Davydov splitting in electronic absorption spectra. In the field of optical activity of chiral compounds, Kuhn and Kirkwood[5] had investigated group-group interactions and proposed the coupled oscillator theory and the group polarizability theory, respectively, which have been extended to the chiral exciton coupling mechanism.

The exciton mechanism has been successfully employed in the studies of chiroptical properties of biopolymers,[6-8] (i.e., proteins, polypeptides, nucleic acids, oligonucleotides, dyes adsorbed on biopolymers, etc), and inorganic metal complexes;[9] it has also been the subject of theoretical treatments.[10,11] Similarly, in the field of organic chemistry, circular dichroism due to the exciton coupling mechanism provides useful and unambiguous information on absolute configuration and conformation.[12-26, 38-46] Since the chiral exciton coupling method is based on sound theoretical calculation, as will be shown in later chapters, the absolute stereochemistry of organic compounds exhibiting typical split CD Cotton effects due to chiral exciton coupling is assignable in a nonempirical manner. The method has thus been extensively used for determining the absolute configuration of natural and synthetic organic compounds.

In the following section we will attempt to explain the mechanism of chiral exciton coupling in CD spectroscopy and the nonempirical nature of the method, and review recent developments of the present method in organic chemistry.

1-2. General Features of the Exciton Chirality Method in CD Spectroscopy and Definition of Exciton Chirality

General features and requirements of the exciton chirality method[18] in CD spectroscopy are as follows:

1. Two identical chromophores exhibiting strong $\pi\to\pi^*$ absorption are located in chiral positions with respect to each other, as exemplified by the dibenzoate depicted in Figure 1-2.

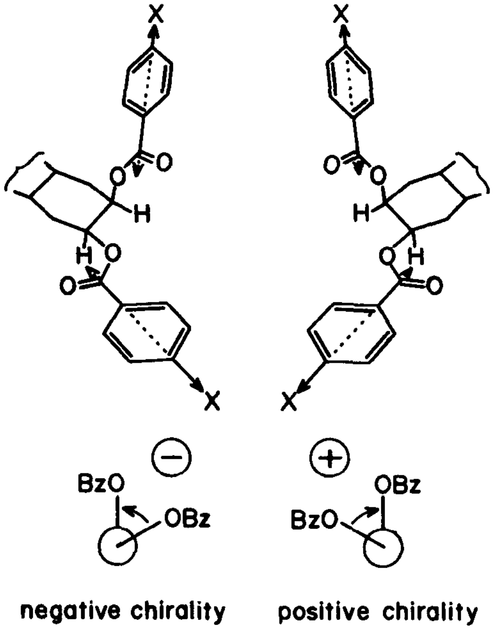

Figure 1-2. Chiralities of α-glycol dibenzoates. [Reprinted from reference 18.]

2. The exciton interaction between the two chromophores i and j splits the excited state into two energy levels, as shown in Figure 1-3. The energy gap $2V_{ij}$ is called the Davydov splitting.

3. Excitations to the two split energy levels generate Cotton effects of mutually opposite signs. As illustrated in Figure 1-4, this leads to a CD spectrum with two component Cotton effects of opposite signs which are separated by the energy gap $\Delta\lambda$ (Davydov splitting). Summation of the component Cotton effects results in the solid curve having two extrema. The extremum at longer and shorter wavelengths are called, respectively, the first Cotton effect and the second Cotton effect. In the case of ORD spectrum, three extrema are obtained by summation, as shown in Figure 1-4.

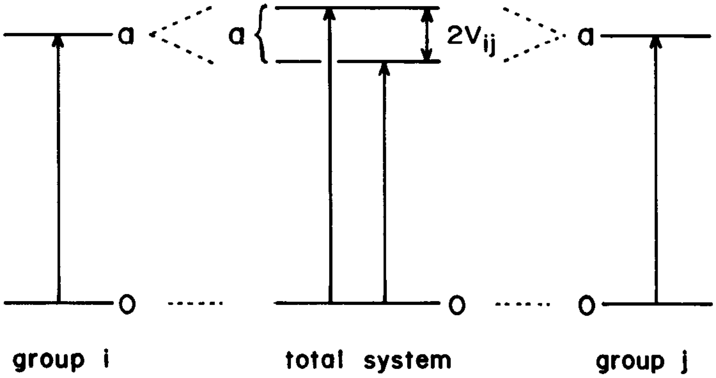

Figure 1-3. By exciton interaction between the two chromophores i and j, excited state splits into two energy levels. The energy gap $2V_{ij}$ *is called Davydov splitting.*