

COMPREHENSIVE CHIROPTICAL SPECTROSCOPY

Applications in Stereochemical Analysis of Synthetic
Compounds, Natural Products, and Biomolecules

VOLUME TWO

EDITED BY

NINA BEROVA • PRASAD L. POLAVARAPU
KOJI NAKANISHI • ROBERT W. WOODY

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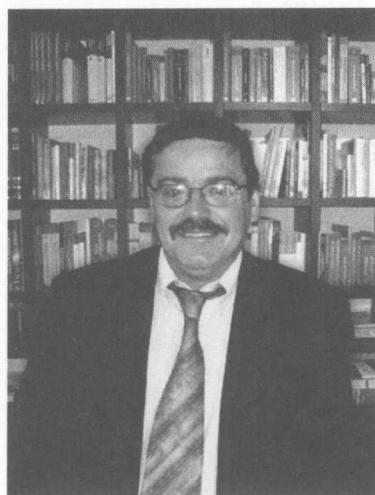
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COMPREHENSIVE CHIROPTICAL SPECTROSCOPY

Volume 2

IN MEMORY OF CARLO ROSINI (1948–2010)



Carlo Rosini obtained his degree in Chemistry (1973) at the University of Pisa, where he completed his thesis on the stereochemistry of Ni(II) complexes. He entered the Italian CNR by joining the group of Professor Piero Salvadori and the research on determination of absolute configuration by Circular Dichroism. Later on, Carlo Rosini spent two years (1977–1979) at the King's College in London, under the supervision of Professor Stephen F. Mason. During this period he studied polarized-light-based spectroscopy and its application to structural determinations. He was appointed as associate professor (1992) at the University of Pisa and then as a full professor (1997) at the University of Basilicata, Potenza. The field of chirality was fundamental to the scientific activity of Carlo Rosini. His broad scientific interests included many aspects of organic stereochemistry, like asymmetric organic synthesis, chiral discrimination mechanisms, chiral stationary phases for enantioselective chromatography, and structural characterization of organic molecules by Circular Dichroism. The last research projects of Carlo Rosini were oriented toward chemical/computational approaches for the determination of absolute configuration by linking experimental and theoretical studies.

We miss his enthusiasm and his charisma, but we will remember his life and his contributions to the science and the chemical community.

Carlo Rosini was one of the first scientists who accepted to contribute a chapter to this volume. Although his premature and tragic death prevented his submission, his spirit never died and is now, not only in the chapter contributed by his co-workers and former students, but also in the minds of all of us who had the privilege to know him and collaborate with him.

PREFACE

Chirality is a phenomenon that is manifested throughout the natural world, ranging from fundamental particles through the realm of molecules and biological organisms to spiral galaxies. Thus, chirality is of interest to physicists, chemists, biologists, and astronomers. Chiroptical spectroscopy utilizes the differential response of chiral objects to circularly polarized electromagnetic radiation. Applications of chiroptical spectroscopy are widespread in chemistry, biochemistry, biology, and physics. It is indispensable for stereochemical elucidation of organic and inorganic molecules. Nearly all biomolecules and natural products are chiral, as are the majority of drugs. This has led to crucial applications of chiroptical spectroscopy ranging from the study of protein folding to characterization of small molecules, pharmaceuticals, and nucleic acids.

The first chiroptical phenomenon to be observed was optical rotation (OR) and its wavelength dependence, namely, optical rotatory dispersion (ORD), in the early nineteenth century. Circular dichroism associated with electronic transitions (ECD), currently the most widely used chiroptical method, was discovered in the mid-nineteenth century, and its relationship to ORD and absorption was elucidated at the end of the nineteenth century. Circularly polarized luminescence (CPL) from chiral crystals was observed in the 1940s. The introduction of commercial instrumentation for measuring ORD in the 1950s and ECD in the 1960s led to a rapid expansion of applications of these forms of chiroptical spectroscopy to various branches of science, and especially to organic and inorganic chemistry and to biochemistry.

Until the 1970s, chiroptical spectroscopy was confined to the study of electronic transitions, but vibrational transitions became accessible with the development of vibrational circular dichroism (VCD) and Raman optical activity (ROA). Other major extensions of chiroptical spectroscopy include differential ionization of chiral molecules by circularly polarized light (photoelectron CD), measurement of optical activity in the X-ray region, magnetochiral dichroism, and nonlinear forms of chiroptical spectroscopy.

The theory of chiroptical spectroscopy also goes back many years, but has recently made spectacular advances. Classical theories of optical activity were formulated in the early twentieth century, and the quantum mechanical theory of optical rotation was described in 1929. Approximate formulations of the quantum mechanical models were developed in the 1930s and more extensively with the growth of experimental ORD and ECD studies, starting in the late 1950s. The quantum mechanical methods for calculations of chiroptical spectroscopic properties reached a mature stage in the 1980s and 1990s. *Ab initio* calculations of VCD, ECD, ORD, and ROA have proven highly successful and are now widely used for small and medium-sized molecules.

Many books have been published on ORD, ECD, and VCD/ROA. The present two volumes are the first comprehensive treatise covering the whole field of chiroptical spectroscopy. Volume 1 covers the instrumentation, methodologies, and theoretical

simulations for different chiroptical spectroscopic methods. In addition to an extensive treatment of ECD, VCD, and ROA, this volume includes chapters on ORD, CPL, photoelectron CD, X-ray-detected CD, magnetochiral dichroism, and nonlinear chiroptical spectroscopy. Chapters on the related techniques of linear dichroism, chiroptical imaging of crystals and electro-optic absorption, which sometimes supplement chiroptical interpretations, are also included. The coverage of theoretical methods is also extensive, including simulation of ECD, ORD, VCD, and ROA spectra of molecules ranging from small molecules to macromolecules. Volume 2 describes applications of ECD, VCD, and ROA in the stereochemical analysis of organic and inorganic compounds and to biomolecules such as natural products, proteins, and nucleic acids. The roles of chiroptical methods in the study of drug mechanisms and drug discovery are described.

Thus, this work is unique in presenting an extensive coverage of the instrumentation and techniques of chiroptical spectroscopy, theoretical methods and simulation of chiroptical spectra, and applications of chiroptical spectroscopy in inorganic and organic chemistry, biochemistry, and drug discovery. In each of these areas, leading experts have provided the background needed for beginners, such as undergraduates and graduate students, and a state-of-the-art treatment for active researchers in academia and industry.

We are grateful to the contributors to these two volumes who kindly accepted our invitations to contribute and who have met the challenges of presenting accessible, up-to-date treatments of their assigned topics in a timely fashion.

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PART I

A HISTORICAL OVERVIEW

THE FIRST DECADES AFTER THE DISCOVERY OF CD AND ORD BY AIMÉ COTTON IN 1895

Peter Laur

1.1. SCOPE: SUBJECTS AND TIME FRAME TO BE REVIEWED

The story of the Cotton effect begins with its discovery in 1895. Although the news was hailed by leading physicists and chemists, studies to extend, exploit, and apply Cotton's findings developed at a slower pace than one might have anticipated. One of the reasons for this delay was simply the necessity of the researchers to construct their own optical apparatus. Gradual technical improvements eventually allowed one, in the 1920s, to take chiroptical measurements in the ultraviolet as well as the visible, thus making accessible in principle a great many Cotton effects in colorless (mostly organic) compounds. Despite the paramount importance of such developments, neither the technical details nor the physics involved will be discussed in the following. Rather, a chemist's view will prevail, paying attention chiefly to experimental results and the application of chiroptics to chemical problems.

Since much of the work during the first 20 or so years after Cotton's discovery was done by physicists and physicochemists, it is not surprising that many investigations were interconnected with or even motivated by the concomitant progress of the theory of optical activity. But also the discussion of this part of (theoretical) physics will be curtailed in the following. The exclusion in this chapter appears justified, because various comprehensive reviews are readily available, as they are for the field of optical instrumentation.

By about 1935, Cotton effect measurements were possible with most organic and inorganic chromophores. It is rather surprising that not much use was made of the chiroptical techniques, especially by organic chemists. On the other hand, physical chemists had demonstrated the feasibility of Cotton effect studies in various classes of chemical compounds, but seemed satisfied with this result. Likewise, the advancement of optical

instruments for chiroptical measurements slowed down. All this led to a certain climax of chiroptical studies in the early 1930s, to be followed by a near standstill. It is not unreasonable to symbolically connect this phenomenon with the death in 1936 of T. M. Lowry, one of the most active scholars in the field.

Arguably, the death of T. M. Lowry ended the first, pioneering period of chiroptical studies. The present chapter will concentrate on reviewing these first "historical" decades.

Some work on the experimental study of the Cotton effect continued after 1936 until World War II on a minor scale, on, for example, organic compounds (S. Mitchell) or platinum complexes (I. Lifschitz). But at exactly the same time, new developments took place in the theory of optical activity and its application to chemical problems: Werner Kuhn's calculation of the absolute configuration of lactic acid in 1935 rang in a new era. The waning interest of the experimentalists contrasts with the increased activity of theoretical chemists like J. G. Kirkwood, E. U. Condon, H. Eyring, or W. Kauzmann, who in the late 1930s advanced different models of optical activity. Still, chemistry had to wait for the period of 1950–1960 for a revitalization of chiroptics. Some reasons for the animation are: (1) the development of X-ray scattering methods for the determination of the absolute configuration, thus anchoring the stereochemistry unambiguously, following J. M. Bijvoet's seminal publication of 1951; (2) the advent of new, commercially available measuring devices of ORD and CD; and (3) growing interest in natural products chemistry and, generally, optically active systems. But to discuss these topics would need another chapter.

1.2. EARLY CHIROPTICAL STUDIES

The discovery of optical activity is credited to the two distinguished French mathematicians, physicists, astronomers, and geodesists (and more) Dominique-François Jean Arago (1786–1853, of Catalan origin) and Jean-Baptiste Biot (1774–1862) [1]. Arago and Biot had been closely associated at least since 1806 in the pursuit of other scientific subjects, and they sometimes published together. Both investigated the optical activity of quartz, and apparently they also shared their equipment to some extent. If, on the one hand, Arago was the first to go into print, Biot, on the other hand, soon became more active in this field and extended the studies. He undoubtedly observed optical activity for the first time in organic compounds such as natural oils and terpenes, or solutions of camphor [2] and cane sugar [3]. Biot continued his research on optical activity throughout his life, later concentrating particularly on tartaric acid. He noticed the wavelength dependence of the optical rotation even at the very beginning of his studies, albeit in a rather qualitative way. Whereas eventually the rotatory dispersion of quartz could be elucidated satisfactorily (which led to Biot's law, stating that the rotation is inversely proportional to the square of the wavelength), similar solution studies were seriously impeded by experimental deficiencies, particularly the lack of suitable monochromatic light sources.

Genuine chiroptical studies were, therefore, rather infrequent until the end of the nineteenth century. One of the most important papers here is a report by the Norwegian physicist Adam Arndtsen, who discussed his studies of aqueous solutions of (+)-tartaric acid [4]. Using sunlight, he was able to visually determine the angle of rotation at some of the principal Fraunhofer lines, that is, C (656), D (589), E (527), b (517), F (486), and e (438 nm). He could confirm and extend Biot's earlier finding that the rotation exhibits a maximum in the spectral region studied, with its wavelength shifting from the