

Contents

Abbreviations	xv
Chapter 1 Theory of Optical Spectroscopy	1
1.1 Electronic Absorption Spectroscopy	1
1.1.1 Exciton Coupling Theory	6
1.2 CD Spectroscopy	11
1.2.1 Units used for CD Spectroscopy	14
1.2.2 Analysis of CD Spectra	17
1.3 MCD Spectroscopy	21
1.3.1 Zeeman Splitting of States	23
1.3.2 MCD Intensity Mechanism, Sign Conventions and Intensity Units	26
1.3.3 Quantitative Analysis of Groundstate and Excited State Magnetic Dipole Moments	31
1.3.4 MCD Spectroscopy of Transition Metal Complexes	34
1.3.5 Qualitative Analysis of MCD Spectra	39
References	40
Chapter 2 Empirical Rules in CD Spectra and Absolute Configuration of Molecules	42
2.1 The Octant Rule	42
2.2 Benzene Sector and Benzene Chirality Rules	47
2.2.1 Benzene Sector Rule	47
2.2.2 Benzene Chirality Rule	50
References	52

Circular Dichroism and Magnetic Circular Dichroism Spectroscopy for Organic Chemists
By Nagao Kobayashi, Atsuya Muranaka and John Mack
© Royal Society of Chemistry 2012
Published by the Royal Society of Chemistry, www.rsc.org

Chapter 3	Representative Systems Analysed by the Exciton Coupling Method	53
3.1	Exciton Coupling among Fewer than Four Identical Chromophores	54
3.1.1	Spectra of 5 α -Cholestane-2 β ,3 β - and 3 β ,6 β -diol <i>Bis</i> (<i>p</i> -dimethylamino-benzoate)	54
3.1.2	Spectra of (6 <i>R</i> ,15 <i>R</i>)-(+)-6,15-Dihydro-6,15-ethanonaphtho[2,3- <i>c</i>]pentaphene	55
3.1.3	Additivity Relationship in the Amplitudes of Exciton-Split CD Curves of Sugar Benzoates	57
3.1.4	Determination of the Absolute Configuration of Oligonaphthalenes	62
3.1.5	Determination of the Absolute Configuration of a Natural Catechol Product, Haematoxylin, using the Phthalocyanine Chromophore	65
3.1.6	Supramolecular Chirality in a Bisporphyrin System Axially Coordinated by a Chiral Guest	69
3.1.7	A Chiral Biscyanine Dye exhibiting an Exciton Couplet with Well-resolved Absorption Bands	72
3.1.8	CD and Absolute Configuration of C ₃ Symmetry Chiral Cyclotrimeratrylenes	75
3.2	Polymer Systems (Systems Consisting of more than Four Chromophores)	78
3.2.1	Helical Structures of N-Alkylated Poly(<i>p</i> -benzamide)s	78
3.2.2	Conformation of Helical Poly(2,3-quinoxaline)s	83
3.3	Exciton Coupling between Non-Identical Chromophores	83
3.3.1	Determination of the Absolute Configuration of Allylic Alcohols: Systems Containing a C=C Double Bond and a Benzoate	86
3.3.2	Application of the Exciton Chirality Method to Conjugated Enones, Esters and Lactones	88
	References	91
Chapter 4	Cyclodextrin Inclusion Compounds	93
4.1	Induced Circular Dichroism of CyDs	94
4.1.1	Inclusion of Pyrene in β -CyD at Room Temperature and in γ -CyD at 70°	95
4.1.2	Inclusion of 2,3-Diaminonaphthalene and 1,8-Diaminonaphthalene in β -CyD	96

4.1.3	Lid-type Inclusion of Pyrene-1,3,6,8-tetrasulphonate Anion by β -CyD	97
4.1.4	Inclusion of 4,4'-Substituted Biphenyls by β -CyD	98
4.1.5	Inclusion of Bipyridyls by β -CyD	99
4.1.6	Disposition of Ferrocene in β - or γ -CyD	99
4.1.7	Chirality of Two Pyrene Molecules in γ -CyD	102
	References	103
Chapter 5 Metal Complexes		104
5.1	Systems which can be Analysed by Excitation Coupling Theory: Absolute Configurations of Metal Complexes Containing <i>o</i> -Phenanthroline, 2,2'-Bipyridyl or Acetylacetonate	104
5.2	CD spectra in the $d \rightarrow d$ Transition Region	110
5.2.1	$[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Cr}(\text{en})_3]^{3+}$	110
5.2.2	Near-IR Absorption and CD Spectra of Ferrocyclochrome <i>c</i> : $d \rightarrow d$ Transitions	112
	References	115
Chapter 6 Circular Dichroism Induced by Optically Active Binaphthyl		116
6.1	Chiral Binaphthyl-Induced CD in Phthalocyanines	116
	References	128
Chapter 7 Analysis of Chiral Systems by Theoretical Calculations		130
7.1	Semi-empirical Calculations	131
7.1.1	Absolute Stereochemistry of (+)-1,8a-Dihydro-3,8-Dimethylazulene	131
7.1.2	Analysis of Naphthalene-diene Derivatives	132
7.2	TD-DFT Calculations	133
7.2.1	Correlation between CD Sign and Conformation in Optically Active Oxo(phthalocyaninato)vanadium(IV)	133
7.2.2	Optically Active Porphyrin Dimers	135
7.2.3	Absolute Configuration and Chiroptical Properties of Three-layered [3,3]Paracyclophane	137
	References	141

Chapter 8	Circular Dichroism of Biomolecules	142
8.1	Protein Chromophores and Electronic Absorption Spectroscopy	143
8.2	CD Spectroscopy of Peptides	147
8.2.1	α -Helix CD	147
8.2.2	β -Sheet and random coil CD	148
8.2.3	β -Turn CD	149
	References	149
Chapter 9	Analysis of MCD Spectra	150
9.1	Examples of the Analysis of Faraday \mathcal{A}_1 Terms	150
9.1.1	Cyclononatetraenide Anion	151
9.1.2	Cycloheptatrienyl (Tropylium) Cation	152
9.1.3	C_{60} Fullerene	152
9.1.4	Identification of the Electronic Origin of the S1 State of Zinc Tetraphenyltetraacenaphthoporphyrin	153
9.2	Examples of the Analysis of Faraday \mathcal{B}_0 Terms	155
9.2.1	Analysis of the Symmetry-split Excited States of Azaporphyrins	155
9.2.2	Analysis of Data Recorded at Cryogenic Temperature: Phthalocyanine Anion Radicals	157
9.3	Examples of Analysis of Faraday C_0 MCD Terms	161
9.3.1	The "Fingerprint" Approach	161
9.3.2	Analysis of Data Recorded at Cryogenic Temperatures	163
9.3.3	The Quantitative Analysis of Magnetisation Curves	167
9.4	Analysis of MCD Spectra based on Molecular Orbital Calculations	168
	References	169
Chapter 10	Michl's Perimeter Model in MCD Spectroscopy	172
10.1	Michl's $4N+2$ -Perimeter Model for Aromatic π -Systems	175
10.2	Michl's $4N$ -Perimeter Model for Antiaromatic π -Systems	179
10.3	Applications of Michl's Perimeter Model	180
10.3.1	Negative Faraday \mathcal{A}_1 MCD Term in a Cyclobutadiene Dianion	180

<i>Contents</i>		xiii
10.3.2	The Effect of Ligand Non-planarity on the Alignment of the Excited State Magnetic Moments of Zinc Tetraphenyltetraacenaphthoporphyrin	182
10.3.3	The Application of the $4N$ and $4N+2$ Perimeter Model to the Spectra of Hexaphyrin(1.1.1.1.1.1)s	183
10.3.4	Using Michl's Perimeter Model to Conceptualise the Optical Properties of Low Symmetry Aromatic π -Systems	185
10.3.5	Analysis of the MCD Spectra of Benzofuran Derivatives Substituted with Group 16 Heteroatoms	187
	References	190
Subject Index		192