

Contents

Foreword	ix
Preface	xiii
CHAPTER 1	
Static stereochemistry	1
1.1 Configuration and chirality	2
1.1.1 Molecular geometry	2
1.1.2 Molecular symmetry	4
1.1.3 Symmetry in simple carbon compounds	6
1.1.4 Classification of molecules according to their symmetry. The Schönflies point group notation	9
1.1.5 Stereoisomerism and chirality	17
1.1.5.1 Classification of molecules by their symmetry	19
1.1.6 Molecular chirality	22
1.1.6.1 The chiral centre	23
1.1.6.2 The sequence rules relating to the chirality centres. The conventions of Cahn, Ingold and Prelog	27
1.1.6.3 The chiral axis	33
1.1.6.4 The chiral plane	36
1.1.6.5 Helices	38
1.1.6.6 Stereoisomerism in penta- and hexa-coordinate compounds	39
1.1.7 Molecules containing more than one centre of asymmetry	41
1.1.7.1 Racemic mixtures	41
1.1.7.2 Open-chain molecules containing several chiral centres	43
1.1.7.3 Stereoisomerism in cyclic molecules. Cyclosteroisomers	50
1.1.8 The experimental determination of configuration. Absolute and relative configuration	54
1.1.8.1 Determination of the absolute configuration	54
1.1.8.2 Determination of the relative configuration	57

1.1.9	Principles relating to the separation of enantiomers	87
1.1.9.1	Mechanical separation (Pasteur's method)	87
1.1.9.2	Resolution through diastereomeric salts and complexes	88
1.1.9.3	Resolution through the formation of diastereomeric compounds	90
1.1.9.4	Resolution by chromatography on optically-active absorbents	90
1.1.9.5	Partial and total resolution. The determination of optical purity	91
1.2	Conformation of carbon compounds	93
1.2.1	The conformation of ethane. Torsional strain	94
1.2.2	The conformation of n-butane. Non-bonding interactions	96
1.2.3	The conformation of cyclohexane	100

CHAPTER 2

Dynamic stereochemistry	112	
2.1	Methods of dynamic stereochemistry	112
2.1.1	Intramolecular symmetry relations between groups of the same structure and position. Topicity	112
2.1.2	Molecular symmetry and n.m.r. spectroscopy	120
2.1.3	Some concepts of reaction kinetics	126
2.1.4	Dynamic n.m.r. spectroscopy	129
2.2	The kinetics of configurational and conformational change	133
2.2.1	Racemization and epimerization	135
2.2.2	Configurational inversion	140
2.2.2.1	Pyramidal inversion at 3-coordinate centres	140
2.2.2.2	Configurational inversion at 5-coordinate centres	149
2.2.3	Hindered rotation	152
2.2.3.1	Hindered rotation about single bonds	152
2.2.3.2	Hindered rotation about double bonds	158
2.2.4	Conformational equilibria in ring systems. Ring inversion	163
2.2.4.1	Ring inversion in six-membered rings	164
2.2.4.2	Conformation and mobility in rings other than those with six members ..	170

CHAPTER 3

Applied stereochemistry	180	
3.1	Reactivity and molecular symmetry	180
3.1.1	The formation of stereoisomers. Intramolecular stereoselectivity	180
3.1.1.1	Transformations involving structurally identical groups	180
3.1.1.2	Transformations involving molecular faces	185
3.1.2	The reactivity of stereoisomers. Intermolecular stereoselectivity	196
3.1.2.1	Configuration and reactivity	196

3.1.2.2	Conformation and reactivity	203
3.1.3	The stereochemistry of concerted reactions. The conservation of orbital symmetry	210
3.1.3.1	The symmetry of molecular orbitals	212
3.1.3.2	Electrocyclic reactions. Conrotation and disrotation	214
3.1.3.3	Cycloaddition and cycloreversion. Suprafacial and antarafacial processes	225
3.1.3.4	Cheletropic reactions	232
3.1.3.5	Sigmatropic rearrangements. Retention and inversion	235
3.2	The stereochemistry of enzymic processes	242
3.2.1	Structural determinants in the stereostructure of enzymes	244
3.2.2	Stereoselectivity in the biosynthesis of steroids	249
3.3	Stereoisomerism in monotonic polymers	260
3.4	Stereoisomerism in some inorganic complexes	265
	References	269
	Subject index	277