

CONTENTS

1. HISTORICAL ASPECTS AND DEFINITIONS	
1.1 The Edward-Lemieux Effect	1
1.2 Anomeric Effect in Sugars	3
1.3 Quantitation of the Anomeric Effect	9
References	13
2. ORIGIN AND CONSEQUENCES OF THE ANOMERIC EFFECT	
2.1 Introduction	17
2.2 The Electrostatic Model of the Anomeric Effect	17
2.3 Solvent Effects on Anomeric Conformational Equilibria	18
2.4 The No Bond-Double Bond Model: Stereoelectronic Interpretation of the Anomeric Problem	22
2.5 The Perfluoro Effect Problem	25
2.6 The Nature of the Lone Pair	26
2.7 Precise Structural Data and the No Bond-Double Bond Model for the Anomeric Effect	30
2.8 Stereoelectronic Effects upon C-H Coupling Constants	35
2.9 Consequences of the Anomeric Effect	39
2.10 The Lone Pair Interaction Model	42
References	44
3. THEORETICAL STUDIES OF THE ANOMERIC EFFECT	
3.1 General Remarks	49
3.2 Nonempirical ab initio Calculations	49
3.3 Semiempirical MO Methods	59
3.4 Quantitative Perturbation Molecular Orbital (PMO) Analysis	61
3.5 Molecular Mechanics Calculations	62
3.6 Extended Huckel Calculations	64
References	67
4. STEREOELECTRONIC EFFECTS ASSOCIATED WITH THE ANOMERIC EFFECT	
4.1 The Gauche Effect	71
4.2 The (Z) Effect at sp ² Centers	82
4.3 Anomeric Effect in Radicals	83
4.4 Further Manifestations of Stereoelectronic Interactions which have been Considered as Related to the Anomeric Effect	90
References	91

5. ENDO AND EXO ANOMERIC INTERACTIONS	
5.1 Working Hypothesis and Definition	95
5.2 Recent Studies of the Exo Anomeric Effect	98
5.3 A Challenge to the Ascendancy of the Exo Anomeric Effect	107
References	110
6. THE ENTHALPIC ANOMERIC EFFECT	
6.1 Conformational Equilibria of 2-Methoxytetrahydropyran – Entropic Contributions	113
6.2 The Enthalpic Anomeric Effect in 2-Substituted Tetrahydropyrans	116
6.3 The Enthalpic Anomeric Effect in Sulfur-Containing Heterocycles	120
6.4 Enthalpic and Entropic Contributions to the S-C-P Anomeric Effect	123
References	127
7. SECOND- AND LOWER-ROW ANOMERIC INTERACTIONS	
7.1 Earliest Observations	129
7.2 The Anomeric Effect in S-C-X Segments	135
7.3 The Anomeric Effect in S-C-P Segments	139
7.4 The Se-C-X Anomeric Effect	161
7.5 The S-S=O Anomeric Effect	163
7.6 Stereoelectronic Effects in O-P-X Segments	164
References	165
8. THE REVERES ANOMERIC EFFECT	
8.1 Discovery, Definition, and Interpretations of the Reverse Anomeric Effect	173
8.2 The Controversy Surrounding the Concept of a Reverses Anomeric Effect	176
References	180
9. THE KINETIC ANOMERIC EFFECT	
9.1 Historical Developments, Concepts, and Relevance	183
9.2 Further Experimental and Theoretical Support for the Antiperiplanar Lone Pair Hypothesis (ALPH)	186
9.3 The Principle of Least Nuclear Motion as an Interpretation of the Kinetic Anomeric Effect	190
References	192
10. APPLICATIONS OF THE ANOMERIC EFFECT IN ORGANIC SYNTHESIS	
10.1 Introduction	195
10.2 Stereocontrolled Synthesis of Spiroketal	195
10.3 Stereoselective Synthesis of Glycopyranosides	202
10.4 Miscellaneous Applications	207
References	210
Author Index	213
Subject Index	225