Contents

| Preface | XV | |
|------------|-------------|-----|
| List of Co | ontributors | XIX |

| 1 | Tautomerism: Introduction, History, and Recent Developments | | |
|-------|---|--|--|
| | in Experimental and Theoretical Methods 1 | | |
| | Peter J. Taylor, Gert van der Zwan, and Liudmil Antonov | | |
| 1.1 | The Definition and Scope of Tautomerism: Principles and | | |
| | Practicalities 1 | | |
| 1.2 | Causes of Reversal in Tautomeric Form: Aromatic Resonance 3 | | |
| 1.3 | Causes of Reversal in Tautomeric Form: Lone-Pair and Dipolar | | |
| | Repulsion 4 | | |
| 1.4 | Causes of Reversal in Tautomeric Form: Selective Stabilization | | |
| | Through "Far" Intramolecular Hydrogen Bonding 5 | | |
| 1.5 | Changes in Tautomeric Form Brought About by Electronegative | | |
| | Substituents 7 | | |
| 1.6 | The Influence of Solvent on Tautomeric Form 8 | | |
| 1.7 | Tautomeric Equilibrium: Historical Overview of an Analytical | | |
| | Problem 9 | | |
| 1.8 | Short Historical Overview of Tautomerization Dynamics 13 | | |
| 1.9 | Conclusions and Outlook 19 | | |
| | References 20 | | |
| 2 | Absorption UV-vis Spectroscopy and Chemometrics: From Qualitative | | |
| | Conclusions to Quantitative Analysis 25 | | |
| | Liudmil Antonov | | |
| 2.1 | Introduction 25 | | |
| 2.2 | Quantitative Analysis of Tautomeric Equilibria 26 | | |
| 2.2.1 | Classical Spectrophotometric Analysis, Limitations, and Early | | |
| | Attempts to Find a Solution 26 | | |
| 2.2.2 | Quantitative Analysis by Using Bands Decomposition 29 | | |
| 2.2.3 | Change in the Environment Affects the Equilibrium: Physical | | |
| | Meaning and Mathematical Expression 33 | | |

| VIII | Contents | | | | |
|---|--|---|--|--|--|
| | 2.3 Analysis of Real Tautomeric Systems 37 | | | | |
| | 2.3.1 | Keto–Enol Tautomerism in 4-(phenyldiazenyl)naphthalen-1-ol: Solvent Effect 37 | | | |
| | 2.3.2 | Keto-Enol Tautomerism in 1-((phenylimino)methyl)naphthalen-2-ol: Verification of the Approach 40 | | | |
| | 2.3.3 Keto–Enol Tautomerism in 1-(phenyldiazenyl)naphthalen-2-ol and 1-((phenylimino)methyl)naphthalen-2-ol: Effects of the Temperatur and the Strength of Intramolecular Hydrogen Bonding 41 2.3.4 Ammonium–Azonium Tautomerism in 4-((4-aminophenyl)diazenyl)-N,N-dimethylaniline: Effect of Protonation and Solvent 43 2.4 Concluding Remarks 46 References 46 | | | | |
| | | | | | |
| | | | | | |
| | 3 Studies of Photoinduced NH Tautomerism by Stationary and | | | | |
| | | Time-Resolved Fluorescence Techniques 49 Alexander Kyrychenko, Jerzy Herbich, and Jacek Waluk | | | |
| | 3.1 | Introduction 49 | | | |
| | 3.2 | Photoinduced Proton/Hydrogen Atom Transfer 50 | | | |
| | 3.2.1 | Direct Intramolecular Proton Transfer Reactions 50 | | | |
| | 3.2.2 | Solvent-Mediated NH Tautomerism 52 | | | |
| | | Fluorescence Techniques for Studying Tautomerism 52 | | | |
| = | | Steady-State Fluorescence Methods 52 | | | |
| | 3.3.2 | Time-Resolved Fluorescence Approaches 54 | | | |
| 3.3.3 Advanced Techniques in Fluorescence Spectroscopy 54 | | | | | |
| | 3.3.3.1 Fluorescence Anisotropy 54 | | | | |
| | 3.3.3.2 Fluorescence Microscopy and Fluorescence Correlation Spectroscopy 55 | | | | |
| | 3.4 | Tautomerism in Bifunctional NH/N Azaaromatics 56 | | | |
| | 3.4.1 | Intramolecular NH/N Tautomerization 56 | | | |
| | 3.4.2 Intermolecular NH/N Tautomerization in Hydrogen-Bonded Dimers 59 | | | | |
| | 3.4.3 Tautomerization in Solute–Solvent Hydrogen-Bonded Complexes 60 | | | | |
| 3.5 <i>Ab initio</i> and DFT Computat | | Ab initio and DFT Computational Methods 67 | | | |
| | 3.5.1 | Reaction Mechanisms and Cooperativity in Proton Migrations 67 | | | |
| | 3.5.1.1 | Concerted versus Stepwise Mechanism 67 | | | |
| | 3.5.2 | Reaction Path Calculations and Energy Barriers for Proton Transfer 69 | | | |
| | 3.5.3 | Challenges for Molecular Dynamics and QM/MM Simulations 71 | | | |
| | 3.6 | NH Tautomerism as a Tool in Biophysics 72 | | | |
| | 3.7 | Concluding Remarks 74 | | | |
| | | Acknowledgment 74 | | | |
| | | References 75 | | | |

| 4 | Femtosecond Pump-Probe Spectroscopy of Photoinduced |
|--|--|
| | Tautomerism 79 |
| | Stefan Lochbrunner |
| 4.1 | Introduction 79 |
| 4.2 | Ultrafast Pump-Probe Spectroscopy 81 |
| 4.2.1 | Time-Resolved Absorption Measurements 82 |
| 4.2.2 | Fluorescence Upconversion 84 |
| 4.2.3 | Ionization Techniques 84 |
| 4.2.4 | Time-Resolved Infrared Spectroscopy 84 |
| 4.3 | Dynamics from Pump-Probe Spectroscopy 85 |
| 4.3.1 | Ultrafast Transient Absorption Signatures of ESIPT 85 |
| 4.3.2 | Data Analysis 87 |
| 4.3.3 | Ballistic Wavepacket Motion 88 |
| 4.3.4 | Coherently Excited Vibrations in Product Modes 90 |
| 4.3.5 | Ultrafast IR Studies 92 |
| 4.3.6 | Other Tautomeric Reactions 92 |
| 4.4 | Reaction Mechanism 93 |
| 4.5 | Reaction-Path-Specific Wavepacket Dynamics in Double ESIPT 96 |
| 4.6 | Internal Conversion 97 |
| 4.7 | Summary and Conclusions 99 |
| | Acknowledgments 100 |
| | References 100 |
| | |
| | |
| 5 | NMR Spectroscopic Study of Tautomerism in Solution and |
| 5 | NMR Spectroscopic Study of Tautomerism in Solution and in the Solid State 103 |
| 5 | |
| 5 5.1 | in the Solid State 103 |
| | in the Solid State 103 Erich Kleinpeter |
| 5.1 | in the Solid State 103 Erich Kleinpeter Introduction 103 |
| 5.1 5.2 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 |
| 5.1 5.2 5.3 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 |
| 5.1 5.2 5.3 5.3.1 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 Ring-Chain Tautomerism 109 |
| 5.1 5.2 5.3 5.3.1 5.3.2 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 Ring-Chain Tautomerism 109 Tetrazole-Azide Tautomerism 111 |
| 5.1 5.2 5.3 5.3.1 5.3.2 5.3.3 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 Ring-Chain Tautomerism 109 Tetrazole-Azide Tautomerism 111 Transannular Tautomerism 111 |
| 5.1 5.2 5.3 5.3.1 5.3.2 5.3.3 5.3.4 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 Ring-Chain Tautomerism 109 Tetrazole-Azide Tautomerism 111 Transannular Tautomerism 111 Keto-Enol Tautomerism 112 |
| 5.1 5.2 5.3 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 Ring-Chain Tautomerism 109 Tetrazole-Azide Tautomerism 111 Transannular Tautomerism 111 Keto-Enol Tautomerism 112 Imine-Amine Tautomerism 116 |
| 5.1 5.2 5.3 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 Ring-Chain Tautomerism 109 Tetrazole-Azide Tautomerism 111 Transannular Tautomerism 111 Keto-Enol Tautomerism 112 Imine-Amine Tautomerism 116 Lactam-Lactim Tautomerism 124 |
| 5.1 5.2 5.3 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 Ring-Chain Tautomerism 109 Tetrazole-Azide Tautomerism 111 Transannular Tautomerism 111 Keto-Enol Tautomerism 112 Imine-Amine Tautomerism 116 Lactam-Lactim Tautomerism 124 Annular Tautomerism of Five- or Six-Membered Heterocyclic |
| 5.1 5.2 5.3 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 5.3.7 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 Ring-Chain Tautomerism 109 Tetrazole-Azide Tautomerism 111 Transannular Tautomerism 111 Keto-Enol Tautomerism 112 Imine-Amine Tautomerism 116 Lactam-Lactim Tautomerism 124 Annular Tautomerism of Five- or Six-Membered Heterocyclic Compounds 126 Nitroso (N-Oxide)-Oxime Tautomerism 128 |
| 5.1 5.2 5.3 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 5.3.7 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 Ring-Chain Tautomerism 109 Tetrazole-Azide Tautomerism 111 Transannular Tautomerism 111 Keto-Enol Tautomerism 112 Imine-Amine Tautomerism 116 Lactam-Lactim Tautomerism 124 Annular Tautomerism of Five- or Six-Membered Heterocyclic Compounds 126 Nitroso (N-Oxide)-Oxime Tautomerism 128 |
| 5.1 5.2 5.3 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 5.3.7 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 Ring-Chain Tautomerism 109 Tetrazole-Azide Tautomerism 111 Transannular Tautomerism 111 Keto-Enol Tautomerism 112 Imine-Amine Tautomerism 116 Lactam-Lactim Tautomerism 124 Annular Tautomerism of Five- or Six-Membered Heterocyclic Compounds 126 Nitroso (N-Oxide)-Oxime Tautomerism 128 Tautomeric Structures in Nucleosides, Nucleotides, and Proteins 129 Tautomerism in Porphyrins 131 |
| 5.1 5.2 5.3 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 5.3.7 5.3.8 5.3.9 5.3.10 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 Ring-Chain Tautomerism 109 Tetrazole-Azide Tautomerism 111 Transannular Tautomerism 112 Imine-Amine Tautomerism 116 Lactam-Lactim Tautomerism 124 Annular Tautomerism of Five- or Six-Membered Heterocyclic Compounds 126 Nitroso (N-Oxide)-Oxime Tautomerism 128 Tautomeric Structures in Nucleosides, Nucleotides, and Proteins 129 Tautomerism in Porphyrins 131 Carbohydrate Tautomerism 132 |
| 5.1 5.2 5.3 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 5.3.7 5.3.8 5.3.9 5.3.10 5.3.11 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 Ring-Chain Tautomerism 109 Tetrazole-Azide Tautomerism 111 Transannular Tautomerism 111 Keto-Enol Tautomerism 112 Imine-Amine Tautomerism 116 Lactam-Lactim Tautomerism 124 Annular Tautomerism of Five- or Six-Membered Heterocyclic Compounds 126 Nitroso (N-Oxide)-Oxime Tautomerism 128 Tautomeric Structures in Nucleosides, Nucleotides, and Proteins 129 Tautomerism in Porphyrins 131 Carbohydrate Tautomerism 132 Azo-Hydrazone Tautomerism 133 |
| 5.1 5.2 5.3 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 5.3.7 5.3.8 5.3.9 5.3.10 5.3.11 5.3.12 | in the Solid State 103 Erich Kleinpeter Introduction 103 Methodologies of NMR Spectroscopy to Study Tautomerism 104 Types of Tautomerism Studied by NMR Spectroscopy 109 Ring-Chain Tautomerism 109 Tetrazole-Azide Tautomerism 111 Transannular Tautomerism 111 Keto-Enol Tautomerism 112 Imine-Amine Tautomerism 116 Lactam-Lactim Tautomerism 124 Annular Tautomerism of Five- or Six-Membered Heterocyclic Compounds 126 Nitroso (N-Oxide)-Oxime Tautomerism 128 Tautomeric Structures in Nucleosides, Nucleotides, and Proteins 129 Tautomerism in Porphyrins 131 Carbohydrate Tautomerism 132 Azo-Hydrazone Tautomerism 133 |

| Acknowledg | 138 | |
|------------|-----|--|
| References | | |
| | | |

| 6 | Isotope Effects on Chemical Shifts as a Tool in the Study of | | | |
|---------|--|-----|--|--|
| | Tautomeric Equilibria 145 | | | |
| | Poul Erik Hansen | | | |
| 6.1 | Introduction 145 | | | |
| 6.2 | Experimental Requirements 148 | | | |
| 6.2.1 | One-Tube Experiments 148 | | | |
| 6.2.2 | Exchange of Isotopes 149 | | | |
| 6.2.3 | Concentric Tubes 149 | | | |
| 6.2.4 | Couplings 149 | | | |
| 6.2.5 | Primary Isotope Effects 149 | | | |
| 6.2.6 | Temperature 150 | | | |
| 6.2.7 | Variation of Solvent 150 | | | |
| 6.2.8 | Isotope Labeling 151 | | | |
| 6.3 | Isotope Effects on Chemical Shifts 151 | | | |
| 6.3.1 | Intrinsic Isotope Effects 151 | | | |
| 6.3.1.1 | Intrinsic Deuterium Isotope Effects on ¹³ C CS 153 | | | |
| 6.3.1.2 | Intrinsic Deuterium Isotope Effects on ¹⁵ N Chemical Shifts | 154 | | |
| 6.3.1.3 | Deuterium Isotope Effects on ¹⁷ O Chemical Shifts 154 | | | |
| 6.3.1.4 | Deuterium Isotope Effects on ¹⁹ F CS 154 | | | |
| 6.3.1.5 | ¹⁸ O Isotope Effects on ¹³ C Chemical Shifts 155 | | | |
| 6.4 | Secondary Equilibrium Isotope Effects on CS 156 | | | |
| 6.4.1 | Isotopic Perturbation of Equilibrium 160 | | | |
| 6.5 | Primary Isotope Effects 161 | | | |
| 6.6 | Solid State 164 | | | |
| 6.7 | Theoretical Calculations 165 | | | |
| 6.8 | Examples 166 | | | |
| 6.8.1 | β -Thioxoketones 166 | | | |
| 6.8.2 | Multiple Equilibria 169 | | | |
| 6.9 | Overview 172 | | | |
| | References 173 | | | |
| 7 | Tautomer-Selective Spectroscopy of Nucleobases, Isolated | | | |
| | in the Gas Phase 177 | | | |
| | Mattanjah S. de Vries | | | |
| 7.1 | Introduction 177 | | | |
| 7.2 | Techniques 177 | | | |
| 7.3 | Guanine 179 | | | |
| 7.4 | Adenine 187 | | | |
| 7.5 | Cytosine 187 | | | |
| 7.6 | Uracil and Thymine 188 | | | |
| 7.7 | Base Pairs 189 | | | |
| 7.8 | Outlook 191 | | | |

| | Acknowledgments 192 References 192 |
|------------|---|
| 8 | Direct Evidence of Solid-State Tautomerism by Diffraction Methods: |
| | Isomers, Equilibria, and Kinetics 197 |
| 0.1 | Panče Naumov and Subash Chandra Sahoo |
| 8.1 8.2 | Application of X-Ray Diffraction to Study Tautomerism 197 |
| 8.2.1 | Examples of X-Ray Diffraction Analysis of Proton Transfer 199 Tautomerism, Proton Transfer, and Resonance-Assisted Hydrogen |
| 0.2.1 | Bonding 199 |
| 8.2.2 | Examples of Thermally Induced Tautomerism 203 |
| 8.2.3 | Photoinduced Tautomeric Processes 208 |
| 8.3 | Other Diffraction Methods Used to Study Proton Transfer |
| | Reactions 211 |
| | References 211 |
| 9 | Dynamics of Ground- and Excited-State Intramolecular Proton Transfer |
| | Reactions 213 |
| | Gert van der Zwan |
| 9.1 | Introduction 213 |
| 9.2 | Transition State Theory 216 |
| 9.3 | Two Examples of Tautomerization 218 |
| 9.4 | The Role of the Solvent 221 |
| 9.5 | Solvent Friction and Solvent Dynamics 224 |
| 9.6 | The Solvent Coordinate: Basics 226 |
| 9.7 | Polarization Fluctuations 229 |
| 9.8 | The Solvent Coordinate: An Application 231 |
| 9.9 | Electronic Rearrangement 233 |
| 9.10 | The Rug that Ties the (Classical) Room Together 234 |
| 9.11 | Quantum and Classical 236 |
| 9.12 | Quantum Decay 239 |
| 9.13 | Coupling Quantum and Classical Motion: A Simple Example 242 |
| 9.14 | Nonlinear Optics 246 |
| 9.15 | Femtochemistry 247 |
| 9.16 | Concluding Remarks 249 |
| | References 250 |
| 10 | Force Field Treatment of Proton and Hydrogen Transfer in |
| | Molecular Systems 253 |
| | Jing Huang and Markus Meuwly |
| 10.1 | Introduction 253 |
| 10.2 | Computational Approaches to Proton Transfer 254 |
| 10.3 | Proton Transfer Reactions with MMPT 256 |
| 10.4 | Applications of MMPT 259 |
| 10.4.1 | Infrared Spectroscopy 259 |

| XII | Contents | |
|-----|----------|--|
| | 10.4.2 | Classical and Quantum Proton Transfer in the Gas Phase 261 |
| | 10.4.3 | Condensed-Phase Proton Transfer 263 |
| | 10.4.4 | MMPT for NMR Properties 264 |
| | 10.5 | Discussion and Outlook 267 |
| | | Acknowledgments 268 |
| | | References 268 |
| | 11 | The Scope and Limitations of LSER in the Study of Tautomer Ratio 277 Peter J. Taylor |
| | 11.1 | Introduction 277 |
| | 11.2 | The Taft–Kamlet LSER Methodology 277 |
| | 11.2.1 | The π^* Scale 278 |
| | 11.2.2 | The β Scale 279 |
| | 11.2.3 | The α Scale 281 |
| | 11.2.4 | The β Value for Water 283 |
| | 11.2.5 | π^* for the Gas Phase 286 |
| | 11.3 | LSER Case Histories in the Field of Tautomerism 287 |
| | 11.3.1 | Enol Formation from β -Diketones and Related Compounds 288 |
| | 11.3.2 | Tautomerism in Schiff Bases and Related Azo Compounds 292 |
| | 11.3.3 | Three-Way Tautomerism in the Pyrazolone 25 295 |
| | 11.4 | Overview 298 |
| | | Appendix 11.A: Earlier Approaches 301 |
| | | References 302 |
| | 12 | The "Basicity Method" for Estimating Tautomer Ratio: A Radical |
| | | Re-appraisal 305 |
| | | Peter J. Taylor |
| | 12.1 | Introduction 305 |
| | 12.2 | Experimental Protocol 307 |
| | 12.3 | The Derivation of Correction Factors 308 |
| | 12.3.1 | Amidines and Related Compounds 308 |
| | 12.3.2 | Conformational Effects on Amidine Correction Factors 309 |
| | 12.3.3 | Lactams: Simultaneous Determination of Δ (NMe) and Δ (OMe) 310 |
| | 12.3.4 | Vinylogous Lactams: Simultaneous Estimation of Δ (NMe) and |
| | 400 = | Δ(OMe) 312 |
| | 12.3.5 | Δ(NMe) in Acylamidines and Imides 313 |
| | 12.3.6 | Δ(NMe) for Compounds with Contiguous Nitrogen Atoms 315 |
| | 12.3.7 | Δ(NMe) for Thiolactams and Their Vinylogues 317 |
| | 12.3.8 | An Attempt at Δ (SMe) for Thiolactams and Their Vinylogues 319 |
| | 12.3.9 | Correction Factors: Summary and Speculations 320 |
| | 12.4 | Regularities Revealed by Correction Factors 320 |
| | 12.4.1 | Benzofusion to Give Benzenoid Structures in Six-Membered Ring Oxoheterocycles 321 |
| | 1242 | Renzofusion to Give Ouinonoid Structures in a Variety of |

Compounds 324

| 12.5 | Complicating Factors in the Use of the "Basicity Method" 326 | | | |
|----------|---|--|--|--|
| 12.5.1 | Complications Caused by Steric and Stereoelectronic Factors 326 | | | |
| 12.5.2 | Complications Caused by Hydrogen Bonding 327 | | | |
| 12.5.3 | Complications Caused by Protonation at the "Wrong Site" 328 | | | |
| 12.6 | Tautomeric Problems to Which the "Basicity Method" | | | |
| | Is Inapplicable 330 | | | |
| 12.7 | Overview 332 | | | |
| | References 333 | | | |
| 13 | Quantum Chemical Calculation of Tautomeric Equilibria 337 | | | |
| | Walter M.F. Fabian | | | |
| 13.1 | Introduction 337 | | | |
| 13.2 | Computational Procedures 338 | | | |
| 13.2.1 | Wave-Function-Based Methods 338 | | | |
| 13.2.1.1 | Independent Particle Methods 339 | | | |
| 13.2.1.2 | Correlated Treatments 340 | | | |
| 13.2.2 | Density Functional Procedures 342 | | | |
| 13.2.2.1 | Overview of Density Functionals 343 | | | |
| 13.2.2.2 | Validation of Density Functionals 346 | | | |
| 13.2.3 | Choice of Basis Set 347 | | | |
| 13.2.4 | Calculation of Spectroscopic Properties 351 | | | |
| 13.3 | Solvent Effects 353 | | | |
| 13.3.1 | Continuum Solvation Models 353 | | | |
| 13.3.2 | Explicit Solvent Models 355 | | | |
| 13.4 | Applications of Quantum Chemical Methods to Tautomeric | | | |
| | Equilibria 357 | | | |
| 13.4.1 | The SAMPL2 Challenge of Predicting Tautomer Ratios 357 | | | |
| 13.4.2 | Lactam-Lactim Tautomerism of 2-Hydroxypyridine 360 | | | |
| 13.4.3 | Annular Tautomerism in Tetrazole 363 | | | |
| 13.5 | Concluding Remarks 363 | | | |
| | References 364 | | | |
| | | | | |

Index 369