

 VOLUME FIFTY

# ADVANCES IN PHYSICAL ORGANIC CHEMISTRY

Edited by

**IAN H. WILLIAMS**

*Department of Chemistry,  
University of Bath,  
Bath, United Kingdom*

**NICHOLAS H. WILLIAMS**

*Department of Chemistry,  
University of Sheffield,  
Sheffield, United Kingdom*



Amsterdam • Boston • Heidelberg • London  
New York • Oxford • Paris • San Diego  
San Francisco • Singapore • Sydney • Tokyo

Academic Press is an imprint of Elsevier



# CONTENTS

|  |            |
|--|------------|
| <i>Contributors</i>  | <i>vii</i> |
| <i>Preface</i>   | <i>ix</i>  |
| <b>1. Equilibrium Effective Molarity As a Key Concept in Ring-Chain Equilibria, Dynamic Combinatorial Chemistry, Cooperativity and Self-assembly</b> | <b>1</b>   |
| S. Di Stefano, G. Ercolani   |            |
| 1. Introduction  | 2          |
| 2. Effective Molarity  | 3          |
| 3. Equilibrium Macrocyclizations   | 10         |
| 4. Dynamic Combinatorial Chemistry   | 22         |
| 5. Cooperativity and Self-Assembly   | 42         |
| 6. Conclusion  | 67         |
| References   | 68         |
| <b>2. Thermodynamic Effective Molarities for Supramolecular Complexes</b>  | <b>77</b>  |
| P. Motloch, C.A. Hunter  |            |
| 1. Introduction  | 78         |
| 2. Effective Molarities for Supramolecular Complexes   | 81         |
| 3. Conclusion  | 98         |
| Appendix: Collection of Thermodynamic Effective Molarity Values for Supramolecular Complexes   | 99         |
| Acknowledgements   | 113        |
| References   | 113        |
| <b>3. Reactivity of Nucleic Acid Radicals</b>  | <b>119</b> |
| Marc M. Greenberg  |            |
| 1. Introduction  | 120        |
| 2. Radical Formation in Nucleic Acids  | 121        |
| 3. The Norrish Type I Photoreaction  | 124        |
| 4. C1'-Radical Generation, Reactivity and Related Mechanistic Implications   | 124        |
| 5. C2'-Radical Generation and Reactivity in DNA, Ribonucleosides and RNA   | 136        |
| 6. C3'-Radical Generation and Reactivity in DNA  | 143        |

|  |            |
|--|------------|
| 7. C4'-Radical Generation and Reactivity in DNA and RNA                                      | 149        |
| 8. C5'-Radical Generation and Reactivity in DNA  | 160        |
| 9. Nucleobase Radical Generation and Reactivity in DNA and RNA                               | 165        |
| 10. Summary and Future Considerations  | 187        |
| Acknowledgement  | 188        |
| References   | 188        |
| <br>   |            |
| <b>4. Computational Studies of Environmental Effects and Their Interplay With Experiment</b> | <b>203</b> |
| B. Mennucci, S. Caprasecca, C.A. Guido   |            |
| 1. Introduction  | 204        |
| 2. Computational Models  | 206        |
| 3. The Interplay With Experiments: The Solvated Molecule and Its Spectroscopic Responses     | 213        |
| 4. Beyond the Solvated Molecule  | 228        |
| 5. Conclusions   | 236        |
| References   | 236        |
| <br>   |            |
| <i>Subject Index</i>   | 243        |
| <i>Author Index</i>  | 253        |
| <i>Cumulative Index of Titles</i>  | 267        |
| <i>Cumulative Index of Authors</i>   | 279        |