J|A|C|S
BOOK REVIEWS

The Nature of the Hydrogen Bond: Outline of a Comprehensive Hydrogen Bond Theory. By Gastone Gilli and Paola Gilli (University of Ferrara, Italy). Oxford University Press: New York. 2009. xii + 318 pp. $130. ISBN 978-0-19-955896-4.

I highly recommend this book to anyone who is truly interested in the hydrogen bond. The title is clearly meant to recall Pauling's classic book, *The Nature of the Chemical Bond*, in which he summarizes his work on chemical bonding. In the current book, the Gillis (father and daughter) summarize the work they have published with their co-workers on the hydrogen bond. As such, the current work differs from other recent books on hydrogen bonds, such as that by Jeffrey, which I previously reviewed (*J. Am. Chem. Soc.* **1998**, *120*, 5604), much as a paper in *Accounts of Chemical Research* differs from one in *Chemical Reviews*.

The book consists of eight chapters. The first, entitled "A century of the hydrogen bond (H-bond)," is a concise, yet critical, introduction and historical review of hydrogen bonding. The Gillis take care to disabuse the reader of many popular fallacies about H-bonds that pervade the literature. For example, Pauling's suggestion that H-bonds are electrostatic in nature was meant only to apply to weak (not all) H-bonds. The second chapter deals with definitions, generalities, and preliminary classification of H-bonds based upon the work of others.

The third and longest chapter covers modeling the H-bond using crystallography. Here, the authors' considerable expertise in crystallography and practical applications of crystallographic databases plays a very important role. They show how careful interpretation of judiciously chosen crystal structures can deepen one's understanding of H-bonding. Roughly two-thirds of this chapter deals with resonance-assisted H-bonds (RAHBs), a class of H-bonding that the Gillis have studied in great detail. These H-bonds can be quite strong and, therefore, important to structure determination. This chapter includes an extensive analysis of a subclass of RAHBs that occurs in tautomers of β-diketones, such as acetylacetone. It also includes further classification of H-bonds, including charge-assisted hydrogen bonds (CAHBs).

In the fourth chapter, the authors discuss modeling H-bonds from a thermodynamic perspective. Detailed discussions of the effects of pK_a matching upon the strength of H-bonds, particularly in the cases of CAHBs, are presented as ways of predicting H-bond strengths from thermodynamic data. Included is a very useful "pK_a slide rule". This is followed by a short chapter on "empirical laws governing the H-bond".

The sixth chapter, "Outline of a novel transition-state H-bond theory (TSHBT)," includes analyses using valence-bond and density functional theory, analyses of the potential surfaces—which generally include double-well potentials—and the application of Marcus theory to these surfaces. The seventh chapter, "The strength of the H-bond: Definitions and thermodynamics," covers the strength of H-bonds in different phases and in aqueous solution. It includes a detailed discussion of the principle of enthalpy/entropy compensation as applied to the H-bond. Finally, in the last chapter, the Gillis discuss the role of strong H-bonds in nature, e.g., the importance of H-bond cooperativity in biochemistry, crystal packing, and water.

No book is perfect, including this one. Among the deficiencies are the choice of an erroneous analysis of the gas-phase electron diffraction of acetylacetone—which did not take the fraction of the sample that is not in the enol form, resulting in the hydrogen atom involved in H-bonding appearing to be considerably out of the molecular plane—instead of what seems to be a more correct one (see Lowery et al. *J. Am. Chem. Soc.* **1971**, *93*, 6399). The following topics are not discussed: (1) trans-H-bond scalar *J*-coupling among the NMR methods used for studying H-bonds, (2) the zero-point vibration's effect upon the experimental structures resulting from surfaces with a low energy barrier in a double-well system; (3) the isotopic substitution method of studying double-well potentials, and (4) the effects of H-bonding on vibrational spectra. Because this book is essentially an overview of the authors' contributions, less space is allotted to those of other groups. However, this should be expected based on analogy to Pauling's book. Another problem is that color plates of some of the most important figures, including the aforementioned "pK_a slide rule," are inserted as a group after page 180, without any explanation or notation in the Table of Contents.

This book should be required reading for biochemists, many of whom seem to have only a superficial idea of what the hydrogen bond really is, as well as for anyone who designs or interprets empirical models that need to reproduce systems where H-bonding is important. On the whole, I believe this book to be a valuable contribution to our understanding of H-bonds. The Gillis should be commended for the considerable time and effort that they must have spent on this endeavor.

J. J. Dannenberg, *City University of New York-Hunter College and The Graduate School*

JA100200Z

10.1021/ja100200z

Comprehensive Organic Name Reactions and Reagents, Volume 1−3. By Zerong Wang (University of Houston—Clear Lake). John Wiley & Sons, Inc.: Hoboken, NJ.2009. xlx + 3662 pp. $595. ISBN 978-0-471-70450-8.

The three-volume set covers 701 named reactions, reagents, and chemical rules. The work is written to function as a resource for graduate students and research scientists with a solid foundation in organic chemistry. Each entry is separated into eight sections: a general description of the reaction, a reaction scheme, the reaction mechanism (accepted or proposed), modifications, applications, related reactions, cited experimental examples, and references. The text also includes several appendices including an index of schematic reactions, a summary of reaction types, a summary of initial publications on named reactions, and the statistics of reaction discovery as well as the standard tables of journal and chemical abbreviations.

Unsigned book reviews are by the Book Review Editor.

The work is extensively referenced with an average of 51 citations per reaction.

In the competitive genre of named reactions, Wang's *Comprehensive Organic Name Reactions and Reagents* has provided a contender. The amount of work that the author has devoted to this text is impressive. Everything about the three-book set reflects this effort, including the number of reactions covered, the breadth of discussion, the extensive references, and, unfortunately, the price. The general descriptions of the reactions are written well with clear discussions of reactivity and mechanism. These sections are packed with references and provide a good synopsis for each transformation discussed. In particular this work is noteworthy for its inclusion of experimental examples, with an average of two examples per reaction. This welcome addition provides researchers with a quick foray into the laboratory characteristics of the chemical transformation of interest. Although the experimental details are consistent throughout the work, three sections—modifications, applications, and related reactions—tend to be spotty and often offer minimal or no information or repeat information previously outlined in the general description section.

Chemists will find this set most useful as a starting point for investigating named reactions. The heavily referenced general descriptions and experimental examples make it a valuable resource for students and researchers who encounter or seek out named reactions. The price of $595 will likely put it out of reach for most students; however, the addition of *Comprehensive Organic Name Reactions and Reagents* to any literature collection will likely lead to frequent use.

Dionicio Siegel, *University of Texas at Austin*

JA100316G

10.1021/ja100316g

Wiley Guide to Chemical Incompatibilities, 3rd ed. By Richard P. Pohanish and Stanley A. Greene. John Wiley & Sons, Inc.: Hoboken, NJ. 2009. xviii + 1110 pp. $175. ISBN 978-0-470-38763-4.

The third edition of this popular reference contains nearly 9000 chemical incompatibility profiles, covering "flammability, violent and explosive binary reactions, incompatibilities, and reactions that may result from physical change". It was designed as a guide for professionals, such as plant managers and first responders, who are responsible for the handling, storing, and transporting of chemicals. In this new edition, each profile was rewritten and expanded rather than simply updated, and 250 new entries were added. Other additions include "more flash points, ... molecular formulas, lower and upper explosive limits, autoignition temperatures, and NFPA-type (Red) numerical fire codes." Information on the effects of chemicals on construction materials has been expanded, and the glossary has been revised to help users with general chemical terms. A short bibliography completes the book.

JA100892B

10.1021/ja100892b

Fluorinated Heterocyclic Compounds: Synthesis, Chemistry, and Applications. Edited by Viacheslav A. Petrov (DuPont Central Research and Development, Wilmington, DE). John Wiley & Sons, Inc: Hoboken, NJ. 2009. xviii + 516 pp. $125. ISBN 978-0-470-45211-0.

Fluorinated Heterocyclic Compounds is an eclectic collection of 10 chapters (Part I) on the synthesis and chemistry of fluorinated heterocycles and 3 chapters (Part II) on some applications of the title compounds. The 17 contributing authors, including the editor, represent a broad spectrum of researchers who have contributed to this field. All authors have topical expertise and experience in the material covered.

The book is organized in a logical fashion, beginning with an introduction to the nomenclature of polyfluorinated compounds, followed by Chapters 1 and 2 on fluorinated three-membered and four-membered heterocycles. Chapters 3 and 4 cover fluorinated five-membered nitrogen and fluorinated five-membered oxygen, sulfur, selenium, and phosphorus heterocycles. Fluorinated sugars and ring-fluorinated pyridines are reviewed in the next two chapters, followed by descriptions of six-membered aromatic heterocycles containing perfluoroalkyl groups and perfluorinated aromatic heterocycles with one or more heteroatoms in Chapters 7 and 8. The following two chapters are reviews of perfluorinated nonaromatic heterocycles and seven-membered and larger ring-fluorinated heterocycles, and the final three chapters cover agricultural products based on fluorinated heterocycles, pharmaceuticals containing fluorinated heterocycles, and lastly practical uses of fluorinated heterocycles. The book contains 1438 references.

As stated by the editor, no effort is made to be a comprehensive treatise of the very large and growing field of fluorinated heterocycles. The book does, however, give the reader a wealth of information on the types of fluorinated heterocycles that are possible and their methods of synthesis, reactivity, and utilization. Having worked in fluorine chemistry and with selected heterocyclic compounds for more than 45 years, I found many familiar examples but also much new material. I think this book will be useful to anyone interested in fluorinated compounds and especially to those interested in heterocyclic compounds. The editor has done a very good job in bringing this book to fruition. It will be useful to many.

Darryl DesMarteau, *Clemson University*

JA100496W

10.1021/ja100496w