

Book Review

Book Review of Asymmetric Organic Synthesis with Enzymes

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Dihydrogen Bonds: Principles, Experiments, and Applications. By Vladimir I. Bakhmutov (Texas A&M University, College Station, TX). John Wiley & Sons, Inc.: Hoboken, NJ. 2008. xiv + 242 pp. \$125.00. ISBN 978-0-470-18096-9.

Bakhmutov describes systems that exhibit significant hydrogen–hydrogen interactions in this book. Such interactions of hydrogen atoms have been labeled as dihydrogen bonds by Crabtree and co-workers in cases where the atoms bear a partial positive and negative charge (*J. Am. Chem. Soc.* **1995**, *117*, 12875). Here, the author extends the use of the term to include even molecular hydrogen. In so doing, he has included such a variety of bond types as to make the label indistinctive, and he spends a great deal of energy exploring what a dihydrogen bond is—a question that is made more complex by including all systems where hydrogen atoms interact with each other. The author writes from the point of view of an uncritical advocate, and I found myself wondering about his objectivity. For example, on page 190 he describes an adduct between the tetrahydroboronate ion and cation complex with pendant hydroxyls: “The structure shows that solid complex **1** forms dimers that are held together by four classical hydrogen bonds complemented by four orthogonal dihydrogen bonds, OH...HB. One can assume that these dihydrogen bonds play a principal role in the formation of these dimer structures.” Also, in an analysis of the intermolecular forces that bind molecules of H₃NBH₃ together, he makes a comparison of the melting point of this molecule with that of CH₃F. He attributes the much higher melting point of H₃NBH₃ to dihydrogen bonding and other factors, without explicitly acknowledging the contributions of a dipole moment, which is nearly three times greater.

The book contains an alarming number of errors, and some of the wording is not very clear. In several instances, the author lists physical techniques and quantum chemical approaches without providing much detail regarding them. The lists serve neither the novice nor the expert well.

Hydrogen is unique among the elements in that it does not possess a core of electrons. If dihydrogen bonds are deserving of a distinctive name, then they must have some unique aspects that are not commonly observed among the heavier elements. The polarizability and size of a hydrogen atom are far more variable as functions of charge than those of the heavier atoms. For this reason, the calculation of bond lengths from electron density data underestimates the X–H bond distance, a point that the author makes. The van der Waals radius of hydrogen has little meaning without its being defined with due regard to charge, a point that is worth noting in viewing structural data.

Bakhmutov does take the *a priori* view that there is a dihydrogen bond distinct from the hydrogen bond and then tries to understand its nature. In this effort, the dihydrogen bond is described in terms of long-standing bonding models. By using this term to describe the interactions, I fear that chemists may be led to treat the dihydrogen bond as something different from the pre-existing models of bonding, in much in the same way

as the hydrogen bond has, in some minds, become a distinctive type of bonding rather than a manifestation of electrostatic and covalent bonding. In his willingness to embrace new nomenclature, Bakhmutov would even have us consider the “H–H bonding” interaction in contrast to dihydrogen bonding.

Whether or not you embrace dihydrogen bonding as a label, the book brings together a range of literature involving an interaction that can be surprisingly strong. As such, the dihydrogen bond joins other noncovalent interactions that play a role in structure and dynamics. It is important to remind the community that hydrogen can play a role as donor as well as acceptor in these sorts of interactions, and this book does just that.

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Asymmetric Organic Synthesis with Enzymes. Edited by Vicente Gotor (Universidad de Oviedo, Spain), Ignacio Alfonso (Universidad Jaime I, Castellón, Spain), and Eduardo García-Urdiales (EMBL-Biocomputing, Heidelberg, Germany). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2008. xiv + 326 pp. \$215.00. ISBN 978-3-527-31825-4.

With their high degree of selectivity and efficiency, enzymes—Nature’s best catalysts—represent the ideal tools for the environmentally friendly formation of chiral, enantiopure, small organic molecules. This book is an excellent collection of 10 chapters, divided into two sections, that present a wealth of data on various methods used to increase the stereoselectivity of enzymatic reactions (Chapters 1–3) as well as on different transformations catalyzed by enzymes (Chapters 4–10). Here the goal is twofold: (1) to inform the reader about novel methodologies, directed evolution to optimize the conditions of enzymatic reactions, and different ways to discover new enzymes, and (2) to serve as a reference of very highly selective and important chemical reactions.

Carrea and Riva begin Section I with a thoughtful review on the various ways to affect enzyme selectivity by modifying the nature of the reaction milieu, best defined as “Medium Engineering”. This chapter covers the past 30 years of research in the field. First, they review the addition of organic cosolvents to aqueous media, the use of organic solvent systems, and the fundamentals of biocatalysis in organic media, i.e., water activity, pH, enzyme form, kinetics, and stability as well as some examples of solvent effects on selectivity. Then they cover more recent trends of utilizing ionic liquids and additives. In the second, timely, informative, and very well-written article, “Directed Evolution as a Means to Engineer Enantioselective Enzymes”, Reetz begins by giving a brief, yet thorough overview of the current molecular biological methods for mutagenesis, e.g., error-prone PCR, DNA shuffling, and iterative saturation mutagenesis. An exhaustive and detailed series of examples of enhancing the enantioselectivity of enzymes (e.g.,

lipases, nitrilases, epoxide hydrolases, and aminotransferases, to name a few) by directed evolution completes the presentation of this powerful approach. As an elegant way to end Section I, Reymond and Streit discuss the different methods available, i.e., mechanism-based enzyme design and metagenomics, to discover novel enzymes with improved properties.

The second and larger part of this book focuses on synthetic applications. This section is divided into six chapters organized by the type of reaction catalyzed by the enzyme. Martín-Matute and Bäckvall first describe the recent and extensive achievements in dynamic kinetic resolutions of racemates catalyzed by metals, bases, acids, aldehydes, and enzymes (Chapter 4). Turner then discusses recent advances in the complementary deracemization and enantioconvergent transformations, two clever ways of achieving the total conversion of a racemate in high yield and enantiomeric excess by optical enrichment of the substrate (Chapter 5). In the next chapter, Chênevert et al. highlight the research from 2000 to 2006 on the transesterification and hydrolysis of carboxylic acid derivatives, alcohols, and epoxides that are catalyzed by hydrolases, the most frequently used biocatalysts in organic synthesis. Gotor-Fernández and Gotor follow in Chapter 7 with a set of examples on the use of lipases for the clean, ecological way to prepare chiral amines and amides by ammonolysis and aminolysis reactions. In Chapter 8, Nakamura and Matsuda mostly review emerging methodologies, i.e., screening of microbes; modification of biocatalysts, substrates, and reaction conditions; and medium engineering, to improve the reactivity and selectivity of enzymatic reductions and to provide some examples of synthetic applications of such reductions. Mihovilovic and Bianchi then discuss novel catalysts for biooxidation and the diverse and exciting biotransformations accomplished by these remarkable enzymes (Chapter 9). Finally, Fessner reviews the state of

development and the most efficient reaction techniques for C–C bond formation by aldolases, with important and relevant synthetic examples (Chapter 10).

Overall, the two complementary sections of this book are useful and give the reader a complete overview of the topic, which is very well described by the title of this monograph. It is rich in illustrations, and therefore pleasing to the eye, and easy to read. Overall the references are timely and appropriate. Because the text covers a wide span of topics and research interests, it is recommended as a learning tool for graduate students in biochemistry and organic chemistry entering the field and as a guide to professionals already enjoying the power of enzymes for producing enantiopure compounds.

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This latest edition of *Organic Reactions* consists of one chapter: “Ionic and Organometallic-Catalyzed Organosilane Reductions” by Gerald L. Larson and James L. Fry. The book concludes with the cumulative chapter titles by volume, an author index, and a chapter and topic index, volumes 1–71.

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