

Book Review

**Book Review of Halogen Bonding: Fundamentals
and Applications. Structure and Bonding, 126**

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J. Am. Chem. Soc., **2008**, 130 (31), 10446-10447 • DOI: 10.1021/ja804186p • Publication Date (Web): 10 July 2008

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Halogen Bonding: Fundamentals and Applications. Structure and Bonding, 126. Edited by Pierangelo Metrangolo and Giuseppe Resnati (Politecnico di Milano, Italy). Springer: Berlin, Heidelberg, New York. 2008. xii + 223 pp. \$229.00. ISBN 978-3-540-74329-3.

Halogen bonding is a highly directional noncovalent interaction between a covalently bonded halogen atom (usually Cl, Br, or I) and a negative site on another molecule or ion, e.g., a lone pair of a Lewis base. It has now been shown that covalently bonded group V and group VI atoms can behave similarly; thus halogen bonding, which has been known the longest, can be viewed as a subset of the class of interactions recently labeled σ -hole bonding.

The articles in this volume specifically address halogen bonding, and two aspects of it in particular: (a) the interactions of halogen and interhalogen molecules (X_2 and XY) with various Lewis bases (B), and (b) the role of halogen bonding in crystal engineering, i.e., the design and preparation of new crystalline materials having certain desired properties. There is very little discussion of the considerable significance of halogen bonding in molecular biology, for example, in molecular recognition, drug design, conformational equilibria, etc. However, the topics that are covered are usually treated exhaustively.

Legon analyzes gas-phase $X_2\cdots B$ and $XY\cdots B$ complexes, with a particular emphasis on their geometries. He does not simply summarize findings but also provides detailed accounts of experimental procedures. Halogen bonding is examined in relation to analogous hydrogen bonding. Particularly interesting is the demonstration of how zero-point energies may determine geometries by overcoming potential energy barriers between conformations.

The crystalline phases of $X_2\cdots B$ and $XY\cdots B$ complexes are surveyed by Pennington et al., with lengthy tabulations of systems and structural data. Bonding arrangements and patterns are identified and discussed separately for various types of Lewis bases. Pennington et al. also include an extensive and detailed summary and evaluation of various computational treatments of such complexes at the molecular level; this complements Karpfen's chapter, which emphasizes theoretical studies of the properties of X_2 and XY interactions with NH_3 and amines.

With the discussions of crystal engineering by Metrangolo et al. and by Fourmigué, we move from $X_2\cdots B$ and $XY\cdots B$ to the much broader category of $RX\cdots B$, where R is some organic moiety, usually containing heteroatoms. By selecting molecules with two or more appropriate halogens—and perhaps having basic sites as well—and combining these with Lewis bases that are also multiply functional, e.g., $Au(CN)_4^-$, it is possible to create one-, two-, or three-dimensional networks of halogen-bonded components. These two chapters illustrate well the vast array of crystal structures that have

been or may in the future be produced. With regard to practical uses of such systems, Fourmigué does make some reference to applications as conducting or magnetic materials, but I would have liked to have seen more about this. Halogen bonding can also be the basis for preparing liquid crystals. This relatively new but potentially important role for it is examined in the chapter by Bruce.

The reader may be wondering why such electronegative atoms as the halogens should interact attractively with negative sites. Brinck et al. showed in 1992 that some covalently bonded halogens have localized regions of positive electrostatic potential along the extensions of their covalent bonds, with negative potentials on their lateral sides. The interaction of such a positive region with a Lewis base accounts for both the occurrence and the directionality of halogen bonding. In 2007, Clark et al. explained the origin of the positive potential as due to the charge deficiency in the outer lobe of the p -type orbital involved in the covalent bond; this is the " σ -hole," a concept later extended to groups V and VI by Murray et al.

The contributors to this volume address the reasons for halogen bonding to various degrees, with Pennington et al. and Metrangolo et al., in their respective chapters, giving essentially the above interpretation; the former include a figure showing the positive potentials on the iodines of I_2 . They ascribe such regions to the charge distributions around the halogens being diminished along the extensions of the covalent bonds (i.e., the σ -holes); they also note that these halogens, having both positive and negative regions, can interact with both nucleophiles and electrophiles. In several of the chapters, there is discussion of factors that influence the strength of halogen bonding to a given Lewis base, such as the polarizability of the halogen and the electron-withdrawing power of the remainder of the molecule.

Some references are made to halogen bonding as a charge-transfer interaction, invoking the treatment developed by Mulliken. This is quite compatible with the electrostatic interpretation given above, which describes the interaction in the ground state of the complex, whereas Mulliken's emphasis was on the transition to the dative excited state. It should also be noted that the occasional suggestion that a halogen to base bond, $RX\cdots B$, involves charge transfer into a σ^* orbital of $R-X$ is inconsistent with the fact, mentioned in Karpfen's chapter, that the $R-X$ stretching frequency sometimes undergoes a blue shift.

Rosokha and Kochi look at charge-transfer spectra and crystal structures associated with halogen interactions with π -systems. They include examples involving a halide ion, such as Br^- , and an arene or olefin in which the π -charge is depleted by the presence of strongly electron-withdrawing groups, e.g., 1,3,5-trinitrobenzene. Such complexes are of considerable interest, but they do not correspond to halogen bonding in the usual sense, since the halogen is acting as the Lewis base.

In the literature on halogen bonding and in this book as well, the reader should be alert to how the words “donor” and “acceptor” are being used. In a complex $RX\cdots B$, RX is the halogen bond donor but the electron acceptor; B is the electron donor and halogen bond acceptor. This is not a problem but must be kept in mind.

The contributions to this volume are reasonably up-to-date, with approximately 13% of the more than 900 references being from 2005–2007. The subject index is not a strong point, but each chapter begins with a detailed table of contents and most of them also provide a list defining abbreviations. In summary, this is a very useful book that contains a great deal of information. I can certainly recommend it.

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JA804186P

10.1021/ja804186p

X-Ray Crystallography of Biomacromolecules: A Practical Guide. By Albrecht Messerschmidt (Max-Planck-Institute for Biochemistry, Martinsried, Germany). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2007. xiii + pp. \$175. ISBN: 978-3-527-31396-9.

Structural biology is a major field within the biological sciences as well as a key component of most modern universities and biotech and pharmaceutical firms. Although NMR spectroscopy plays a growing role as a tool of structural biology, X-ray crystallography remains the mainstay of the discipline. In the past, X-ray analyses of protein structures were largely the purview of professional crystallographers. Today, the existence of experimental core facilities and robust analytic software has allowed a broader range of scientists to use this powerful method. It is not uncommon for a research group to crystallize and, with some help, solve a macromolecular structure of central interest to it. Such users may want to acquire a theoretical background in X-ray diffraction to understand the method itself and to enable them to analyze their data and their molecular model critically.

To address this need, there are currently a number of books available that provide a background on protein crystallography. These include *Principles of Protein X-ray Crystallography* by Drenth; *Crystallography Made Crystal Clear: A Guide for Users of Macromolecular Models* by Rhodes; *Practical Protein Crystallography* by McRee; and *Outline of Crystallography for Biologists* by the late Blow. This abundance raises a question about the role for Messerschmidt's book.

The first part of the book, “Principles and Methods”, is laid out largely like many other books on crystallography. It begins with a review of crystal growth, moves on to a discussion of X-ray generation and equipment, and then covers the theory of diffraction, phasing, and special techniques. The treatment here is unusually rigorous—overly so, in my opinion, for the likely audience for the book. For example, in Chapter 3, Messerschmidt describes wave addition algebraically, factoring away to develop complex expressions for the resulting amplitude and phase. I feel this is more opaque and less useful for many budding crystallographers than is the more common Argand vector analysis, although the result is the same. Later in the chapter, he discusses diffraction from an electron, beginning with Maxwell's equations. Again, this level of analysis is

unnecessary for most readers, although it will be of interest to a few specialists. I could extend this list considerably, but the point is clear: this book contains many more rigorous derivations of X-ray phenomena than do most other books in the area. I think that many biochemists or molecular biologists would find the treatment by Blow, for example, to be far clearer and more illuminating for their needs; it gives a better “feel” for the subject. Ironically, despite the general level of mathematical rigor, Messerschmidt does not develop convolution theory. My experience in the classroom is that this powerful tool is one of the most useful in the field.

Part II of the book, “Practical Examples”, is quite different in tone. The author presents very practical details of how to run and interpret some of the most common and useful software in the field, such as MOSFLM, SHARP, and elements of CCP4. The level could almost be characterized as “hand-holding” and seems somewhat out of place compared to Part I. In any case, this section should be very useful for a range of practitioners, even though it may rapidly become obsolete given the pace of software development.

In summary, this book is reasonably well organized and covers all of the relevant theory and much of the practical applications of the field. My opinion is that the theoretical rigor is unnecessarily high for most casual users, although the examples in the Part II could be very useful to them. On the other hand, I think that having at least one copy of this book available would be a benefit to many laboratories specializing in protein crystallography. It could provide the details necessary for a deep analysis of crystallographic problems and also for understanding the design and functional intricacies of modern diffraction equipment. The practical examples of Part II could also be helpful for training students and more occasional users of the technique.

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JA8027586

10.1021/ja8027586

Computational Modeling for Homogeneous and Enzymatic Catalysis: A Knowledge-Base for Designing Efficient Catalysts. Edited by Keiji Morokuma and Djamaladdin G. Musaev (Emory University, Atlanta). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2008. xx + 378 pp. \$215. ISBN 978-3-527-31843-8.

The availability of powerful computers and the development of efficient and reliable computational methods and algorithms in the past decade have provided useful tools for understanding catalysis. Although most computational studies of catalysis have been driven by curiosity, others have been motivated by economic considerations. Virtually all industrially produced chemicals rely upon catalysts; thus, it is sometimes possible to design more efficient catalysts, given a greater knowledge base. This latter point is the basis of the subtitle of the book.

Morokuma and Musaev, two of the leading experts in the field of computational modeling of catalysis, have assembled an excellent collection of timely reviews. The scope of the book includes the application of computational methods to the modeling of homogeneous, heterogeneous, and enzymatic catalysis. The 15 chapters, written by 35 computational chemists from academia and industry, cover a broad range of topics,

including biocatalysis, C–H bond activation, nitrogen fixation, oxidations, and, among other topics, polymerization.

The first three chapters provide very readable summaries of recent research on three distinct biological and enzymatic catalytic processes. These chapters set a high standard that is maintained throughout. In the remaining 11 chapters, there is very heavy emphasis on the role of transition metals as efficient tools for organic synthesis. The extensive coverage of computational studies of transition metal catalyzed reactions and metalloenzyme catalyzed reactions is the strongest feature of the book. This is very fitting given the rapid development of organometallic chemistry and its impact on organic synthesis. Nevertheless, there are a few current topics in catalysis that have not been included, such as nontransition metal catalyzed condensation reactions that are an important aspect of synthetic strategies in organic chemistry. The inclusion of chapters on the use of proline and thiourea, for example, would have made the book an even more essential reference work, while keeping its size within reason.

From a technical perspective, the book is very well produced. The quality of the figures is high, and the general layout is attractive. There are a few awkward sentences, but the scientific content is clear.

In summary, this book represents a substantial contribution and will be an important source of information for all researchers with an interest in catalysis. Furthermore, it will be an excellent starting point for new researchers in the field. This book should be included in all research libraries.

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JA8046975

10.1021/ja8046975

Handbook of RAFT Polymerization. Edited by Christopher Barner-Kowollik (University of New South Wales, Sydney, Australia). Wiley-VCH GmbH & Co. KGaA: Weinheim. 2008. x + 544 pp. \$245. ISBN 978-3-527-31924-2.

Reversible addition–fragmentation chain transfer (RAFT) polymerization has only been developed over the past decade, but has quickly found wide application in polymer synthesis, spawning many new polymer compositions, architectures, and materials. The RAFT method of polymerization relies on the fast, reversible chain transfer processes of thiocarbonylthio compounds to mediate the growth of polymer chains in radical polymerization. Its use can result in significant control over molecular weight, create narrow distributions in the molecular weight of the polymer, and provide polymers with chain-end functionality that allows for a variety of postpolymerization reactions to occur, including block copolymer synthesis, peptide conjugation, (nano)particle surface modifications, and so on. Such a broad range of chemistries and materials, coupled with

the fact that RAFT polymerizations are generally easily performed, means that RAFT polymerization can be utilized by many in the chemical community.

This book provides a timely overview of all aspects of RAFT polymerizations, including an excellent summary of RAFT-related mechanisms and materials. It covers a wide range of topics, beginning with historically related thiocarbonylthio processes (e.g., Barton–McCombie deoxygenation), structure–reactivity correlations, polymerizations in a variety of media (e.g., emulsions), RAFT kinetics and mechanisms, complex polymer architectures and functionality, and finally examines the potential of RAFT polymerization in areas such as drug/gene delivery, optoelectronics, tissue engineering, alternative energy, etc.

The book contains contributions from key researchers in the field and is uniformly well written and edited. Most chapters are of a good length and depth and are correspondingly well referenced. Because RAFT polymerization is relatively new, most references are recent, including some from 2007. The authors have generally done an excellent job of making digestible specific subjects that could easily become burdensome for individuals not working in those specific fields. In all, it is an excellent book, and I suspect that workers (and students) from many fields—not just those working in the polymer area—will find this a constantly useful reference for many years to come.

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JA804579V

10.1021/ja804579v

Annual Review of Physical Chemistry, Volume 59, 2008. Edited by Stephen R. Leone (University of California, Berkeley) and Associate Editors: Jay T. Groves (University of California, Berkeley), Rustem F. Ismagilov (University of Chicago), and Geraldine Richmond (University of Oregon). Annual Reviews: Palo Alto, CA. 2008. xvi + 804 pp. \$84. ISBN 978-0-8243-1059-2.

Volume 59 of *Annual Review of Physical Chemistry* contains 30 chapters covering the latest research in this broad field, from biophysical investigations of collapse mechanisms of biological thin films to research in sonoluminescence and cavitation by ultrasound irradiation, to coverage of quasicrystal surfaces. The opening chapter “A Fortunate Life in Physical Chemistry” is an autobiographical account by Stuart Rice of his “evolution as a physical chemist.” A Cumulative Index of Contributing Authors, Volumes 55–59 and a Cumulative Index of Chapter Titles, Volumes 55–59 complete the book.

JA804861J

10.1021/ja804861j