Stirring Stuff

Stimulating Concepts in Chemistry. Edited by *Fritz Vögtle, J. Fraser Stoddart*, and *Masakatsu Shibasaki*. WILEY-VCH, Weinheim 2000. xvii + 396 pp., hardcover DM 98.00.—ISBN 3-527-29978-5

The modern world has embarked with much fanfare into the new millennium, and many people, faced with a reality more sober than the glitter of the festivities had promised, are looking for some guidance. Chemists can turn to

chemistry books, which abound in examples with inescapable titles marking the event. What a pleasant surprise, then, to find a book that follows a different lead. The refreshingly new twist of



Stimulating Concepts in Chemistry is its emphasis on the conceptual reasoning behind those research areas in (organic) chemistry which have emerged in recent years as inspirational new directions. The 24 contributions in this book are therefore not just reviews of specific topics, but rather essays in which respected leaders in their fields illustrate the important ideas behind their individual areas of research. The conceptual approach is also apparent in the layout and the structure of each essay: each one of them is introduced by a two-sentence statement outlining the main concept, one illuminating figure, and a short

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abstract of the ideas that are to be developed in the following highly structured text. Keywords running vertically along the margin of the introductory pages to each essay facilitate orientation. Many citations, including the titles of the publications, conclude each essay.

The essays in this book are loosely grouped into four sections, "Design and Synthesis", "Architecture, Organisation and Assembly", "Molecular Devices and Material Properties", and "Biological Aspects".

"Design and Synthesis", the largest section in the book, consists of 10 essays. The first three essays address new developments in environmentally benign organic chemistry. S. Kobayashi, for example, describes the development and uses of water-stable Lewis acid catalysts, R. Novori discusses supercritical fluids in organic synthesis, and D. Curran describes the advantages of fluorous techniques for the synthesis of organic molecules. Efficiency in organic synthesis is the topic of two essays by L. F. Tietze and J. A. Ellman. While the former highlights the power of domino reactions to construct complex organic molecules from relatively simple precursors, the latter focuses on combinatorial libraries for drug development. Five essays in this section are devoted to various aspects of catalysis. K. Houk reflects on the computational modeling of enzymes (theozymes) and their use in catalyst design (chemzymes), A. Pfaltz introduces his concept of asymmetrical P,N ligands in enantioselective catalysis, M. Shibasaki explains his approach to mimicking enzymes by asymmetric two-center catalysis, and T. Shiori describes efforts to combine asymmetric catalysis with phase-transfer catalysis. This section is concluded by an essay from A. H. Hoveyda in which he highlights asymmetric catalytic CC, CO, and CN bond forming reactions in target-oriented synthesis.

The section "Architecture, Organisation and Assembly" contains five con-

tributions from the work of F. Diederich, Y. Rubin, F. Vögtle, J. Rebek, J. F. Stoddart, and M. D. Ward. While Diederich and Rubin summarize synthetic developments in the area of fullereneand acetylene-based molecular carbon allotropes, Vögtle and co-authors take the reader into the macromolecular world of dendritic architectures. Three essays on supramolecular chemistry follow, one in which J. Rebek outlines the concept of chemical encapsulation in self-assembling capsules, a second one where J. F. Stoddart describes rotaxane and hemicarcerand superarchitectures formed by slippage and constrictive binding, and finally a third in which M. D. Ward highlights his group's efforts in crystal engineering with guanidinium disulfonates as molecular host frameworks.

Six essays by J. M. Tour, V. Balzani, M. N. Paddon-Row, G. R. Desiraju, A. P. de Silva, and K. Müllen constitute the section named "Molecular Devices and Material Properties". J. M. Tour discusses the synthesis and uses of molecular wires based on alkynylbenzenes and alkynylthiophenes. V. Balzani gives an overview of various approaches to molecular-level devices and machines, and M. N. Paddon-Row outlines his concept of electron and energy transfer over large distances through nonconjugated media. The essay by G. R. Desiraju, which is concerned with the supramolecular synthon in crystal engineering, appears to be somewhat misplaced in the light of the content of the previous section. The topic of A. P. de Silva's contribution is luminescent logic and sensing, in which he describes molecular devices capable of controlled and specific photoinduced electron transfer. The final word in this section comes from K. Müllen, who presents nanochemical architectures based on the benzene nucleus.

The last section in this collection, entitled "Biological Aspects", is surpris-

ingly short, with only three essays by A. J. Kirby, C. H. Wong, and H. Waldmann. A. J. Kirby builds on an earlier review on enzyme mimics, C. H. Wong describes the rational design of enzyme inhibitors, and H. Waldmann discusses the fertile interplay between organic synthesis, cell biology, and biophysics, with RAS protein as an example.

The editors have achieved an admirable degree of homogeneity in this multiauthor collection of essays. The figures and schemes are, with a few exceptions, of very high quality and almost free of errors, as also is the text. The individual essays are well written and are an exciting and indeed stimulating read for all those fascinated by key developments in (organic) chemistry. Certainly, individual readers' personal tastes and views might have dictated a different selection and weighting of topics. In the introduction the editors express their wish that this book should be the start of a "Concepts in Chemistry" series that would include other subdisciplines of chemistry which have not been considered (enough) here. The good start that has been made with this "inaugural volume" certainly makes one look forward to such a continuation, and that would retrospectively justify the overly comprehensive title of the book. Stimulating Concepts in Chemistry should be available in academic libraries and is recommended for advanced students and curious professionals.

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Metabolic Pathways of Agrochemicals. Parts 1 & 2. Edited by *Terry R. Roberts* and *D. H. Hutson*. Royal Society of Chemistry, Cambridge 1999. 2326 pp., hardcover £ 425.00.—ISBN 0-85404-489-2

When planning to use new plant protection agents (agrochemicals) or to test compounds of potential value, it is essential to have a knowledge of their breakdown pathways and the intermediate and final products. Toxicological laboratories, mainly in industry, devote much effort to identifying the com-

pounds thus generated. Very often, and sometimes unexpectedly, this gives new insights into the metabolic pathways of plants and bacteria (including soil bacteria). However, this knowledge is not easily accessible to scientists who are not accustomed to using the patent literature. Enzymologists do not usually read the journals Weed Science or Pesticide Science, and do not know the trivial names of the compounds. Consequently, they miss much potentially useful information about breakdown pathways (and also breakdown inhibitors). However, this book is concerned with reactions and contains no enzymology, let alone the associated molecular biology. Studies of the mechanism of action of pesticides have often made important contributions to understanding the biochemistry of the target species and the biosynthetic pathways that the agents interfere with (one thinks of the role of herbicide studies in research on photosynthesis, or of the shikimic acid pathway). In the same way, investigating breakdown mechanisms should give fresh insights into less obvious degradation pathways.

Knowledge about the metabolic pathways of pesticides, leading to either breakdown or detoxification, yields insights into aspects such as their range of applications, selectivity, mechanism of action, and possible risks to the environment. (Detoxification is not the same as breakdown; for example, the deactivation of Metribuzin by in vivo formation of the N-glycoside is not a breakdown process.) There is, of course, specialist literature about many pesticides, but this information is inaccessible to many scientists. These two volumes go a long way towards filling the gaps described above. Nevertheless, one notices that "unpublished" occurs frequently in the citations. The chemistry of pesticide breakdown often turns out to be surprising, as also does the manner of breakdown by biological systems. These two volumes are a mine of information on those topics.

The *Pesticide Manual* published by the British Crop Protection Group (my copy of which is dated 1997) lists over 1100 compounds, and serves as the reference point for these two volumes. Of those in the manual, Volume 1 lists 153 insecticides, a few pheromones and synergists, and 108 fungicides, nematocides, and

rodenticides, while Volume 2 lists 158 herbicides (more than the number listed in the herbicides handbook of the Weed Science Society), and a few safeners and plant growth regulators, about 470 compounds altogether. The products described in the introduction to each class are not necessarily the market leaders, and, for example, the same breakdown route is sensibly not repeated for all the ureabased herbicides. On the other hand, the compilation includes some compounds that have only a small market niche, or some that are at present only potential pesticides and have not yet been used commercially. The data given in the introduction to each compound are brief: the chemical and trivial names. CA registration number, molecular mass, chemical structure, some physicochemical data such as partition ratio or lipophilicity (important for studies of QSAR, quantitative structure-activity correlation), and a few additional lines on the mechanism of action. This information is already available in the specialist books on the subject, whereas the present work concentrates on the breakdown pathways, which those publications rarely mention. The predominant breakdown mechanisms described are chemical, especially photochemical, in the application environment and in the soil. Next in importance are biological mechanisms involving metabolic pathways in soil bacteria or in plants. These are described clearly, precisely, and in detail—at least so far as they are known, as there are still many gaps in knowledge.

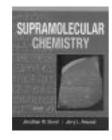
The compounds are grouped according to their modes of activity and are arranged alphabetically within those groups, a system which works well in finding one's way. Space is used generously, with excellent clear page layouts, but this has probably made the volumes thicker than was really necessary. These are useful works of reference that can be thoroughly recommended; as such, however, they are not books for relaxed reading.

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Supramolecular Chemistry. By *Jonathan W. Steed* and *Jerry L. Atwood.* John Wiley & Sons Ltd., Chichester 2000. 746 pp., softcover £ 29.95.—ISBN 0-471-98791-3

Books on the new field of supramolecular chemistry available up to now, such as the recently published monograph by Schneider and Yatsimirski (*Principles and Methods in Supramolecular Chemistry*, Wiley, New York 1999),

or the well-known book by J.-M. Lehn (Supramolecular Chemistry, VCH, Weinheim 1995), are specialist books intended mainly for those engaged in re-



search in the area. In contrast, Steed and Atwood have produced the first textbook on supramolecular chemistry that is written mainly for students.

An introduction, in which the authors explain important concepts and definitions, is followed by a chapter on the supramolecular chemistry of the living world. This chapter succeeds well, awakening the reader's interest straight away, and this not solely due to the section about Viagra. The importance and ubiquitous presence of supramolecular structures in biology is emphasized and lucidly explained, with examples such as the chemistry of photosynthesis and DNA. After this interesting start, the authors introduce the reader to the various types of host molecules. They begin with the classical cation hosts, then progress to the more complicated molecules that can bind anions and neutral species.

From host – guest chemistry the reader then moves on to the more complex phenomena of self-organization. A chapter on "Crystal Engineering" is followed by a section dealing with templates and self-assembly. The discussion touches on catenanes, rotaxanes, self-replicating systems, and other topics. A section headed "Molecular Devices" deals with supramolecular photochemistry, molecular machines, sensors, molecular electronics, nonlinear optical materials, and dendrimers. The next section, on "Biological Mimics", is mainly concerned with enzyme model systems.

Lastly the authors discuss liquid crystals and clathrates.

The subject matter is systematically arranged, with a logical structure. All important aspects of modern supramolecular chemistry are addressed, and the authors have avoided overemphasizing their own areas of research. Literature references, mainly secondary literature and review articles, are incorporated into the text so that the reader can dig deeper on topics of special interest. In addition there is a list of primary literature references at the end of each chapter; this is concise and relevant, giving only the most important papers on the subject. It is pleasing to note that the literature references are very up-to-date, including publications up to the end of 1999. A few exercise problems are given at the end of each chapter to test the reader's newly gained knowledge and provide additional insights. Solutions to these were to have appeared on the authors' web page [http://www.CH.KCL. AC.UK/SUPRAMOL/TEXTBOOK.

HTM], but at the time of writing this review (November 2000) they could not be found. However, the web page does provide some further information, including a detailed list of the book's contents, the authors' preface, and three-dimensional structures for a few of the supramolecular complexes described. The latter are very useful, especially for complex molecules where twodimensional representations are inadequate, and they will help students to gain a better impression of the complete structure. The layout of the work is mainly clear and informative. Only a few of the figures are not very clear (e.g., pp. 292, 382, 453). Here some judicious use of color would have been an advantage. Some additional detailed information, for example about analytical methods for studying molecular interactions, is presented in "boxes" distinguished by a gray background. Unfortunately, however, the text in these is printed in such small type that it is difficult to read on the gray background.

There are a few small printing errors, but they do not detract significantly from the very good overall impression. On the other hand, in textbooks it is especially important that students should not be confused by errors in structural formulas. For completeness, therefore, it has to

be mentioned that on page 113 one finds a hexavalent carbon atom, and that on pages 518 and 523 the formulas show a few too many electric charges, whereas on page 4, in formula 1.3, the hydrogen atoms that should be on the nitrogen atoms have been omitted.

Summarizing the verdict, the book is thoroughly recommended for all advanced students of chemistry with an interest in the highly topical and exciting area of supramolecular interactions. The word *advanced* must be emphasized, since to understand the contents one should have a thorough knowledge of the fundamentals of inorganic, organic, and physical chemistry, together with some basic knowledge of biochemistry and organometallic chemistry.

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Chemical Separations. Principles, Techniques, and Experiments. By *Clifton E. Meloan*. John Wiley and Sons Inc., New York 1999. xv+752 pp., hardcover £ 64.50.—ISBN 0-471-35197-0

In the preface to this book the author (not its editor!) writes that the aim is to describe the basic principles of the most commonly used chemical (and physicochemical) separation techniques, the apparatus needed, and some special applications (detailed descriptions of experiments). Essentially it can be said that the author has succeeded in that aim, with over 700 pages, in encyclopedic format, of which over 200 are occupied by the experiments.

The separation methods are described in eight main chapters. However, not all those that are discussed can qualify as separation techniques in the strictest sense. Also some of the methods that are mentioned, presumably in the interest of completeness, are not so widely applicable as to deserve detailed description in a laboratory handbook that is partly intended for use by undergraduates.

The chapter entitled "Separations involving phase changes" describes the various distillation techniques (including azeotropic and extractive distillation, molecular distillation, and sublimation), as well as zone melting and freeze drying. This is followed by "Separations involving extraction", which describes the classical extraction methods (including the relatively little used technique of countercurrent extraction chromatography), together with the more chromatography-related techniques of solidphase extraction (SPE) and extraction by supercritical gases. True chromatographic methods are described in great detail in the following chapter of 150 pages. A separate chapter is devoted to ion-exchange chromatography. chapter "Separations involving electric fields" describes electrogravimetry and field-flow fractionation, and also, of course, treats classical electrophoresis techniques and capillary electrophoresis in much detail. As one would expect, this comprehensive description of separation methods also includes membrane techniques, foam fractionation, centrifugation, and classical Orsat analysis.

Each chapter contains a brief but adequate account of the basic theory of the method, with worked examples of calculations where possible. The apparatus is described and discussed in detail with text and figures, whether it involves only simple matters such as different types of coolers, materials for recovering spilled mercury, or capillary cutting devices for gas chromatography, or more complex details such as detectors for chromatography. The latter are treated thoroughly, covering the different detection principles and types of applications, illustrated by clear figures. Each chapter is accompanied by a detailed list of questions. However, the most useful extensions to the chapters are the experiments, which are described in detail with all the necessary apparatus and chemicals. The experiments chosen are highly topical and relevant to practical needs. Typical examples are experiments to determine the breakdown products of aspartame by capillary electrophoresis, or vitamin C in drinks by ion chromatography.

The book can be recommended for everyone with an interest in separation techniques, whether the purpose is to prepare a lecture course or to make practical use of the methods. Readers will appreciate the many instructive figures, the data, the practical advice, and—not least—the detailed descriptions of experiments. The book should be available in every laboratory library (including organic chemistry departments, as the flash chromatography that is favored there is also treated in detail). All chemists need to be familiar with separation methods and to be able to carry them out correctly; this book will give them quick access to valuable advice about practical problems.

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Color. A Multidisciplinary Approach. By *Heinrich Zollinger*. Helvetica Chimica Acta, Zürich, and WILEY-VCH, Weinheim 1999. x + 258 pp., hardcover DM 198.00.—ISBN 3-906390-18-7

The author—already known from his books about color (Color Chemistry, 2nd edition, VCH, 1991; Farbstoffchemie, 3rd edition, VCH, 1982), and diazo chemistry (Diazo Chemistry, I and II, VCH, 1994 and 1995)-now presents a book about general aspects of work with colors. The author's intention, mentioned in the introduction (10 pp.), was to write a book for reading throughout rather than a dictionary for reference. It was not to be an unconnected collection of special topics; instead it was meant to be appropriate not only for scientists, but also for laymen. Accordingly, the chapters deal with very different aspects of color. The book begins with chapters on the various areas of natural sciences, starting with physics (29 pp.). Aspects covered include refractive indices, the explanations for primary and secondary rainbows, and the question of how the feathers of peacocks can show so many different colors. Chemical aspects follow next (21 pp.), with topics from inorganic, organic, and theoretical chemistry. Since a book devoted to this area has already been published by the author, the topics are treated here in a very concise and simple manner. A chapter about the measurement of colors (15 pp.) deals

with the additive and subtractive mixtures of colors and dyes, and the diagram showing the specifically human view of color. There is also a historical part, mentioning, for example, Newton's speculations about the relationship between color and a musical key (in this case the first, Dorian mode). The biological aspects of color vision follow, with special emphasis on human vision (42 pp.). Anatomical and biochemical aspects are dealt with, as well as several disorders of vision. A section about animal vision finishes this extensive part. There then follow chapters concerned with the humanities and cultural aspects, and the arts. The first of these considers the psychological and cultural aspects of the naming of colors in different languages (36 pp.). Relationships with art and other cultural areas follow (70 pp.). Besides the historical aspects of European and Japanese cultures concerning paintings, including stained glass church windows, the psychological aspects are briefly mentioned again, as also are synesthetic aspects, as well as Goethe's Zur Farbenlehre and his arguments against Newton. The book ends with an epilogue (11 pp.).

Scientific texts may often be divided into two groups, one aiming at a specialized and technically orientated readership, and one intended for a general readership with a concise and simplified presentation. The middle course of the scientifically based description of a broadly defined general subject, as chosen by this author, is nowadays rare, not only in the area of chemistry. Of course, one cannot expect a complete description of so many different aspects of color in just 258 pages. Instead the book aims to present suggestions which show the connection between the different topics. and leave it to the reader to follow the ideas further. Accordingly, the author also tries to present the many different aspects of color research which fascinate him, and to discuss different hypotheses that are still in contradiction to each other. Minor inaccuracies or misunderstandings are therefore hard to avoid in a text with limited space and aimed at so many directions. Thus, for example, protonated iminium ions with conjugated double bonds are equated with cyanines, and the abbreviations of Figure 5.4 are hard to understand on reading

through the main text. One of the most noticeable mistakes in the otherwise flawless printing is the shift of printed colors in the picture on page 187.

However, these criticisms do not detract significantly from the usefulness of the book and the stimulating ideas that it offers. Unfortunately the high price of the book is a matter for concern, especially since it is not meant to be a specialized book with a small readership. Certainly this does not reflect the author's intentions, nor does the wasteful style of page layout, in which the text occupies only 40 % of the space. The rest of the space has been used for illustrations in only about 1/7 of all pages, and five pages are left completely blank. Nevertheless, the book is highly recommended to everybody who is not deterred by its price and has interests in the general area of color.

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Hydrodesulfurization and Hydrodenitrogenation. By *Toshiaki Kabe, Atsushui Ishihara* and *Weihua Qian.* WILEY-VCH, Weinheim 1999. xii+374 pp., hardcover DM 268.00.—ISBN 3-527-30116-X

Hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are timely subjects. With new, very strict legislation about the permissible limits of sulfur and nitrogen in fuels coming under discussion for 2005, research on HDS and HDN catalysts as well as catalytic processes is attracting ever more attention in industry and academia. Even though some critical remarks can be made, this book fills a gap and is a must for everyone in the hydrotreatment field. This is the first comprehensive work published since the standard text Sulphide Catalysts, Their Properties and Applications by Weisser and Landa. It contains a wealth of information for the beginner as well as for the expert. The extensive references to the Japanese literature are an advantage for scientists from other parts of the world, who ought to have kept up with this literature as well but have not always done so.

The book has five chapters: 1. Introduction to HDS and HDN; 2. Reaction profile in HDS and HDN; 3. Structure of HDS and HDN catalysts; 4. Development of novel HDS and HDN catalysts; 5. Process engineering. Each chapter has an impressive number of references: 95, 408, 392, 501, and 212, respectively. Whereas Chapters 3 and 4 refer to literature starting in the seventies, Chapter 2 refers to articles that were published as long ago as the sixties. Since the authors or editors chose to put a list of references at the end of each chapter rather than at the end of the book, many of them are repeated. This probably reflects the fact that each of the three authors was responsible for one or two

The book is well presented; the layout makes a good impression, and the English is of a high standard. My only complaint to the publisher is that the quality of the paper is so poor that the print on one side of the page is clearly visible on the other side.

The book starts with a short (16 pp.) introduction to the subject. Although an introduction to Chapters 2–4 is certainly needed, 16 pages are not enough to introduce all the aspects discussed in the book, but are too many if several of the points must be introduced in the respective chapters anyway. The major part of the book is distributed over Chapters 2–4 (104, 80, and 91 pp., respectively).

Chapter 2 discusses the HDS and HDN reactions from an applied point of view. The descriptions and discussions of the mechanisms, effects of substituents, and effects of hydrogen sulfide and kinetics are thorough. Kinetic equations are presented without much critical discussion. Although it is clear that the authors can cover much more ground by taking such an approach, I wonder whether this approach will prove attractive to the readers. Students should learn to ask critical questions about the results presented in the literature, and textbooks are a good place to teach them to do so.

The effect of alkyl groups in deep HDS is well presented, although the excellent review by Whitehurst, Isoda, and Mochida in Adv. Catal. 42 (1998) on the HDS of polyaromatic sulfur compounds is not discussed, because the book was finished in July 1998. For more or less the same reason, the relevant chapters in the Handbook of Heterogeneous Catalysis, edited by G. Ertl, H. Knözinger, and J. Weitkamp, and published in 1997, have also not been taken into account. With the book being finished in 1998, it was also impossible for the authors to pay much attention to theory, because the very interesting results using density functions (Norskov, Raybaud, and van Santen) were published only in recent years.

Whereas the description of HDS mechanisms is elaborate and at a good level, HDN mechanisms are not dealt with as thoroughly. There is a general tendency to discuss mechanisms from an overall, engineering point of view. For instance, the term hydrogenolysis is used for gross bond cleavage. Although this is correct in principle, it does not contribute anything to our understanding; a chemical, mechanistic picture would have been welcome.

Chapter 3 describes the structure of the catalysts and the methods that were used to derive the relevant information. It bears some resemblance to chapters in the book *Hydrotreating Catalysis* by H. Topsøe, B. S. Clausen, and F. E. Massoth, published in 1996. Given the research interest of the authors, a fair amount of information on radiotracer experiments was to be expected; nevertheless, this reviewer is of the opinion that more emphasis should have been placed on spectroscopic techniques.

Chapter 4 presents alternative ways of developing HDS and HDN catalysts. Supports other than alumina and promoters such as B, P, and F are discussed. Metal carbides and nitrides deserved more space than just two pages. The major part of this chapter deals with research results of the authors, as exemplified by 80 % of the figures. The book ends with a 35-page description of aspects of the relevant processes.

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