Additions and Corrections

The Effect of a Peptide Helix Macrodipole on the pK_a of an Asp Side Chain Carboxylate [*J. Am. Chem. Soc.* **1996**, *118*, 12038−12044]. HEMANT V. JOSHI AND MARK S. MEIER*

After the publication of our article, we became aware of a paper by Doig and Baldwin[1] in which anomalous Asp pK_a values were observed in helical peptides. In the Baldwin paper, a series of Asp-containing peptides (some N-protected, some N-unprotected) were titrated by CD and an N-terminal Asp was found to have a lower pK_a than Asp residues located at other positions in similar peptides. This paper should have been cited and discussed in our article, and we regret the oversight.

(1) Doig, A. J.; Baldwin, R. L. *Protein Sci.* **1995**, *4*, 1325−1336.

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Book Reviews

Perspectives in Supramolecular Chemistry, Volume 1. The Lock and Key Principle. The State of the Art−100 Years on. Edited by Jean-Paul Behr (Université Louis Pasteur de Strasbourg). John Wiley & Sons: Chichester. ix + 325 pp. ISBN 0-471-93902-1.

This book, the first in a series on supramolecular chemistry, pays tribute to the seminal insights of Emil Fischer, who in 1894 compared enzyme−substrate interactions to a lock and key. One hundred years later this simple but elegant idea has paved the way toward understanding a variety of molecular recognition processes. The book contains an eclectic mix of topics spread over eight chapters: their link is that they all deal with biological applications of the lock and key principle. Chapter 1 is written by Friedrich Cramer and is an overview of his research on supracellular chemistry. In an interesting way, Cramer relates his work on fundamental molecular recognition questions to the transformation in lock and key mechanisms from the classic lock based on chirality and shape of the late 19th century to the magnetic tape locks of the 1990s. Chapter 2 is a fairly detailed theoretical treatment of molecular recognition in protein−ligand interactions and is written at a level for specialists in this area. Chapters 3−5 are concerned with specific applications of biomolecules to molecular recognition. The authors do a nice job in minimizing the overlap between chapters, and thus, taken together, they offer a nice review of the field. The sixth chapter is an excellent discourse on crystal growth and chirality by Leiserowitz, Lahav, and co-workers. This chapter will be of interest both to experts in the field and to people who would like to learn some aspects of crystal engineering. The well-designed diagrams and pictures enhance the clarity of the material. The last two chapters are more general in content: Chapter 7 discusses the origin of life and its relationship to molecular recognition. The last chapter by Lehn gives a short overview of the field of supramolecular chemistry. While this chapter does an excellent job of giving a perspective on supramolecular chemistry, it is not significantly different from some of the other reviews published recently by the same author. In summary, this book is a good start to this new series on supramolecular chemistry. It is geared to scientists who have some knowledge of this field and would be a welcome addition to their libraries.

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JA955156R

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Gas Chromatography and Mass Spectrometry−A Practical Guide. By Fulton G. Kitson, Barbara S. Larsen, and Charles N. McEwen (E.I. du Pont de Nemours & Co., Wilmington, DE). Academic Press Inc.: San Diego. 1996. xii + 381 pp. $49.95. ISBN 0-12-483385-3.

The authors preface this book by stating that "it is designed to be a valuable resource to the GC/MS user by incorporating much of the practical information necessary for successful GC/MS operation into a single source". The book certainly includes some of the information needed for successful GC/MS operations. It is divided into four parts, namely, Fundamentals of GC/MS, GC Conditions, Derivatization and MS Interpretation of Specific Compound Types, and Ions for Determining Unknown Structures, and 12 appendices.

The Fundamentals is just that in 40 pages, including an adequate list of references to more detailed works. The meat of the book consists of specific information for running GC/EIMS on 33 classes of compounds−all the common functional groups, plus industrially important compounds such as common drugs and their metabolites, common pesticides, plasticizers, and prostaglandins. Section 3 lists possible formulas of ions, or their parent compounds, up to *m/z* 200, as well as ions resulting from a loss of up to 200 Da from molecular ions. The appendices compromise a potpourri of trouble-shooting tips, definitions, and information, primarily aimed at the nonspecialist.

The contents of the book are a mixed bag. The textual material is generally well written and provides a wealth of practical, useful information collected from 30 years of work by Fulton Kitson. However, the standard of editing and the quality of drawings used to represent chemical structures can only be described as primitive. Most errors are in the figures, such as the labeling of an electrostatic mass analyzer as a momentum analyzer, whereas it is correctly described in the text. There are numerous examples of pentavalent nitrogen atoms. Many derivatization procedures are given as recipes, with no comments on the chemistry or on possible interferences. Some compounds are sloppily named, not usually to the point of being ambiguous, but possibly misleading for the inexperienced. For example, benzimidazole is referred to as "1,4-benzimidazole" and 1,4-phenylene diisocyanate as "1,4-diisocyanate benzene". The index is spotty; if it were more complete, it would significantly enhance the value of the book.

Perhaps the most disappointing aspect of this book is its production. The paper is "acid-free", but is thin and poorly bound (wire spiral, hidden by a light cardstock cover). If used as intended in the laboratory, this book will most likely fall to pieces long before unwashed paper would have disintegrated.

On balance, this book collects a wealth of practical data. It is different from two possible competitors, namely, G. M. Message's *Practical Aspects of GC/MS* and J. R. Chapman's *Practical Organic Mass Spectrometry* in that it gives relatively little information on the technical aspects of operating a gas chromatograph or a mass spectrometer. The book will be most useful for GC/MS laboratories specializing in analyses.

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Modern Techniques in Electroanalysis. Series: Chemical Analysis, Vol. 139. Edited by Petr Vanýsek (Northern Illinois University). Wiley: New York. 1996. xvii + 369 pp. $79.95. ISBN 0-471-55514-2.

In the preface to this book, Editor Petr Vanýsek comments that contemporary electroanalytical chemistry is largely defined by three concurrent streams of research activity: detection of chemical species, studies on the structure and composition of interfaces, and advancements in instrumentation. The goal set forth for the present volume (the 139th monograph in a series on analytical chemistry and its applications), is to provide a central resource for information scattered throughout the current primary literature (usually because the work described is so recent). In this regard, each of the eight chapters presented here succeeds in providing an overview of a timely topic of interest to the electrochemical community at large.

The first chapter presents an overview of vacuum surface techniques as applied to the study of electrode surfaces and the neighboring region of solution. The authors (M. Soriaga and J. Stickney) are experts in this area and are well-known in the electroanalytical community. They begin with a discussion of experimental techniques and procedures, followed by a critical analysis of issues associated with removal of an electrified interface from solution (emersion) for characterization. Several case studies follow which demonstrate the types of information available from these experiments. The authors make a concerted effort to preface each study with a concise explanation of the motivation for the work and its likely general importance.

The next chapter by J. Pemberton and A. Garvey focuses on applications of vibrational spectroscopic methods in electrochemical studies. The material presented goes beyond a compilation of the authors' well-known work in this area. Instead, the case study approach of the first chapter continues. For example, the results from a number of papers on the use of infrared techniques to study electrooxidation of formic acid published over the course of several years are combined into a focused discussion. Several other well-chosen examples follow, including mention of Raman emersion studies, providing an essential tie-in to the first chapter. It is also commendable that the authors provide the full title for each of the 148 references cited, a practice which would have been welcomed in the rest of the volume.

A chapter by M. Ward and H. White follows on the use of scanning tunneling (STM) and atomic force microscopies (AFM) for characterizing interfaces. A critical and thoughtful comparison is made of the strengths and weaknesses of the relatively new family of scanning probe techniques to classical surface techniques that provide atomic-level information about the interfacial region. After a brief, intuitive summary of the underlying principles of STM and AFM (with appropriate pointers to the relevant physics literature), an excellent discussion is presented on the interactions between the probe tip and a sample surface and how they can influence data, in some cases even driving *in situ* phase transitions. Again, several well-considered case studies follow, including the use of tunneling spectroscopy to study semiconductor surfaces.

Unfortunately, the case study approach is absent from the subsequent chapters dealing with stripping analysis (H. Dewald) and automated detectors (M. Trojanowicz). Adopting a more conventional approach of providing a fairly complete review of each area, a wealth of information is provided on each topic. The sixth chapter, by C. Zoski, brings together a substantial amount of theoretical work that has been accomplished in the area of steady-state voltammetry for electrodes of various geometries. The majority of the chapter focuses on single, uncomplicated heterogeneous reactions (the *E* mechanism). Although brief mention (1.5 pages) is made of coupled solution reactions, no specific chemical examples are shown or discussed. A brief chapter by D. Gosser on electrochemical simulations is included. Some of the material presented will be familiar to readers of Gosser's earlier book on this topic, but the final section on the use of noise analysis to monitor the robustness of fit to experimental data is notable. The volume concludes with a chapter of the Editor himself on the subject of charge transfer reactions at liquid−liquid interfaces. The seminal experimental work in this area (co-authored by the Editor) is presented, and later developments are noted (including the theoretical contributions of Marcus), building to the most recent work involving the use of scanning electrochemical microscopy to lend spatial resolution to these interesting studies.

Finally, the unusually large number of typographical errors (including one mis-sequenced figure) in this book must be noted. Although quite distracting, such miscues will likely not dilute the impact this volume will have on the electroanalytical literature. Brevity in future journal articles could be greatly facilitated by referring readers to any one of these chapters for background information and a suitable entry into the existing literature. Individual volumes in established monograph series are usually more valuable to libraries for occasional use than to the individual. This book is an exception and will be a much used addition to the personal bookshelf of many practicing electrochemists.

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Infrared Spectroscopy of Biomolecules. Edited by Henry H. Mantsch (Institute of Biodiagnostics) and Dennis Chapman (Royal Free Hospital). Wiley-Liss: New York. 1996. xi + 359 pp. $89.95. ISBN 0-471-02184-9.

With the addition of new time-resolved infrared techniques and high-throughput FTIR this technique is becoming popular for the study of kinetics and structure in biological systems. In particular, new sample cell geometries that reduce the interference of water in biological infrared spectra has created a renewed interest in this technique. This is a very good book for workers in the field of infrared spectroscopy of biomolecules.

This book does not contain general chapters designed to educate a novice in the field. It is arranged along the line of a series of review articles on specific topics associated with infrared spectroscopy, not unlike the format of an ACS symposium series. The chapters are well prepared and contain extensive, up-to-date references. The chapters are (1) Theoretical Analysis of the Amide I Infrared Bands of Globular Proteins by H. Torii and M. Tasumi, (2) Fourier Transform Infrared Spectroscopy of Enzyme Systems by J. Alben, (3) Light-Induced Fourier Transform Infrared Difference Spectroscopy of the Primary Electron Donor an Photosynthetic Reaction Centers by E. Nabedryk, (4) Equipment: Slow and Fast Infrared Kinetic Studies by F. Siebert, (5) Ultrafast Infrared Spectroscopy of Biomolecules by B. Cohen and R. Hochstrasser, (6) Infrared Spectroscopy of Nucleic Acids by J. Liquier and E. Taillandier, (7) Fourier Transform Infrared Spectroscopy in the Study of Hydrated Lipids and Lipid Bilayer Membranes by R. Lewis and R. McElhaney, (8) Fourier Transform Infrared Spectroscopy of Cell Surface Polysaccharides by K. Brandenburg and U. Seydel, (9) Fourier Transform Infrared Spectroscopic Studies of Biomembrane Systems by P. Haris and D. Chapman, (10) What can Infrared Spectroscopy Tell Us About the Structure and Composition of Intact Bacterial Cells by D. Naumann, C. Schultz, and D. Helm, (11) Biomedical Infared Spectroscopy by M. Jackson and H. Mantsch, (12) New Trends in Isotope-Edited Infrared Spectroscopy by H. Fabian, D. Chapman, and H. Mantsch.

There are two areas of concentration in this book. They are ultrafast kinetics and the relatively new field of infrared spectroscopy of biofilms.

This monograph is an excellent work for those in the field of infrared spectroscopy of biomolecules and for those trained in infrared spectroscopy desiring to enter the field.

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JA965636Y

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Advances in Inorganic Chemistry, Volume 42. Edited by A. G. Sykes (The University Newcastle-upon-Tyne). Academic Press: San Diego. 1995. vii + 408 pp. $99.00. ISBN 0-12-023642-7.

This new addition to the long-running series continues its focus on bioinorganic chemistry. A timely report on methane monooxygenase by Liu and Lippard describes the structural and mechanistic differences between the two most studied soluble forms from *M. capsulatus* and *M. trichosporium.* Included is a compilation of structural characterizations and reactivities, as well as recent Mossbauer data on short-lived, reactive intermediates in the catalytic cycle. Mechanistic alternatives are discussed in comparison to the much studied cytochromes P-450. Of appeal to biocoordination chemists is Hancock and Martell's somewhat mistitled chapter, Lewis Acid/Base Behavior in Aqueous Solution. It is rather a survey of the coordinating properties of ligands in terms of the HSAB with emphasis on explaining metal selectivity

in biology. Among their many examples is a proposed redox role for the substrate-coordinated Fe in aconitase, and an examination of the reverse chelate effect in systems which selectively bind a substrate between two metals. Of more general interest is the review of Substitution Reactions of Solvated Metal Ions by Lincoln and Merbach, which updates this classic field of study. A good exposition is given on the use of volumes of activation to differentiate substitution mechanisms, and such data are utilized throughout the survey of solvated metal-ion types. Recent references include work on lanthanide complexes and oxo- and sulfido-cluster complexes. Lickiss offers a substantial chapter on the synthesis and structure of organosilanols, concentrating on well-defined monomeric species. In the crystalline state, these industrially important reagents form a myriad of hydrogen-bonding networks, and an attempt is made to elucidate the common structural motifs. Parkin offers a review of more traditional coordination chemistry in the chapter on poly(pyrazolyl)borato complexes of the s- and p-block elements. Emphasis is on the structure and reactivities of monomeric terminal alkyl, hydride, and hydroxide derivatives. Continuing the biocoordination theme, the Zn(OH)tris(pyrazolyl)borate derivative is discussed as a functioning model for carbonic anhydrase reactivity, and the Lewis-base reactivity is shown to extend to phosphatase and peptidase activities. Parkin also uses the Zn derivatives to demonstrate controlled crystallographic disorder, the origin of the infamous "bond-stretch" isomerism, by intentionally doping crystals with structurally similar molecules. This systematic study illustrates the need for precaution when attempting to determine true bond lengths from crystallographically disordered data sets.

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Indoles. Series. Best Synthetic Methods. By Richard J. Sundberg (University of Virginia). Academic Press: San Diego. 1996. xv + 175 pp. $45.00. ISBN-0-12-67645-1.

The *Best Synthetic Methods* series published by Academic Press provides concise but authoritative surveys on a broad range of important reagents and methodologies in the field of organic chemistry. With the lastest volume, *Indoles*, this series inaugurates a new subseries with a focus on heterocyclic compounds and their synthesis and characteristic chemistry. The author of this lastest volume is Professor Richard J. Sundberg of the University of Virginia, noted indole chemist and author whose 1970 book, *The Chemistry on Indoles*, still sets the standard against which all other texts in the field are measured. Although the need for such a comprehensive text on the subject may have been largely supplanted by more recent coverage in reference sources such as *Comprehensive Heterocyclic Chemistry* and *The Chemistry of Heterocyclic Compounds*, or by timely reviews on specific indole related topics, there still exists a need for a complete but inexpensive monograph for the chemist's bookshelf. The volume *Indoles* serves just such a purpose, providing as it does an overview of all the methods for construction of the indole ring as well as the methodologies available for the selective functionalization of this heterocyclic nucleus. In keeping with standard practices for the *Best Synthetic Methods* series, methods are illustrated by experimental procedures drawn from the literature and by tables involving examples chosen to indicate both the scope and applicability of the methodology. Moreover, *Indoles* maintains the most valuable feature of all volumes in this series, in that they are as accessible to the novitiate in the subject described as they are useful to the seasoned practitioner.

The greatest challenge in presenting such a concise but authoritative survey of the synthesis and reactions of indoles lies in the development of a logical ordering of the subjects, such as methods of synthesis. To this end, the author has conveniently chosen to base the organization of the text on the retrosynthetic concept of identifying the bond(s) formed in the process, and within each chapter further disconnections identify potential starting materials for the actual construction of such bonds. Using that guideline, the book first describes methods for the construction of the indole ring, while the later chapters are devoted to the characteristic chemistry of this heterocycle.

Following the introductory chapter which describes the importance and general reactivity of indoles, the following six chapters focus on methods for construction of the indole ring from benzenoid precursors while Chapter 8 then addresses the newer and less utilized preparative route to indoles from pyrroles. In each chapter, the author does a masterful job of illustrating and updating the classical indole syntheses and introducing reliable newer methodologies (latest references are 1995), and despite the concise format of the book, coverage of each topic tends to be remarkably complete and up to date. For instance, the discussion of the Fischer indole cyclization in Chapter 7 describes the reaction, its mechanism and catalysis, recent mechanistic postulates, methods for effecting regioselective cyclizations of unsymmetrical arylhydrazones, anomalous reactions, and useful applications.

Chapters 9, 10, and 11 describe methods for substitution on the ring positions N, C-2, and C-3, respectively, while Chapters 12 and 13 are devoted to modification of substituents on the pyrrole ring including the introduction of the tryptamine and tryptophan side chains. Chapter 14 deals with functionalization of the carbocyclic ring of the indole nucleus while Chapter 15 describes indole specific oxidation—reduction processes. Finally, Chapter 16 illustrates methods for elaboration of indoles via cycloaddition, employing the indole as the diene component in Diels—Alder processes via vinylindoles or quinodimethane type intermediates.

While this volume is unquestionably a valuable asset to the practicing heterocyclic chemist, there are subtle ways by which the text might have been made more user friendly. For instance, the reaction schemes are not referenced within the text, so at times it is not clear that what is being read is actually illustrated. Another source of confusion pertains to the experimental procedures, which list only the name of the compound prepared but not the method being employed. Finally, the tables, while doing much to emphasize the scope and generality of the reactions described, might have been made clearer had reaction schemes been included above most tables. However, these cosmetic flaws are by no means fatal and detract little from this well-researched and well-presented monograph.

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