Additions and Corrections

Scalar Relativistic Effects on ^{17}O NMR Chemical Shifts in Transition-Metal Oxo Complexes. An ab Initio ECP/DFT Study [*J. Am. Chem. Soc.* **1995**, *117*, 1851−1852]. Martin Kaupp,* Vladimir G. Malkin, Olga L. Malkina, and Dennis R. Salahub

Page 1851: Due to a conversion error, the experimental ^{17}O shifts (second column, Table 1) were given incorrectly. The correct numbers should read from top to bottom 871, 576, 456, 1255, 786, 605, 1142^{f}, 832. This change does not alter the findings of the paper.

JA955017+

Book Reviews

Structure Correlation, Volumes 1 and 2. Edited by H.-B. Bürgi (University of Bern) and J. D. Dunitz (ETH, Zürich). VCH: Weinheim, Germany. 1994. xxvii + 888 pp. $235.00. ISBN 3-527-29042-7.

Structure correlation is the analysis of all available structural data for a given chemical fragment in different environments and the correlation of these data with molecular structure and reactivity. A famous correlation of this type is the "Dunitz−Bürgi trajectory" for nucleophilic additions, but the concept is applicable to a wide range of chemical phenomena. As Roald Hoffmann noted, the "geometrical structure... provides us with the starting point for the understanding of every physical, chemical and biological property of the molecule." This volume presents the results of 15 years of progress in structure correlation, edited by two pioneers in this area of research, Jack D. Dunitz and Hans-Beat Bürgi. They have brought together experts in their fields to summarize the principles and applications of structure correlation in organic, inorganic, and supramolecular chemistry and in structural biochemistry.

The book is organized into four parts: Basics, Molecular Structure and Reactivity, Crystal Packing, Proteins and Nucleic Acids. Part 1 opens with two chapters written by the editors, dealing with methods for descriptions of the geometrical structure of molecules, including coordinate systems, symmetry, and vibrational analysis. Chapter 3 (F. H. Allen, O. Kennard, and D. G. Watson of the Cambridge Crystallographic Data Center) provides an overview of the Cambridge Structural Database (CSD) and details of software for searching this resource. Chapter 4 (R. Taylor and F. H. Allen) gives examples of extracting the information in the CSD for structure correlation analysis and describes statistical and principal component analysis and cluster analysis of the results. Chapter 5, by Bürgi and Dunitz, gives a general discussion of the principles of structure correlation and the relationship with physical concepts.

Part 2 is devoted to the elucidation of reaction pathways by analysis of structure−structure and structure−energy correlations. Chapter 6 (A. S. Cieplak) gives an extensive and excellent overview of the theory and structural data revelant to addition and elimination reactions involving carbonyl derivatives. Chapter 7 (H.-B. Bürgi and V. Shklover) demonstrates the ubiquity of the three-center−four-electron system $X-MR_3-Y$ in organic and inorganic substitution reactions. Chapter 8 (T. Auf der Heyde) deals with substitution reactions and ligand rearrangements (*e.g.*, pseudorotation) in inorganic compounds. Chapter 9 (W. B. Schweizer) summarizes the most important studies on conformational preferences in typical organic fragments like esters, furanoside rings, and a few others.

Part 3 covers structure correlations in extended systems: Chapter 10 (I. D. Brown) reviews the bond-length−bond-valence relationship in inorganic solids, Chapter 11 (J. Bernstein, the late M. C. Etter and L. Leiserowitz) discusses the role of hydrogen bonding in molecular assemblies, and Chapter 12 (A. Gavezzotti) addresses the problem of correlating molecular and crystal properties and eventually predicting the crystal structure of a given molecule of known structure.

Finally, Part 4 gives examples for the extension of the structure correlation concept to proteins and nucleic acids. Chapter 13 (G. Klebe) discusses the mode of action of enzymes with the help of reaction path data and structure correlations derived from "small" molecules. Chapter 14 (W. L. Duax, J. F. Griffin, and D. Ghosh) describes the empirical approach of mapping the active sites of steroid hormone receptors and steroid-binding proteins by analyzing crystallographic data of more than 1000 steroids or steroid-like compounds. Chapter 15 (E. G. Hutchinson, A. L. Morris, and J. M. Thornton) is concerned with structural patterns in globular proteins and contains useful analysis of a host of different common arrangements. Chapter 16 (T. L. Blundell) addresses the question of the correlation between the primary and tertiary structure in families of homologous proteins, while Chapter 17 (C. Broger and K. Müller) deals with the predictability of protein folding from local hexapeptide sequence patterns. Chapter 18 (M. Egli) gives a collection of structural patterns in nucleic acids and in short oligonucleotide fragments, including intercalated aromatic and DNA-protein binding. An extensive appendix (106 pages) with a selection of typical interatomic distances in organic and organometallic compounds from X-ray data rounds off the book.

The editors have succeeded in presenting a work of great substance and magnitude. The graphical presentation is unusually homogeneous for a book with so many different contributors. The editing is excellent, and very few minor problems or omissions were detected. Both crystallographic data and the results of *ab initio* calculations are covered in some of the chapters. This work will be of considerable value for every chemist, even those with only a vague interest in structure and reactivity. It should be found in every research library.

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JA9451269

Topics in Fluorescence Spectroscopy. Volume 4. Probe Design and Chemical Sensing. Edited by Joseph R. Lakowicz (University of Maryland). Plenum Press: New York and London. 1994. ISBN 0-306-44784-3.

This is a stimulating and very timely book. Its 14 chapters reflect a good fraction of the research going on in the area of fluorescence-based chemical sensing. It is complimentary in many aspects to the 1991 two-volume book *Fiber Optic Chemical Sensors and Biosensors* edited by O. S. Wolfbeis.

Chapter 2 is on fluorescent probes for ion recognition and is very readable and informative. The important mechanisms that lead to molecular recognition between ion and fluorescent probes are discussed in great claritm, and the references cited indicate an excellent knowledge of the literature. This chapter is a must for everybody interested in sensing clinically important electrolytes. Chapter 3 is similar in that it covers fluorescent chemosensors for cations, anions, and neutral analytes. There is some overlap with Chapter 2. The title suggests a broad review, but in fact, it refers to probes derived from 9-aminomethylanthracene only, which is a UV-excitable fluorophore and of little practical utility in sensor design. Fortunately, the sensing schemes described for these probes are likely also to hold for other (more longwave) probes. I found the chapter to be of particular significance because it demonstrates how species as different as metal cations, inorganic anions, polyanions such as DNA, and heparin may be sensed with fairly high specificity by smart chemical modification of a single basic fluorophore.

Chapters 4 and 5 cover the design and application of luminescent probes, the first on transition metal complexes and the second (and less thrilling) one on twisted intramolecular charge transfer states (which usually result in large Stokes' shifts). In Chapter 4, the use of such probes for sensing oxygen, and methods for immobilizing them in polymers including silicone, are being described as well. Parts of Chapter 5 are trivial, with chemical structures and spectra being reproduced from the Handbook of a major manufacturer of fluorescent probes.

The significant trend toward red and near-infrared fluorometry and fluorescent probes is described in Chapters 6 and 7. The two chapters are very useful and stimulating to read. They may have been combined into one chapter, though, so to avoid some overlap. I missed a statement that most infrared dyes cited in the two chapters have rather short lifetimes and are not easily amenable to lifetime-based sensing. Chapter 12 (on instrumentation for red−near-infrared fluorescence) may have been included here as well.

Chapters 9 (on real-time chemical sensing employing luminescence techniques) and 10 (on lifetime-based sensing) may have been combined as well. The title of Chapter 9 is wrong in that it covers lifetime-based methods only and ignores all other schemes including sensors based on measurement of intensity, polarization, energy transfer, inner filter effects, and combinations thereof. Both are first-class articles, though, on this particular subject, and a highly recommended source of information.

The applications part starts with a chapter on fluorescence sensing as applied to bioreactors. Authors describe sensors for optical measurement of pH, oxygen, carbon dioxide, glucose, and the like. After all, it does not come as a surprise that most methods described are lifetime-based and come from the authors lab, while a wealth of information from other sources is ignored. Even worse, all the results presented are based on cuvette measurements only, although others have reported the use of optical sensors for monitoring bioreactors (and in real fermentation broths), albeit not making use of fluorescence lifetime. However, this should not have made authors ignore such valuable work. Similarly, the applicability of fluorescence resonance energy transfer (FRET) for sensing glucose using doubly labeled concanavalin A is discussed, but no reference is made to the fact that the scheme has been experimentally verified already by Meadows and Schultz in 1988.

The contents of the chapter on various methods of fluorescence immunoassay may be found in other books as well. I expected it to focus more on methods for *continuous* monitoring (i.e., sensing). The remarkable work of W. G. Miller which goes into this direction may have been discussed in more detail in a book which is on sensors (rather than tests).

My major criticism is on Chapter 1 which covers Emerging Biomedical Applications of Time-Resolved Fluorescence. Indeed, the potential of lifetime sensing is huge, but the author fails to put lifetime methods into perspective with other methods including measurement of intensity or polarization. These more "conventional" methods have received a high degree of sophistication now and—if applicable—can successfully compete with lifetime sensing.

The strong emphasis on lifetime methods becomes annoying when the author is referring to a statement on the advantages of (*all* kinds of) fluorimetric methods but means lifetime only. On p 1 it is correctly stated that "*...there is a continuing use of fluorescence detection to replace analytical methods based on radioactivity*". Correct, but to the least extent for lifetime methods: except for the DELFIA immunoassay, all widely used tests are based on either intensity, polarization, or energy transfer, but not lifetime, and this holds not only for immunoassay but also to DNA testing, sequencing, and sensors. Lifetime is the future, no doubt, but this should not make one ignore the state of the art!

Indeed, blood gas sensing appears to be the "Holy Grail" in optical sensing. The question (raised on p 7) "*how can phase modulation fluorometry contribute to this health care need?*" cannot be been answered without referring to intensity-based fluorosensors being on the market, their precision and accuracy being more than adequate. Similarly, optical blood septicemia tests are on the market and work very well. The above question therefore better be formulated as "*How can phase modulation fluorometry contribute to improve intensity-based fluorosensors?*" It is not radiometric methods which need to be put into perspective to lifetime, but rather intensity-based fluorometric methods.

It should have been stated at some point that there are several aspects in this method which are critical but are not adequately addressed: (a) many pH and ion binding probes have too small a difference in the lifetimes of free and bound forms to be of analytical use; (b) the real challenge in sensor chemistry is the temporal instability of the sensing material, be it a p*K* value or a quenching constant. The resulting drift in the work function over time cannot be compensated for by either kind of measurement, and this of course includes lifetime.

Figure 1.1 is incorrect. Such calibration plots are sigmoidal only if the *log* of the analyte concentration [ANALYTE] is plotted against optical signal. An intensity ratio plot (*A*/*B* vs [ANALYTE]) cannot be linear! The title of chapter 1.3.2. ("Non-invasive Transdermal Glucose Sensing") is misleading. One may not call a method noninvasive if it requires a sensor patch to be placed in the body, even though the actual measurement may be performed transcutaneously. On the other side, methods for real transcutaneous sensing of oxygen via lifetime (by placing a sensor patch on the surface of the skin heated to 42 °C) are known (*Proc. SPIE* **1993**, *1885*, 217−227) but not cited.

In conclusion, the book deserves a good place in the library of everybody interested in the subject. It covers most of the important aspects of optical chemical sensing, but also with a more than strong emphasis on lifetime-based methods, a substantial overlap between certain chapters, and incomplete citation of prior art. Intensity-based methods, even if commercially extremely successful, are widely ignored. If I had edited a book on such a timely topic, I would have combined some of the chapters to one and included a chapter on what the editor himself calls the holy grail in sensing, namely blood gas and pH analysis. Such a chapter is badly missed, along with another covering the important area of enzyme-based sensing.

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JA955102H

Analytical Electrochemistry. By Joseph Wang (New Mexico State University). VCH: New York. 1994. xi + 198 pp. $59.95. ISBN 1-56081-575-2.

The stated goal of the book is to cover the full scope of modern electroanalytical techniques and devices. The anticipated readers are graduate students, advanced undergraduates, and nonexperts in the field. The book is organized into six chapters which contain short examples sections with illustrative calculations for equations in the chapter. The fundamentals are presented briefly and the general description of applications includes illustrations and references with citations through 1994, many of them to the author's own work.

The first chapter, Fundamental Concepts, distills the theory behind amperometric measurements. The first two sections, Why Electroanalysis? and Faradaic Processes, include a short general discussion of controlled potential techniques. The chapter includes sections on mass transport controlled reactions which introduces Nernst−Planck and Fick's equations, on potential step and potential sweep experiments where the current expressions are introduced, on processes controlled by the kinetics of electron transfer which includes a brief discussion of Butler−Volmer kinetics and a section entitled Activated Complex Theory, which briefly introduces the kinetic model in common use. The chapter concludes with sections on double-layer and electrocapillary effects with brief theory and equations. At the end of the chapter a supplementary reading section precedes the standard reference section.

The second chapter, Controlled-Potential Techniques, gives a general discussion of chronoamperometry, a comprehensive discussion of polarography theory and experiment, and a brief description of pulse voltammetry theory with applications of square wave and introduces ac voltammetry. The remainder of the chapter is devoted to theory and applications of stripping analysis including sections on anodic, potentiometric, and adsorptive stripping, with many references from the author's own work, and to flow analysis. The flow analysis section is comprehensive and includes sections on principles, cell design, including detector design for CZE, mass transport, and detection modes.

The third chapter, entitled Practical Considerations, has sections on electrochemical cells, supporting electrolytes and oxygen removal, instrumentation, and working electrodes. The instrumentation section lists current suppliers of voltammetric analyzers and contains an abbreviated diagram of a three-electrode potentiostat which in view of its brevity appears erroneous. The final working electrodes section describes the dropping and static mercury electrodes in some detail, as well as carbon and metal electrodes, and includes a section on modified, micro, and composite electrodes. The modified electrodes are discussed as preconcentrating, permselective, and conducting polymer electrodes with references from the author's and selected other work.

The fourth chapter is dedicated to Potentiometry and contains sections on principles of potentiometric measurements, ion-selective electrodes with extensive discussion of glass electrodes, and in addition liquid membrane, solid state, and coated wire electrodes as well as on-line potentiometric measurements. The description of ion-selective electrodes is practical minded with some discussion of interference effects and brief references to theory.

The fifth chapter, Electrochemical Sensors, has a section on electrochemical biosensors including enzyme-based electrodes (amperometric and potentiometric) which outlines enzyme immobilization and basics of response, a section on enzyme electrodes of analytical significance including glucose sensors, ethanol, urea, tissue, and bacteria electrodes, and a brief section on affinity biosensors including immuno and receptor-based sensors. In addition there is a section on gas sensors including carbon dioxide and oxygen sensors and a section on solid-state devices with a discussion of microfabrication of solid-state sensor assemblies and sensor arrays.

The final chapter of the book, entitled Study of Electrode Reactions, has a section on cyclic voltammetry including a brief description of data interpretation, a study of electrode mechanisms and adsorption processes, and quantitative applications. There are also sections on spectroelectrochemistry focused on UV−vis, scanning probe microscopy including scanning tunneling, and atomic force microscopy with selected references from the author's and other work and a brief section on scanning electrochemical microscopy and electrochemical quartz crystal microbalance.

The book is easy to read as a general reference to be supplemented with more thorough and comprehensive texts and references. Unfortunately the book editing is very sloppy with many errors in the text, equations, terminology, and text referencing. More thorough figures and captions would have given a more finished look to the text. Overall the text could be a welcome addition to the library for those with an interest in the basics of electrochemical sensors and sensing.

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JA9451224

Diazo Chemistry I. Aromatic and Heteroaromatic Compounds. By Heinrich Zollinger (Eidgenossische Technische Hochschule). VCH: Weinheim, New York. 1994. xiv + 453 pp. DM198. ISBN 3-527-29213-6.

Heinrich Zollinger's *Diazo Chemistry I. Aromatic and Heteroaromatic Compounds* is a lengthy and comprehensive treatise describing the development of ideas about the structure and reactivity of aromatic and heteroaromatic diazo compounds beginning with their discovery in 1858. There are over 1700 references dating between 1620 (!) and 1992. (The reference from 1620 is to Francis Bacon. The earliest reference to diazo compounds is from 1860.)

The author presents a historical approach to the development of the major ideas about structure and reactivity of diazo compounds, beginning with the first work and continuing with discussions of the important work in the field—both correct and incorrect—through 1992. There is a heavy emphasis on the physical organic concepts used to elucidate mechanisms. Important topics are discussed in terms of kinetics, substituent effects, isotope effects, solvent effects, and MO calculations.

Methods for the preparation of aromatic and heteroaromatic diazo compounds are presented in Chapter 2, while the kinetics and mechanism of diazotization are presented in Chapter 3. The opposite order of presentation might have been preferable, so that the reader could place the various techniques for preparing diazo compounds in the context of an understanding of mechanism. Chapter 4 presents both experimental and theoretical investigations of the structures of diazonium compounds. Subsequent chapters deal in substantial detail with aspects of the reactivity of diazonium ions, including acid−base reactions, isomerization reactions, addition of various nucleophiles, dediazoniation reactions, host−guest complexation of arenediazonium salts, and azo coupling reactions. The final chapter addresses the formation and reactions of triazenes.

A failing of many books of this type is the tendency to simply list conclusions as reported by the authors without any critical analysis. This author does an excellent job of discussing the basis for the conclusions presented and of placing each piece of work in the context of the field at the time. There are several interesting accounts of conflicts in interpretation of data that in some cases lasted for decades.

Because of the prodigious amount of information presented, this book is most suited to those with a special interest in diazo chemistry, rather than a general audience which might wish for a more concise description of the current status of the field. However, the book should be useful to a wider audience for two reasons. First, the book provides many examples of the use of physical organic chemistry to solve mechanistic problems which should nicely complement existing physical organic textbooks. Second, the book is a (highly technical) history of a subfield of organic chemistry and contains interesting insights into the development of scientific ideas in the context of the state of knowledge at the time and into the sometimes unfortunate perpetuation of conclusions drawn too soon.

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JA9450519

Symmetry and Topology in Chemical Reactivity. By Pieter Schipper (University of Sydney). World Scientific: Singapore, New Jersey, London, and Hong Kong. 1994. xii + 272 pp. $58.00. ISBN 981-02-1542-8.

This book is the author's development of a formal, unified theory of chemical reactivity based on group theoretical concepts. By utilizing the Born−Oppenheimer approximation, the author separates the symmetry constraints which are imposed upon a reaction coordinate into a set controlling nuclear motion on the potential energy surface, the classical (geometric) constraints, and a set controlling the electronic reorganization which occurs during a chemical reaction, the quantum (electronic) constraints. Using the classical constraints and projection operators from group theory, the author is able to generate structures along any symmetry-allowed reaction coordinate from reactant to products, including the transition state. Using the quantum constraints, he is able to evaluate the reaction coordinate to determine if it is symmetry allowed or forbidden.

The first two chapters of the book review the fundamentals of chemical reactivity including transition state theory, potential energy surfaces, and reaction coordinates. Chapters 3 and 4 present the formal theory behind the classical constraints in a mathematically rigorous fashion. Once the formal theory has been established, Chapter 5 presents a practical procedure for applying the classical constraints to a given reaction. Finally, Chapter 6 completes the presentation of the classical (geometric) constraints by applying them to a series of reactions including chiral rearrangements, electrocyclic reactions, cycloaddition reactions, and aliphatic nucleophilic substitutions. Chapters 7, 8, and 9 develop the theory of the quantum (electronic) constraints which reflect symmetry limitations on the reorganization of electrons as a reaction proceeds from reactant to products. After establishing the formal theory in Chapter 7, Chapter 8 develops a practical procedure for applying the quantum constraints to any reaction. Chapter 9 concludes the presentation of the quantum constraints by presenting a simplified version of the previous procedure for π systems which the author entitles the Constrained Perturbation Molecular Orbital (CPMO) method, after Dewar's PMO method. Chapters 10−12 summarize the material developed earlier by sequentially applying the classical and quantum constraints to a series of reaction coordinates representing addition reactions, inorganic rearrangements, and substitution reactions.

Those chemists interested in the theoretical foundations of chemical reactivity and reaction mechanisms will find that this book succeeds in unifying a number of concepts which are used to evaluate reaction coordinates. The book is copiously illustrated with diagrams to assist the reader in understanding the theoretical concepts, and the bibliography is adequate. Unfortunately, these attributes fail to make the theory accessible to the nonspecialist. The reader must have a reasonable background in group theory to evaluate the methods presented, so too a knowledge of quantum mechanics and applied molecular orbital theory is required. This book is an ambitious undertaking; the line of reasoning tends to be terse at several places. There are some interesting, provocative comments concerning the orbital noncrossing rule and reactivity. Overall, this will be a useful book for specialists in the field.

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