and examples are presented in a tutorial fashion, providing guidance in properly constructing input files and in correctly interpreting the output files. General background material is presented on the underlying theoretical concepts for the computational methods. A reference list is provided at the end of the manual for those individuals wanting to pursue greater details of the computational methods. The manual also contains a chapter on how to use and customize the GUI. On-line help is also available within the GUI. Customer support from Semichem is readily accessible over the phone or by electronic mail. Dr. Holder, in fact, was usually the one who promptly responded to my questions about the GUI or the computational methods.

Overall, AMPAC 4.5 provides a solid semiempirical molecular orbital package which will be of great interest to both academic and industrial users. The graphical user interface is a practical and helpful feature, but the real power of this software package is its computational capabilities. Simulated annealing is the most exciting computational feature, allowing the user to quickly and reliably explore the conformational space of a monomer unit which may be of importance in polymeric materials. Semichem is a young company that is constantly improving its product. The additions and enhancements to the computational module as well as the graphical user interface between versions 4.0 and 4.5 have impressed me, and I expect a similar performance from this company in the future.

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Book Reviews

Fundamentals of Photoinduced Electron Transfer. By George J. Kavarnos. VCH Publishers: New York. 1993. viii + 360 pp. $75.00. ISBN 0-89573-751-5.

Photoinduced electron transfer has become one of the key unifying reactions of the various subdisciplines of chemistry. As such, it has attracted voluminous contributions both to the original and review literature. (A brief listing of a number of these reviews can be found in the editor's introduction to the special issue on electron transfer in *Chemical Reviews* published in May of 1992.) It is entirely appropriate, therefore, that Kavarnos has prepared a text with a strong pedagogical bent. The author describes in the preface his goal in writing the text: as a primary or secondary text in introductory and advanced chemistry courses at the undergraduate and graduate level. In this niche, the book fulfills its mission very well.

Chapter 1 is an introductory discussion of elementary concepts of organic and inorganic photochemistry. It is followed by a chapter on the use of spectroscopic methods for characterization of oxidized and reduced intermediates and radical ion pairs. Chapter 3 provides many examples of organic transformations initiated by photoinduced electron transfer. Chapter 4 deals with physical aspects of photoinduced electron transfer, covering such topics as through-bond and through-space coupling and electron transfer occurring through rigid and flexible bridges. Chapter 5 focuses on the use of organized assemblies and interfaces for controlling electron transfer. Chapter 6 provides a clear presentation of both the classical and quantum mechanical theories used routinely to describe both thermal and photoinduced electron transfers.

As is consistent with its pedagogical orientation, the text includes at the end of each chapter suggestions for further reading which are selected articles and reviews dealing with the topics considered in each chapter. The section is followed by problems whose solutions can be found by reference to the original literature. Although a subject index is included, an author index is not, making it unnecessarily difficult to locate particular investigations.

The interested reader should approach this book as a text rather than as a monograph in order to avoid disappointment. The literature cited is far from comprehensive, and it was often unclear to this reader why particular examples were chosen rather than others. Attribution for work was often weak, and although a reference is cited for each topic, the choice of topics is sometimes rather arbitrary. In an advanced text, one would expect to have identified the key players in a research area by name in a monograph text. In other cases, key contributors to the topics being considered are either neglected completely or at least undercited with respect to their key experiments: among the many significant omissions in the text is a lack of emphasis on a work by Farid and Gould on electron transfer in ion pairs and of Mataga on intra- and intermolecular electron transfer. The work of Fujishima and Honda, which stimulated much of the work on water splitting on semiconductor surfaces, is neglected, and the many contributions of Grätzel and Fendler, among others in this area, are undercited. Many of the figures included within the text cite a review by Kavarnos in *Topics in Current Chemistry* rather than the original literature. This reviewer often also found the absence of chemical or quantum yields distracting in discussions of the applicability of photoinduced electron transfer as a synthetically viable method.

For optimal teaching value, the chapter on theory should have appeared earlier and more practical applications should have been emphasized. For example the pioneering work of Closs and Miller on long distance electron transfer seems to be missing from the place one would have expected it in dealing with long distance electron transfer (Chapter 4). Instead, one finds it in Chapter 6. Similarly, the reader would have to guess that one of the principal applications to have emerged from semiconductor-mediated photoinduced electron transfer is in photocatalytic oxidative degradation, for this topic is not covered at all in Chapter 5. The section on photosynthesis similarly neglects the elegant work of Norris, Fleming, and others in characterizing the operative pathways in photosynthetic reaction centers.

All of these omissions, however, can be overlooked if one considers the book as a beginning text which does provide, indeed, an interesting overview of the fundamental scientific concerns of this important area. It is quite appropriate for use in a special topics course for students who have completed a year of undergraduate organic and physical chemistry.

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Catalysis by Metal Complexes. Volume 14. Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds. Edited by K. Kalyanasundaram and M. Gratzel (Swiss Federal Institute of Technology of Lausanne). Kluwer Academic Publishers: Dordrecht, Boston, and London. 1993. xvi + 465 pp. $192.00. ISBN 0-7923-2261-4.

This monograph comes at an opportune time to complement the recent monographs *Photosensitive Metal–Organic Systems—mechanistic principles and applications* in the Advances in Chemistry series (C. Kutal and N. Serpone, Vol. 238, American Chemical Society, 1993), *Charge Transfer Photochemistry of Coordination Compounds* (O. Horvath and K. L. Stevenson, VCH Publishers, 1993), and *Fundamentals of Photoinduced Electron Transfer* (G. J. Kavarnos, VCH Publishers, 1993). Other related monographs are *Supramolecular Chemistry* (V. Balzani and L. De Cola, NATO ASI Series C371, Kluwer Academic Publishers, 1992) and the earlier series of volumes *Photoinduced Electron Transfer* (M. A. Fox and M. Chanon, Elsevier, 1988). The present monograph will be an excellent addition to a researcher's personal library.

This monograph is basically organized into four parts. In the first part (Chapter 1), A. W. Adamson recounts some historical perspectives of the birth of inorganic photochemistry from the work in his laboratory (Adamson's Rules, the thexi state, redox quenching, etc.) and those of others since the 1950s; it is mixed with some nostalgia about the *good old days* when the inorganic photochemical community was a relatively small family which met at informal gatherings, now full-fledged international symposia. As Prof. Adamson aptly put it: inorganic photochemistry has come a long ways from our first, unintentional photochemistry in 1950. The next three chapters (Part 2) consider the basic principles and concepts that govern electron and energy transfer (V. Balzani and M. Maestri) which have been covered extensively by the authors in several other fora, photocatalysis by Hennig and co-workers, and the chemistry of charge transfer excited states by Vogler and Kunkely. The five chapters of Part 3 cover the photochemistry of classical Werner-type transition metal complexes and their applications (e.g., photoreduction of CO_2 and CO, and photosensitization of large bandgap semiconductors). Polypyridine complexes such as rubipy, $Ru(bpy)_3^{2+}$, and its analogs have received the greatest attention, building up to polynuclear/supramolecular devices based on the rubipy systems and subsequently represented by the metalloporphyrin units. The following and last five chapters (Part 4) focus on several inorganic and organometallic systems (polyoxometallates, metal carbonyls, organometallics, ground-state complexes of inorganic salts, and electron donor/acceptor complexes of organometallics such as metal alkyls and metallocenes) where photocatalytic transformations of organic substrates have been demonstrated. As noted by the editors, the emphasis in these contributed chapters was placed on basic principles and features of the system(s) rather than on a comprehensive survey. Although the intent was respected somewhat, nevertheless the articles do cover some recent material in a minireview style which, however, does not detract from the benefits that novice readers and seasoned researchers will find in this monograph.

Following the contribution by Balzani and Maestri, which also briefly presents such things as light emission sensitizers (LES) and light absorption sensitizers (LAS), Hennig and co-workers examine the nontrivial definition of photocatalysis which has also been entertained by others (Salomon, Chanon, Wubbels, Kutal, among others); these authors also attempted to simplify the definition and to classify the various terminologies meant to describe reaction types. At the end of it all, however, as also inferred by others, the term *photocatalysis* is best taken in its broadest sense when no mechanistic implications are possible. Various good examples illustrate the terminologies. The next chapter examines the charge transfer (LMCT, MLCT, MMCT, LLCT, ILCT) excited state chemistry of transition metals possessing different electronic configurations.

The photoredox and photosensitization (and photocatalytic) processes involving transition metal polypyridine complexes are discussed by Kalyanasundaram; specifically, topics include types of excited states encountered and tuning of their properties and light-induced electron and energy transfer reactions and their applications. The concepts are illustrated with selected examples of mononuclear complexes. Polynuclear polypyridyl complexes based on rubipy are discussed by Scandola and co-workers; they are viewed as simple photochemical molecular devices. Topics that relate to these devices are also addressed, namely spectral sensitization, photoinduced charge separation, antenna effect, remote photosensitization, and the antenna-sensitizer function. Applications of 2,2′-bipyridine and 1,10-phenanthroline complexes of cobalt(II), ruthenium(II), rhenium(I), and iridium(III) in the photoreduction of carbon dioxide and in the water-gas shift reaction are taken up by Ziessel. The usefulness of the more complex polynuclear devices as photosensitizers of TiO_2-based photoelectrochemical cells and the mechanism(s) of sensitization are entertained in the chapter by Gratzel and Kalyanasundaram. It would appear that TiO_2 electrodes coated with $Ru(dcbpy)_2(SCN)_2$ are the most efficient among the several mononuclear systems examined and that the trinuclear system $[(CN)(bpy)_2–Ru–CN–Ru(dcbpy)_2–NC–Ru(bpy)_2(CN)]$ has good sensitization properties. It was unfortunate that the photochemical stability of many of these photosensitizers was not addressed by the various authors that labor in this area. It would also seem that simple adsorption of the sensitizer onto a wide bandgap semiconductor electrode is preferable (gives higher photonic efficiencies) to chemical derivatization, the photochemical instability notwithstanding. The progress made in the assembly of porphyrin derivatives into supramolecular systems is reviewed by Harriman in a chapter in which he also describes the aptitude(s) of such assemblies to photosensitize particular reactions. The work recounted was primarily concerned with trying to reproduce, under controlled conditions, some of the important features of photosynthetic reaction center complexes.

The photocatalytic and photoredox properties of an interesting assembly(ies) of early transition metal oxide clusters, so-called polyoxometallates (negatively charged condensed oligomeric aggregates of oxide ions and transition metal ions usually in their d^0 electronic configuration), are examined by Hill et al. The chemistry of these clusters is still in its infancy; there is much to occupy interested researchers to bring it to maturity (dehydrogenation of organic substrates, aerobic catalytic oxidation of organic substances, selective oxidations in the presence of oxygen, among others). The assemblies possess properties that could be utilized to address new catalytic transformations, photoredox chemistry (the redox potentials of some assemblies in their ground states vary between -1 and $+1$ V, while the potentials of the corresponding excited states can reach up to ca. 3 V), and eventually the construction of sophisticated single-molecule multifunctional devices capable of several temporally linked functions. Kolle addresses the photocatalytic transformations of organics using inorganic salts and complexes of Cu(I), Cu(II), and others; mechanistic details of the reactions and subsequent classification problems are also explored. The contribution by the Santa Barbara group (Ford and co-workers) focuses on those photocatalytic reactions that implicate simple mononuclear and polynuclear metal carbonyls, $M_y(CO)_x$, together with mixed ligand complexes where several CO's are in the coordination sphere of a single metal center. The role of photochemistry in facilitating catalysis in C–H activation by generating coordinative unsaturation by photoextrusion of a ligand (CO, H_2) in organometallic systems is addressed by Crabtree. In the last chapter, Bockman and Kochi explore electron donor/acceptor (EDA) interactions and photoinduced electron transfer in organometallic compounds which can span redox potentials between -2 and $+2$ V. Discussed are the properties of typical organometallic compounds that are relevant to EDA complex formation and to electron transfer, the electronic and structural changes attendant on complex formation, and the consequences of photoinduced electron transfer from the donor to the acceptor by illumination into the charge transfer band(s) of the EDA complexes.

The references in each of the chapters, though not exhaustive, are representative of the various fields touched upon in this monograph. The lists are a good starting point for the novice and more seasoned researchers to accumulate more detailed literature in those specific areas of interest. Other monographs that review polypyridyl complexes, in particular, and other topics germane to those described here, in general, should wait a few years to allow development and maturity of some of the concepts and chemistry examined here and elsewhere. The reader will find in the present monograph several research ideas worth pursuing. If only for this, the monograph is definitely worth having in one's personal library.

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Carbocyclic Cage Compounds: Chemistry and Applications. Edited by E. Osawa and O. Yonemitsu. VCH Publishers: New York. 1992. 409 pp. $95.00. ISBN 0-89573-728-0.

This volume, which is part of the series Methods in Stereochemical Analysis edited by A. P. Marchand, contains 13 chapters written by different authors.

The first and largest chapter, written by A. P. Marchand, is a general survey of polycyclic cage molecules as useful intermediates in organic synthesis and in mechanistic studies; an example is the photothermal metathesis (cycloaddition followed by fragmentation) of Diels–Alder adducts between cyclopentadiene and *p*-benzoquinones to yield triquinanes. Tabular surveys allow rapid access to many interesting and useful reactions.

Chapter 2 by K. Naemura describes high-symmetry chiral cage-shaped molecules such as the tricyclics (twistane and brexane), tetracyclics (ditwist-brendane and ditwistane), and pentacyclics (C_2-bishomocubane and D_3-trishomocubane). Both theoretical and practical problems connected with the synthesis of such molecules are described.

A brief chapter by H. Kroto and D. R. M. Walton is dedicated to post-fullerene organic chemistry. The high yield of the dehydration/dehydrogenation reaction affording corannulene is interpreted as the discovery of a new round world of post-Buckminsterfullerene chemistry to complement the pre-Buckministerfullerene flat one.

F. Matsuda and H. Shirahama present a new look at natural product chemistry in three dimensions, concentrating on (i) stereocontrolled transannular cyclizations of macrocyclic compounds, namely biogenetic and biomimetic reactions of terpenes and on transannular Diels–Alder reactions, and (ii) stereoselective intermolecular reactions of macrocycles, namely the total synthesis of periplanone B and other remote asymmetric inductions using macrocyclics.

Propellanes are systematically reviewed by Y. Tobe (who made significant contributions to [*m.n.*2]propellanes) updating earlier surveys.

J. Nishimura discusses the formation of cyclophanes from vinylarenes. [2 + 2] photocyclodimerizations of divinylbenzenes, trivinylbenzenes, or related compounds such as 1,3,5-tristyrylbenzene, afford cyclophanes in satisfactory yields. The four-membered rings thus obtained may be cleaved by Birch reduction, affording cyclophanes with tetramethylene bridges. Another approach consists in cationic cyclocodimerizations in the presence of triflic acid under high-dilution techniques.

The synthesis of prismanes is surveyed by G. Mehta and S. Padma, whose experimental contributions to this field are significant. Whereas [3]-, [4]-, and [5]prismane have been synthesized both as unsubstituted and susbtituted compounds, [*n*]prismanes with $n \geq 6$ are still unknown. This is rather surprising because [3]prismane with a half-life of 11 h at 90 °C is more strained than the [*n*]prismanes with $n = 6–8$. Strained prismanes are "angry tigers unable to break out of paper cages" owing to the Woodward–Hoffmann rules, which should make them kinetically stable.

H. Higuchi and I. Ueda describe recent developments in the chemistry of cubane. Direct functionalization can occur via metallocubanes (mercury, zinc, lithium, and magnesium are the most useful metals) or via photosensitized substitution. Release of steric strain in cubanes may lead to valence isomerization and ring enlargement; e.g., tertiary cubyl carbinols yield homocubanes under acid conditions, and analogous cubane-1,4-biscarbinols afford bishomocubanes or *6H*-azulenones. Pyramidalized olefins such as cubene are even more strained. The cubane skeleton, when polynitrated, may serve as high-energy density material. A list of yet unknown cubane derivatives is offered as a challenge to synthetic chemists.

Another progress report encompassing the years 1986–1990 is authored by W. L. Dilling and refers to 1,1- 1,2-, 1,3-, 1,3′-, and 1,4-bishomocubanes. It describes systematically theoretical calculations, formation, and reaction of these systems.

C. Ganter reviews briefly his approach to adamantane rearrangements; instead of using Lewis-acid-catalyzed isomerizations to enter "Adamantaneland" using Schleyer's well-trodden path, he generates carbocations from alcohols and Brønsted acids and uses ionic hydrogenation agents such as Et_3SiH. The mechanistic conclusions complement those of Schleyer, Olah, and Farcasiu.

The reflex and antireflex effects introduced by G. Ourrisson and his school are described by Josette Fournier and B. Waegell with the implication for polycyclic cage compounds. The compromise between electrostatic effects in cyclohexanone rings with polar α-substituents gives rise to the effects mentioned in the title.

T. Miyashi, Y. Yamashita, and T. Mukai review photochemical syntheses and reactions of cage molecules, including information on photocyclizations which do not occur, such as those that would lead to hexaprismane.

The final chapter by K. Hirao, A. Yamashita, and O. Yonemitsu is a very brief review on the valence isomerization between norbornadiene and quadricyclane, which so far has not ripened into a viable solar energy conversion system. Information is provided on homogeneous and heterogeneous catalysts for the ring-opening reversion of quadricyclanes.

Minimal overlap between the chapters was unavoidable, and cross-referencing would have been useful. As a general conclusion, this is an extremely useful source of information for all chemists interested in up-to-date accounts, with extensive literature coverage, for a variety of topics connected with carbocyclic cage compounds.

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Drug Stereochemistry: Analytical Methods and Pharmacology. Second Edition, Revised and Expanded. Clinical Pharmacology Series/18. Edited by Irving W. Wainer (McGill University and Montreal General Hospital). Marcel Dekker, Inc.: New York. 1993. xvi + 424 pp. $165.00 ISBN 0-8247-8819-2.

This new edition has been impressively revised and expanded and is comprised of 16 chapters divided into four major sections: Section I, Introduction; Section II, The Separation and Preparation of Stereochemically Pure Drugs; Section III, Pharmacokinetic and Pharmacodynamic Differences Between Drug Stereoisomers; and Section IV, Perspectives on the Use of Stereochemically Pure Drugs.

The first three chapters of the book have not been updated and basically provide an early history of stereochemistry, an overview of stereochemical terms and concepts, and a section on enantiomer analysis by competitive binding methods.

Chapter 4 (Indirect Methods for the Chromatographic Resolution of Drug Enantiomers: Synthesis and Separation of Diastereomeric Derivatives) has been vastly expanded with new sections on 3-aminoquinuclidines and isoindoles and additional material added to the existing sections on carbamates, isothiocyanates, chiral esters, formation of amides, and resolution via derivatization of epoxides and cyclophosphamide.

Chapter 5 (The Direct Resolution of Enantiomeric Drugs by Chiral-Phase Gas Chromatography) contains new material regarding chiral diamide phases and cyclodextrin derivatives. This chapter also has an excellent discussion on the application of enantioselective gas chromatography to pharmaceuticals with examples of amino alcohols, amines, amino acid type drugs, heterocycles, and essential oils as well as miscellaneous section. Over 50% of the references in this chapter are from the recent literature.

Chapter 6 (HPLC Chiral Stationary Phases for the Stereochemical Resolution of Enantiomeric Compounds: The Current State of the Art) has been vastly updated with 46% of the references appearing in the literature since 1988. Chapter 7 (Synthesis of Enantiomerically Pure Drugs) has unfortunately not been updated. Chapter 8 (Enzymatic Synthesis and Resolution of Enantiomerically Pure Compounds) is a new chapter and contains an excellent discussion on enzyme-based production of homochiral compounds via (1) oxidoreductase (oxidation), (2) oxidoreductase (reduction), (3) transferases, (4) hydrolases, (5) lyases (C–C formation, amino acid, acyloin, cyanohydrin), (6) lyases (C–O formation, C–N formation), and finally (7) isomerases.

Section III of the book has undergone extensive revision and begins with a chapter on stereoselective biotransformations and their toxicological consequences and implications. This is an excellent chapter exploring the stereochemical factors that impact most heavily on biotransformation. There is an excellent section on stereoselectively and toxicity and the role of biotransformation, in which the stereochemistries of various drugs are evaluated with regard to efficacy and toxicity. This section also directs attention to the pharmacokinetic differences that exist between various stereoisomers. Other topics included in this chapter are mixed function oxidases, polymorphism, flavin-containing monooxygenases, glutathione transferases, epoxiide hydrolases, glucuronyl transferases, sulfotransferases, and cysteine conjugate β-lyase.

Chapter 10 discusses stereoselective transport of drugs across the epithelia. This is a new chapter which describes the transport mechanisms by which many drugs cross epithelial barriers. There is also a brief description of the properties of the epithelial cell and more specific comments on the transport of sugars, amino acids, nucleosides, organic cations, and organic anions. There is a brief discussion of the importance of the kidney in the regulation of water, electrolyte and nutrient balance, and the excretion of metabolic waste and foreign substances as well as a brief discussion of the epithelia of the small intestine and liver.

Chapter 11 (Verapamil: A Chiral Challenge to the Pharmacokinetic and Pharmacodynamic Assessment of Bioavailability and Bioequivalence) is very interesting reading which points to the need for evaluating the relevance of stereospecific assays and the need for enantiospecific data for racemic drugs in the current clinical and regulatory environment.

Chapter 12 is on the enantioselective binding of drugs to plasma proteins and explores the impact drug binding to plasma proteins may have on pharmacokinetic and pharmacodynamic properties of drugs and in particular how enantiomers differ in these respects.

Section IV (Perspectives on the Use of Stereochemically Pure Drugs) of the book has been completely revised and consists of four chapters. Chapter 13 (FDA Perspective on the Development of New Stereoisomeric Drugs: Chemistry, Manufacturing, and Control Issues) is a superb chapter which gives an excellent introduction to this particular section of the book. It discusses general policy, analytical control methods and specifications for chiral drugs such as stereochemical identity, systematic nomenclature, and proof of stereochemical structure.

Chapter 14 (Stereochemically Pure Drugs: An Overview) considers the advantages and disadvantages of racemic vs enantiopure drugs. It delves into the pharmacodynamic and toxicity considerations, situations where enantiomers are equipotent, and the situation where most of the ativity resides in a single enantiomer. There are also examples given where there is a clear advantage in the use of a racemic drug. There is also an interesting section on pharmaceutic consideration and regulatory concerns at the close of the chapter.

Chapter 15 (Stereoisomeric Drugs in Therapeutics: Clinical Perspectives) opens with a short introduction and then classifies racemic drugs into four general groups: (1) those which are a mixture of an active and relatively inert isomer, (2) those which are mixtures of isomers with different and unique pharmacodynamic activities, (3) mixtures with opposing pharmacodynamic activities, and (4) those which are mixtures with similar pharmacodynamics but with different potency. Examples of each are given. The chapter concludes with a discussion on stereoselective pharmacokinetics in disease states and aging.

Chapter 16 (Development of Stereoisomeric Drugs: An Industrial Perspective) addresses the issues that face the pharmaceutical industry during the development stages of stereoisomeric drugs. It is an excellent illustration of the technical and regulatory considerations that must be considered during drug development. As with many of the other chapters in this text, this chapter and particularly this section are a must for new students of medicinal chemistry.

The chapters in this book are well written and referenced with an adequate index. It is certainly a must for libraries; however, the price will likely keep it off the shelves of most scientists who no doubt would find it useful in their own personal libraries.

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