Dessau, *ibid.*, **88**, 1589 (1966); (e) E. Wenkert and B. L. Mylari, *ibid.*, **89**, 174 (1967).

(7) Fisch and Ourisson, ref 6b, report transannular hydrogen transfer in a substituted cyclodecyl radical, but the precise positions involved were not determined.

(8) H. J. Urech and V. Prelog, *Helv. Chim. Acta*, **40**, 477 (1957); V. Prelog, W. Küng, and T. Tomljenovic, *ibid.*, **45**, 1352 (1962).

(9) The reactions were performed in 50% aqueous methanol by reduction of hydroxocobalamin with $NaBH_4$, addition of the corresponding alkyl tosylate or iodide, then precipitation of the B_{12} product with acetone. It was washed with acetone, and then cleaved by Br_2 in CH_2Cl_2. Cyclodecyl bromide was isolated in ca. 7% overall yield, and identified by VPC, mass spectrum (d_1), and NMR spectra.

(10) M. Tada and H. Ogawa, *Tetrahedron Lett.*, 2639 (1973); F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Am. Chem. Soc.*, **92**, 1414 (1970).

(11) The decomposition is probably homolytic, but the resulting radical–B_{12r} pair recouples to only a small extent, consistent with the low yield in the original alkylation. Thus further cyclodecyl radical rearrangement is not detectable.

(12) B_{12s}^- is a powerful reducing agent.[5] While iodide and tosylate are comparable leaving groups in simple displacements, the C–I bond is much more easily reduced.

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Received November 25, 1975

Book Reviews

A Dictionary of Spectroscopy. By RONALD C. DENNEY (Thames Polytechnic). Halsted Press, John Wiley & Sons, Inc., New York, N.Y. 1973. xv + 161 pp. $8.95.

A dictionary of spectroscopic terminology could be quite useful. The diverse techniques and concepts of spectroscopy are anything but deficient in jargon and nomenclature of dubious descriptive value. I would be grateful to Dr. R. C. Denney for his dictionary if it were not flawed by unnecessarily trivial and specialized entries, important omissions, and physically unsound discussions. This dictionary is clearly directed at individuals who are not interested in understanding spectroscopy.

Analytical atomic, infrared, and mass spectroscopy are particularly well represented, but Delves cup, gallium cut-offs, and McLafferty rearrangements, for example, seem out of place. Chromatography, except in its connection to mass spectroscopy (Watson–Biemann separation), appears to have been excluded. Other omissions include Hund's rules and coupling cases, Faraday, Kerr, and Stark effects, a distinction between Rydberg and valence states, and a discussion of resonance-enhanced Raman spectroscopy.

Following are excerpts from several of the more misleading definitions:

> *Bonding Orbitals.* "If the two electrons have opposite spins the electron cloud of the molecular orbital is mainly between the two nuclei .... This constitutes a bonding orbital. If, however, the two electrons have identical spins, the molecular orbital is formed with a nodal plane between the two nuclei and the charge is localized at each end of the bond." Spin is confused with phase of the atomic orbital.
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> *Brewster Angle.* "The Brewster angle is the angle at which the incident light is totally reflected if in one polarization and totally refracted if in the opposite polarization." Although total transmission does occur for one polarization, *total* reflection at Brewster incidence does not occur for the other polarization.
>
> *Ground State.* "When electrons in an atom or molecule occupy the vibrational levels [?] in the lowest possible energy levels, the condition is referred to as the ground state."
>
> *Population Inversion.* "This is the name given to a situation in which the number of active species occupying a particular energy state is greater than that predicted by the Boltzmann ratio. This is of special consideration in lasers in which excited states of extended lifetimes are produced and population inversions deliberately created." An inversion is more than a departure from equilibrium; an upper level must have a larger population than a lower energy level. Upper laser levels do not necessarily have extended lifetimes.
>
> *Raman Effect.* ".... after being raised to an excited state, some of the excited molecules returned to a higher or lower vibrational level in the ground electronic state. The lifetime of the Raman excited state is about 10^{-12} s and only about 1 in 10^6 molecules exhibit the effect at any particular moment." The excited state in the Raman effect is not a *real* but a *virtual* level. The Raman effect might be approximately 10^6 times weaker than fluorescence excited from a *real* upper level.
>
> *Schrödiger Wave Equation.* "Solutions of the equation are only possible for finite, non-zero, unique values of E; such solutions are termed eigenvalues and correspond to the energy states developed from the Bohr Theory of the atom." No comment.
>
> *Triplet State.* "The triplet state can only arise from the promotion of one of the two π electrons, forming part of an unsaturated system, to an upper unoccupied orbital." There are many other ways of forming triplet states.

Perhaps a physical chemist specializing in diatomic molecular spectroscopy is too much of a purist to properly review this dictionary of spectroscopy.

Robert W. Field, *Massachusetts Institute of Technology*

Structure and Bonding. Volume 20. Edited by J. D. DUNITZ (Zurich), P. HEMMERICH (Kontanz), R. H. HOLM (Cambridge, Mass.), J. A. IBERS (Evanston), E. G. JØRGENSEN (Geneva), J. B. NEILANDS (Berkeley), D. REINEN (Marburg), and R. J. P. WILLIAMS (Oxford). Springer-Verlag, New York, N.Y. 1974. 167 pp. $27.10.

This is the latest in a series of volumes "issued at irregular intervals, according to the material received". This volume was given the secondary title "Biochemistry". All four of the review articles in this volume deal for the most part, at least, with the physical and chemical properties of certain metal ions in proteins and smaller polypeptides. Moreover, the last three articles all cover aspects of naturally occurring, iron-containing compounds.

The first article entitled "The Role of Divalent Cations in the Mechanism of Enzyme Catalyzed Phosphoryl and Nucleotidyl Transfer Reactions", by A. S. Mildvan and C. M. Grisham, both summarizes and critically examines experimental findings on the enzymes staphylococcal nuclease, DNA polymerases, pyruvate kinase, phosphoenolpyruvate carboxylase, fructose diphosphatase, creatine kinase, phosphoglucomutase, alkaline phosphatase, and (Na^+ and K^+) adenosine 5′-triphosphatase. In each case the authors speculate on possible roles of divalent metal ions in coordinating with either the atom or group which attacks (or leaves from) the transferred phosphoryl moiety, or in coordinating with the transferred phosphoryl moiety itself.

The second article, "The Enzymatic Reduction of Ribonucleotides", by H. P. C. Hogenkamp and G. N. Sando, is a thorough summary of the chemistry and biochemistry of the currently dynamic area of research which is examining how nature provides the deoxyribonucleotide precursors needed in DNA synthesis. The authors correlate information gathered in a variety of different systems and show where some common themes have emerged. In some cases the authors postulate possible intermediates in some of these reductase reactions.

The third and fourth articles, "The Electronic State of Iron in Some Natural Iron Compounds: Determination by Mössbauer and ESR Spectroscopy", by W. T. Oosterhuis, and "Mössbauer Spectroscopy on Heme Proteins", by A. Trautwein, are much more physical in content. Oosterhuis correlates Mössbauer, ESR and, in some cases, x-ray crystallographic findings on ferrichrome A, deferoxamine, various hydroxamic acid complexes of ^{57}Fe, mycobactin P, enterobactin, and transferrins. He points out a dilemma which has emerged: "How can one get $g = 4.3$ in ESR and Mössbauer spectra indicative of a *rhombic* environment when the complexes are known (from x-ray crystallographic studies) to be *trigonal* (axial)?"

Trautwein's well-written article focuses on recent findings on the deoxy, oxy, and carbomonoxy forms of myoglobin and hemoglobin. He begins with a simplified model explaining the Mössbauer effect based on an earlier description by H. Frauenfelder. Following a summary of experimental findings, he launches into a discussion of using molecular orbital theory to interpret experimental Mössbauer and susceptibility data.

The first two articles should be of primary interest to biochemists and the latter two articles to biophysicists; moreover, the topics covered are rather diverse. In the future, better service to the scientific community could be provided if the articles within a given volume could be tied together by some common theme and the volume given a more explicit secondary title to describe that common theme.

George L. Kenyon, *University of California, San Francisco*

Zerovalent Compounds of Metals. By L. MALATESTA and S. CENINI. Academic Press, Inc., London. 1974. 241 pp. £7.50 ($19.75).

The authors of this book have chosen to review the chemistry of zerovalent metal compounds, excluding those which contain exclusively carbon monoxide as ligands but including those compounds which contain both carbon monoxide and other ligands. Compounds containing unsaturated hydrocarbons are also omitted. Their literature search covers the period up to the end of 1972.

The book contains two major parts. Part I contains current thought on the important factors that contribute to the stabilization of transition metals with low oxidation states (especially zero) as well as the physical methods the chemist utilizes to study compounds of this type. The authors thoroughly discuss and illustrate with facts such ideas as σ-donor and π-acceptor properties of ligands, and the physical means whereby these properties are studied, i.e., ir, NMR, ESCA, Mössbauer, and even kinetic and thermodynamic data.

Part 2 contains a detailed survey of complexes with tricovalent P, As, and Sb derivatives which are so prevalent in this type of chemistry. The chapters discuss the Ni, Co, Fe, and Cr triads in separate sections. Each section contains an incredible amount of information about the myriads of complexes of this type that exist today. The authors attempt to review the information available as well as compare the results and then give the reader an overall view of where the research in this area is in 1972 as well as the direction it seems to be taking.

Finally a small but detailed section containing the chemistry of isonitrile derivatives is presented.

This book is an excellent volume for those interested in the organometallic chemistry of transition metals, especially those in the low oxidation states. It is useful for both the industrial and academic chemist alike and should be included in libraries which chemists of these areas utilize.

Philip H. Merrell, *Bowdoin College*

Modern Molecular Orbital Theory for Organic Chemists. By WESTON T. BORDEN (University of Washington). Prentice-Hall, Inc., Englewood Cliffs, N.J. 1975. xiv + 305 pp. $14.95.

A qualitative introduction to molecular orbital theory in the first portion of the book appears to be a necessary approach to give the students an intuitive grasp of the concepts of symmetry, orbital shape, relative energy levels, and the meaning of α and β based on the concept ionization potential and electron affinity. The merit of this text exists in the introduction of perturbation theory, concepts about σ and π orbital energies (p 62) explained through semiquantitative analytical formulas such as $\beta = \beta_0 \exp[-A(r - r_0)]$, $E_\sigma = (k_\sigma/2)(r_0' - r)^2$, general solutions for cyclic systems, a discussion of alternate hydrocarbons, the Woodward–Hoffmann rules, group theory, and especially to self-consistent field theory, PPP theory, extended Hückel theory, etc.

Having had a course in physical chemistry, the student should understand wave functions and Schroedinger's equation applied to simple systems. The author states that "only in the second half, when the students had developed a good physical 'feeling' for molecular orbital theory, did the course become more mathematical". Although a qualitative approach suffices at first, the question of how one obtains numerical results ultimately arises. The discussion on applications of Hückel theory (Chapter 3), although well organized, could be improved by examples which actually include a solution of an eigenvalue problem. This technique, which results from the variational principle, is fundamental to quantum mechanics, and especially molecular orbital theory. While reading the first portion of the book one may wonder, for example, why the energy for pentadienyl is found to be $4\alpha + 5.46\beta$ for the cation and $6\alpha + 5.46\beta$ for the anion (p 59), whereas $E^+ = 4\alpha + 5.24\beta$ and $E^- = 6\alpha + 6.48\beta$ (p 61) for cyclopentadienyl. Energy levels and coefficients of the molecular orbitals are not listed prior to this discussion nor later in the text, and, consequently, the reader *must* accept these values as well as some of the other results on faith.

By introducing Chapter 3 with the traditional approach to Hückel theory with a wave function written as a product of one-electron orbitals and showing that the total energy is a sum of molecular orbital energies, by using zero-differential overlap and defining an effective one-electron Hamiltonian operator resulting in $\alpha = (\chi_A, h_{eff}\, \chi_A)$ and $\beta = (\chi_A, h_{eff}\, \chi_B)$, would not only prepare the student for the more advanced but related mathematical topics with the explicit inclusion of electron repulsion (Chapter 7) and self-consistent field theory (Chapter 8) but would also answer very explicitly the quantum-mechanical basis of molecular orbital theory. This text introduces modern approaches and should be used, but the lecturer will most likely have to supplement the material in the first portion of the text.

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The Shikimate Pathway. By E. HASLAM (University of Sheffield). John Wiley & Sons (Halsted Press), New York and Toronto. 1974. 316 pp. $29.00.

Though small in size, the titled volume looms large in the wealth of copiously referenced information made available by the author. This cross-discipline presentation skillfully melds disparate elements of natural-product organic chemistry, biochemistry, botany, and plant physiology into a cohesive presentation that should provide valuable source material to anyone seriously interested in the metabolism of aryl compounds.

The topic is covered in six chapters, with the opening chapter devoted initially to a delineation and consideration of some mechanistic studies of the common pathway—from carbohydrate to chorismate, thence to the various branch points from chorismate to essential metabolites. The second chapter emphasizes the chemistry of important intermediates and draws attention to the ways in which key isotopically labeled precursors may be prepared. A detailed consideration of the biosynthesis of the various isoprenoid quinones, phenolic metabolies, *p*-aminobenzoic acid, and the folic acid coenzymes (Chapter 3) is followed by a discussion of the metabolism of the aromatic amino acids, with emphasis on oxidative pathways and particular reference to higher organisms and microorganisms (Chapter 4). The terminal portion of the book (Chapters 5 and 6) deals with the shikimate pathway in higher plants with emphasis on plant phenols and the phenylpropanoid pool. As the author has stated: ". . . identical compounds in the chemical sense are often synthesized in different ways in different organisms and the shikimate pathway provides many examples of metabolites of this type. . . ."

The writing style is clear and the reader is left with a definite understanding of what is reasonably well established, what is doubtful or speculative, and what is unknown or remains to be established.

In addition to its usefulness to diverse research groups, the reviewer would judge the text an admirable vehicle for the presentation of a topic too long neglected in teaching biochemistry.

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