

0.568, 0.650, 0.302, 0.281, 0.271. In order to obtain a comparison with the expectations of the axial model with the same LSR-substrate distance used in the simulation, the converged average ratios for *each* of the 20 computer runs were treated as *observed* ratios and *R* values<sup>2</sup> were calculated. These ranged from 9.8 to 0.6% and averaged 4.4%.<sup>25</sup> In most cases closer agreement with an axial model could be obtained by allowing the Ln-O distance to vary from that employed in the simulation. Insofar as the present model may represent reality, this finding implies that LSR-substrate distances determined from nmr experiments by *assuming* an axial model may not reliably reflect the actual values of these quantities and deviations up to 0.5 Å and more are not unlikely. The average shift ratios for 20 runs on isoquinoline<sup>26</sup> were, for protons a-g (see structure 2) respectively: 1.000, 1.000,<sup>27</sup> 0.252 (4), 0.144 (6), 0.154 (8), 0.248 (13), 0.439 (19). These may be compared with the axial ratios calculated from the model employed: 1.000, 1.000, 0.250, 0.141, 0.150, 0.243, 0.432. The *R* values calculated as described above ranged from 9.9 to 0.7% and averaged 4.6%.

An alternative model,<sup>12,28</sup> which assumes that shift reagent adducts in solution largely maintain the structure and properties found in the solid state, has certain inadequacies which are overcome by the present model. Although the earlier model accounted<sup>12</sup> quite well for the 4-methyl shifts of 4-picoline in the Ln(dpm)<sub>3</sub>(4-pic)<sub>2</sub> systems, it predicted 2- and 3-proton

(25) It should be noted that the ratios for the simulated individual contributing forms depart markedly from the expectations of axial symmetry. For example, in a run which yielded an *R* value of 0.6% the ratios for protons b-g respectively fell in the following ranges: -0.502 to 0.600, -1.698 to 0.827, -1.114 to 1.072, -0.693 to 0.541, -0.458 to 0.365, -0.398 to 0.431, while the converged average values were respectively: 0.389, 0.573, 0.653, 0.304, 0.282, 0.272.

(26) Ln-N = 2.53 Å, coordination along nitrogen lone pair axis, β = 45°.

(27) For each iteration a C<sub>2</sub> rotation of the substrate was performed and the results were averaged; this accounts for the identity of the calculated a and b proton shifts.

(28) R. E. Cramer and R. Dubois, *J. Amer. Chem. Soc.*, **95**, 3801 (1973).

(29) J. P. Sipe, III, Ph.D. Thesis, The Pennsylvania State University, 1973. For instance using eq 1, the susceptibility tensor data for Eu(dpm)<sub>3</sub>(4-pic)<sub>2</sub> of ref 12 (η = 18°) and geometric factors were calculated from the solid state structural data; dipolar shifts for the 4-picoline protons 2-H, 3-H, and 4-CH<sub>3</sub> were calculated to be -18.0, -5.4, and -2.5

shifts which were too large.<sup>29</sup> In addition, even the 4-methyl resonance shift was in poor agreement for the thulium system. Using a particular random number sequence and the experimental susceptibility tensors<sup>12</sup> for the Ln(dpm)<sub>3</sub>(4-pic)<sub>2</sub> series, Ln = Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, and Yb, we calculate the following shifts for the 1-proton (a) of isoquinoline in the above sequence: 30.2, 14.5, 2.2, -12.7, 203.6, 244.9, 110.7, -42.0, -139.8, -31.7 ppm (298°K, β = 45°). The calculated negative Tm shift is larger than that of the Er and Yb systems, as is observed experimentally.<sup>30</sup> It should be noted that in its prediction of effective axial symmetry<sup>24</sup> the present model is completely independent of adduct stoichiometry.

While it is obvious that (with the qualification of a slight bias) an *infinite* number of randomly chosen isomers (a biased uniform distribution of substrate ligands with respect to the principal magnetic axes) would conform exactly to the expectations of axial symmetry, we have demonstrated that a dynamic equilibrium between a relatively small number of interconverting forms will lead to shift ratios which will approximate, but in general do *not exactly equal*, those derived from an axial model. Many of the details of the simulation are not necessarily realistic, *viz.*, unit weights for all contributing isomers, arbitrary angular constraints, and choice of susceptibility tensor components. However, the major finding, that resonance shift ratios will, within reasonably broad limits, conform to an axial<sup>24</sup> model, can be expected to be independent of the parameters employed.

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ppm, respectively, at 298°K, when the nonequivalent 2-H and 3-H shifts are averaged. Variation of the η parameter failed to improve the agreement with the room temperature solution shift data (-12.0, -4.2, -3.0 ppm).

(30) W. D. Horrocks, Jr., and J. P. Sipe, III., *J. Amer. Chem. Soc.*, **93**, 6800 (1971).

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## Book Reviews

**Organic Chemistry. Third Edition.** By R. T. MORRISON and R. N. BOYD. Allyn and Bacon, Inc., Boston, Mass. 1973. ix + 1258 pp. \$17.95.

The third edition of this textbook is a result of a conservative and effective expansion, with a few deletions and modifications, of the second edition. The previous editions of this textbook have traditionally been well liked by students because of their clarity and organization. You will find no radically different methods for presentation of fundamental material in the third edition. The basic organization and approach have not been altered.

There must, however, be some changes in a new edition, and I will try to briefly mention those which came to my attention. (a) The initial discussion of resonance is presented much earlier in Chapter 6 on alkenes. As a result, the discussion of allyl radical

stability and 1,4-addition reactions of conjugated dienes can be presented to the student much more easily and in a clearer manner. In the previous edition, resonance was not initially introduced until Chapter 10 in the discussion of aromaticity. (b) Some of the chapters in the earlier edition have been combined. Ethers and epoxides are discussed together in Chapter 17, and the discussion of glycols is now included in the chapter on alcohols. The small chapter on diazonium salts in the second edition has been incorporated into one of the chapters on amines. The chapter on dicarboxylic acids is now included in Chapter 18 on carboxylic acids, and the separate chapter on keto acids has been deleted.

Slight feelings of nostalgia set in when one realizes that Körner's method of absolute orientation of benzene, balancing oxidation-reduction equations, and classical molecular weight determination

methods are no longer included. In their place, you will find discussions of some new material such as the synthesis of acids and esters using 2-oxazolines and organoboranes, the thallation reaction, and a discussion of enamines.

Part II (Chapters 25–32) contains most of the completely new material. There is a new chapter on macromolecules which includes a considerably expanded treatment of polymers. Another new chapter on rearrangements and neighboring group effects includes some old material such as the discussion of the Hofmann rearrangement taken from the chapter on amines. Nonclassical ions and neighboring group effects are discussed in the same simple, easy-to-read Morrison and Boyd fashion, which incorporates some of the controversies that have highlighted this area.

There is also a new chapter on molecular orbitals and orbital symmetry. This chapter, which includes discussions on sigma-tropic shifts and electrocyclic and cycloaddition reactions, contains excellent illustrations. Included at the end of this chapter are six pages of problems. The inherent quality of the textbook and the reason for the high student-appeal are well illustrated by the authors in this chapter. Here one sees clearly that the authors are able to distill out the basic principles and present them in a simple manner which should be easy to read and understand by most students.

Part III of the textbook (Chapters 33–37) entitled "Biomolecules" includes chapters on fats, carbohydrates, amino acids, and proteins. Some of this material is a result of the rearrangement and regrouping of material found in other chapters of the older edition.

The last chapter in the textbook is also new and is entitled "Biochemical Processes." This chapter gives the impression that it may have been quickly added as an afterthought, and in my opinion it does not measure up to the standards set by the rest of the book. It includes a discussion of the mechanisms of enzyme action, biosynthesis of fatty acids, and biological oxidation mechanisms. Nucleic acids are also discussed in this chapter.

The success of this textbook can perhaps be summarized on the basis of endurance alone. I was taught organic chemistry from the first edition. I am presently using the third edition to teach students who, if the trend continues, will be teaching additional students from the fourth or fifth edition.

Costello L. Brown, *California State University, Los Angeles*

**Organic Phosphorus Compounds. Volumes 1–5.** Edited by G. M. KOSOLAPOFF (Auburn University) and L. MAIER (Monsanto Research S. A.). Wiley-Interscience, New York, N. Y. Volume 1: 1972. xiii + 545 pp. \$29.95. Volume 2: 1972. v + 508 pp. \$29.95. Volume 3: 1972. v + 500 pp. \$29.95. Volume 4: 1972. v + 531 pp. \$29.95. Volume 5: 1973. v + 329 pp. \$29.95.

This treatise is an updating of Professor Kosolapoff's 1950 volume of the same title. When complete the total work will consist of 21 chapters, each covering specific types of phosphorus compounds. The individual chapters discuss synthetic methods, reactions, and physical properties and include, at the end, a listing of all known compounds containing the phosphorus functionality under consideration.

Chapters of Volume 1 are: Primary, Secondary, and Tertiary Phosphines; Organophosphorus-Metal Compounds, Biphosphines, Triphosphines, Tetraphosphines, Cyclopolyphosphines, and Corresponding Oxides, Sulfides and Selenides; Phosphine Complexes with Metals. Volume 2: Phosphite, Phosphonite, and Aminophosphine Complexes; Quaternary Phosphonium Compounds. Volume 3: Phosphine Alkylenes and Other Phosphorus Ylids; Penta- and Hexaorganophosphorus Compounds; Tertiary Phosphine Oxides. Volume 4: Tertiary Phosphine Sulfides, Selenides, and Tellurides; Halo- and Pseudohalophosphines; Phosphonyl- (Thiono-, Seleno-) and Phosphinyl- (Thiono-, Seleno-) Halides and Pseudohalides; Phosphonous Acids (Thio-, Seleno-Analogs) and Derivatives; Phosphinous Acids and Derivatives. Volume 5: Organic Derivatives of Hypophosphorous, Hypodiphosphorous, and Hypophosphoric Acid; Organic Derivatives of Phosphorous Acid and Thiophosphorous Acid. Future volumes are scheduled to contain the following chapters: Phosphinic Acids and Derivatives; Organic Derivatives of Phosphoric Acid; Phosphorus(V)-Nitrogen Compounds with Phosphorus in Coordination Number Four; Cyclophosphazenes; Phosphonic Acids; Organic Derivatives of Thio (Seleno-, Telluro-) Phosphoric Acid.

The treatise has neither a subject nor an author index. This is not as disconcerting as it might seem as compounds are listed in the tables in a systematic manner, and the references given at the end of each chapter are in alphabetical sequence by the first author's name. Not counting review literature, the total number of references cited

in the first five volumes is in excess of 10,000. The editors claim the literature is covered completely through 1969, with selected citations from the 1970 and 1971 literature.

There are a few complaints the individual user might have. For example, the organometallic chemist might find it annoying that the complexes are tabulated according to the phosphorus ligands rather than by the metal present. A few of the compound tables are somewhat difficult to use. All in all, this is an absolutely indispensable reference work. It should be available in every chemistry library and within arm's reach of every chemist seriously participating in organophosphorus research. The editors and authors are to be commended for their contribution to this monumental work. Considering the price and the fact that the entire work was printed by reproduction from typewritten copy, the contribution of the publishers was apparently minimal.

Carl R. Johnson, *Wayne State University*

**Structure and Bonding. Volume 10.** Edited by P. HEMMERICH (University of Konstanz), C. K. JØRGENSEN (Genève), J. B. NEILANDS (University of California, Berkeley), R. S. NYHOLM (University College, London), D. REINEN (University of Marburg), and R. J. P. WILLIAMS (Oxford University). **Volumes 11 and 13.** Edited by J. D. DUNITZ (Federal University, Zürich), P. HEMMERICH, J. A. IBERS (Northwestern University), C. K. JØRGENSEN, J. B. NEILANDS, R. S. NYHOLM, D. REINEN, and R. J. P. WILLIAMS. Springer-Verlag, New York, N. Y. Volume 10: 1972. 190 pp. \$18.10. Volume 11: 1972. 170 pp. \$17.20. Volume 13: 1973. 254 pp. \$26.70.

The first of these three additions to this established series of chemical review publications, subtitled "Inorganic Chemistry," contains seven articles which are typically essays rather than exhaustive literature surveys. The articles and their authors are: "Kinetics and Mechanism of Alkali Ion Complex Formation in Solution," by R. Winkler, a review emphasizing complex formation of the alkali ions with specific biological carriers; "Intra- and Inter-Molecular Bonding and Structure of Inorganic Pseudohalides with Triatomic Groupings," by Z. Iqbal, a review of structure and spectra of azides, fulminates, cyanates, and thiocyanates; "Spectra and Bonding in Metal Carbonyls, Part A: Bonding," by P. S. Braterman, an article covering electron and orbital bookkeeping, bent bonds, and metal-metal bonds; "On The General Theory of Magnetic Susceptibilities of Polynuclear Transition-metal Compounds," by J. S. Griffith, a definitive and scholarly essay with many useful tables of theoretical expressions and with applications to two-iron two-sulfur proteins such as spinach ferredoxin; "Thermochemistry of the Chemical Bond," by V. Gutmann and U. Mayers, an article reexamining the Pauling postulates relating to bond energies, electronegativities, and ionic character; "Vibrational Spectra and Structural Properties of Complex Tetracyanides of Platinum, Palladium, and Nickel," by S. Jerome-Lerutte, an article featuring comparisons of vibrational frequencies in solids for different cations; and "Electronic Spectra and Structural Properties of Complex Tetracyanides of Platinum, Palladium, and Nickel," by M. L. Moreau-Colin, a review closely related to the preceding one, but dealing instead with electronic absorption and emission spectra. As four of these seven articles deal with compounds containing the related ligands CO, CN<sup>-</sup>, and the triatomic pseudohalides, there is a reasonable degree of unity to the volume, making it of particular value to those interested in organometallic chemicals.

Volume 11 in this series is subtitled "Biochemistry," and contains four articles all dealing with the role of transition metal ions and their complexes in biology. The articles and their authors are: "Complexes Related to *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. An Anti-Tumour Drug," by A. J. Thompson, R. J. P. Williams, and S. Reslova, a review featuring photochemistry and the interaction of the metal complexes with amino acids, proteins, and nucleotides; "The Chemistry of Vitamin B<sub>12</sub> Enzymes," by J. M. Wood and D. G. Brown, a review emphasizing esr and nmr studies of B<sub>12</sub> compounds and B<sub>12</sub> enzymes of both methyl-transfer and hydrogen-transfer types; "Molybdenum-Containing Enzymes," by R. C. Bray and J. C. Swann, an article focusing on studies of milk xanthine oxidase, but also covering the role of molybdenum in other enzymes; and "Evolution of Biological Iron Binding Centers," by J. B. Neilands, a short but important essay discussing our present knowledge of the role of iron compounds in protist organisms, plants, and animals. The close relationship of these four articles makes this volume of particular value to those wishing to become more acquainted with this rapidly advancing field of research.

Subtitled "Rare Earths," Volume 13 in this series contains four articles covering various aspects of the crystal structure and elec-

tronic properties of rare earth and actinide ions in condensed phases. The articles and their authors are: "Structural Systematics in Actinide Fluoride Complexes," by R. A. Penneman, R. R. Ryan, and A. Rosenzweig; "Spectra and Energy Transfer of Rare Earths in Inorganic Glasses," by R. Reisfeld, in which ligand field theory is applied to the interpretation of absorption spectra, energy transfer, and emission spectra for ions in glasses; "The Crystal Chemistry of the Rare-Earth Silicates," by J. Felshe; and "The Inner Mechanism of Rare Earths Elucidated by Photo-Electron Spectra," by C. K. Jørgensen, a somewhat rambling but nonetheless very readable and delightful account of the entire history of the discovery of the rare earths, the establishment of their place in the periodic chart, and the interpretation of photoelectron spectral data for both the filled 3d inner shell and the partially filled 4f shell. The pair of articles on crystal structures, one on actinide fluorides and the other on rare-earth silicates, comprise 152 of the 254 pages in this volume and are both extremely valuable compilations of data together with extensive discussion of their systematics. As with Volume 11, the close relationship of the four articles in this volume makes it a particularly valuable contribution to the literature and an indispensable reference work for researchers in this field.

With regard to all of the volumes in this "Structure and Bonding" series, it should be noted that they are supplied with a high quality soft cover rather than with a hard cover. Furthermore, unlike other research volumes published today, they do not contain indexes to the authors whose research papers are cited in the reviews.

Lawrence L. Lohr, Jr., *University of Michigan*

**The Chemistry of the Transuranium Elements. Volume 3.** By CORNELIUS KELLER (Institute for Radiochemistry Nuclear Research Center and University). Verlag Chemie, D-6940 Weinheim/Bergstr. 1971. xv + 675 pp. DM 188.

This is the third volume of a series dealing with the chemistry of the transuranium elements. The book addresses itself primarily to the readers interested in actinide chemistry as a whole and provides rather detailed information regarding production and synthesis of mostly inorganic compounds and some organometallic complexes. The treatment of the subject matter in this volume, while comprehensive, is very well organized, remarkably complete, and very readable by the materials scientists and inorganic, nuclear, and radio chemists. Chapters in both of the two parts are arranged in conveniently short subsections with informative and particular headings. Conciseness and simplicity mark the writing, and the author's thorough understanding of the field is skillfully used for emphasis and comparison between the actinides and lanthanides and their compounds. Among the virtues of the book are the numerous references to the Russian literature, which seems to have been thoroughly covered, the large number of tables summarizing data for families of related compounds, and appreciable flow schematic and phase relationship diagrams for manufacturing technology and other engineering data necessary for production and alloying of transuranium metallic and inorganic nonmetallic materials. In addition to the aforementioned qualities, an excellent balance of theoretical and experimental approach is maintained by the author throughout the volume. All these qualities make this book attractive for study and teaching. As a reference book, it contains much useful information. Altogether this book is an excellent, up-to-date chemistry of the actinide series which deserves a wide distribution and usage.

K. S. Mazdiyasi, *Air Force Materials Laboratory*

**Biochemistry of the Developing Brain.** Edited by WILLIAMINA HIMWICH (Galesburg State Research Hospital). Marcel Dekker, Inc., New York, N. Y. 1973. 388 pp. \$24.50.

This book represents Volume I of a projected two-volume series dealing with the biochemistry of early brain development. It contains seven chapters written by different authorities on selected topics judged to be of special interest in the area of developmental neurobiochemistry. This book will be of value to those searching for reviews of recent developments in this area. There is a thorough discussion by Davis and Himwich of available information regarding amino acid and protein content of developing brain. The GABA system in brain during ontogeny is dealt with by Haber and Kuriyama. Agrawal and Davison review myelination and the effects of undernutrition upon this peculiar form of cellular development. Berl discusses the issue of metabolic compartmentation with respect to brain development. This reviewer found the chapter by Balasz and Richter on the effects of hormones on the biochemical maturation of the brain to be a particularly valuable synthesis of a complex area.

The value of this type of edited volume is that it permits selected writers to discuss in depth their concepts of significant progress in areas of interest. As such, this book can hold its own in the field. It is not to be recommended as an introduction to developmental biochemistry since it will be overwhelming to the student wishing a birdseye view. Another perennial problem with volumes of this type is that by the time of publication and distribution, there is a 3- to 4-year gap between manuscript preparation and the date of reading. This limits its usefulness to researchers interested in current work.

Workers in the area of developmental biochemistry should be aware of this volume as it contains the most comprehensive available reviews in this rapidly evolving field.

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**Energy Transfer Parameters of Aromatic Compounds.** By ISADORE B. BERLMAN (Hebrew University of Jerusalem). Academic Press, New York, N. Y. 1973. ix + 379 pp. \$20.00.

"Energy Transfer Parameters of Aromatic Compounds" is primarily a compilation of Förster radii ( $R_0$ ), molar concentrations of acceptor species for which there is an average of one acceptor molecule inside a sphere of radius  $R_0$  about the donor molecule ( $C_0$ ), and donor fluorescence-acceptor absorption overlap integrals for dipole-dipole energy transfer phenomena between various donor-acceptor pairs selected from 210 aromatic molecules. The introductory part of the book contains about 70 pages of textual material consisting of a concise, well-written outline of the history, foundations, and current trends of thought in all aspects of energy transfer phenomena. The literature is well covered in this section, and conflicting interpretations of experimental results are noted. This section should be of value to graduate students as introductory or supplemental reading on the subject of energy transfer. The final chapter of the introductory section (Chapter 7) contains explicit instructions on the intelligent use of the compilations of energy transfer parameters in Chapter 8. The compilations of energy transfer parameters refer almost exclusively to solutions in cyclohexane and in a few cases to ethanolic and benzene solutions. This may somewhat limit the value of the tables to biological scientists. However, the variety of aromatic ring systems, functional groups, combinations of functional groups, and isomers, represented in the donor and acceptor molecules listed, is extensive and thus a great deal of information not available elsewhere in a single source is contained in this work. The book will be a worthwhile addition to the libraries of spectroscopists and photochemists.

Stephen G. Schulman, *University of Florida*

**Theory of Electric Polarization.** By C. J. F. BÖTTCHER (University of Leiden). Completely revised by O. C. VAN BELLE, P. BORDEWIJK, and A. RIP (University of Leiden). Volume I: Dielectrics in Static Fields. Elsevier, New York, N. Y. 1973. xx + 377 pp. \$38.50.

The 1952 edition of this book by Professor Böttcher has now been extensively revised and expanded by his senior collaborators, thus resulting into the above Volume I and the projected Volume II. The present volume treats subjects such as: theory of dipoles and multipoles; concepts in electrostatics; problems of polarization, energy, and the reaction field; statistical-mechanical and the continuum approaches to the dielectric constant; and, finally, a treatment of nonlinear effects in dielectrics. Three extensive appendices describe some of the mathematical skills (vector and tensor calculus; solution of Laplace's and Poisson's equations; some properties of the Legendre polynomials) needed to understand completely the textual material.

As the name clearly indicates, the book deals mainly with the theoretical aspects. The book is tightly written with a heavy emphasis on the mathematical formulation of arguments, with relatively little effort at developing the intuitive appreciation of the various concepts presented. This is one of the classic texts in the field of dielectrics and is clearly useful in all graduate courses involving significant discussions of the theory of dielectrics. The book should also be of interest to chemical physicists in areas (such as double-layer theory, colloid and surface science, ionic and non-ionic solutions, molecular spectroscopy, etc.) in which an understanding of the dielectric properties of molecules or molecular clusters is essential. It should perhaps be added that topics such as dynamic behavior of dielectrics, determination of permanent dipole and multipole moments, and the polarization of solids, etc., would be discussed in the projected Volume II.

Ashok K. Vliji, *Hydro-Quebec Institute of Research*