

BOOK REVIEWS

Orbitals in Atoms and Molecules. By CHR. KLIXBÜLL JØRGENSEN, Cyanamid European Research Institute, Cologny, Geneva, Switzerland. Academic Press, Inc., (London) Ltd., Berkeley Square House, Berkeley Square, London, W.1, England. 1962. v + 162 pp. 15.5 × 23.5 cm. Price, \$6.00.

This book is an interesting blend of a number of apparently unrelated topics, which are, to some extent, brought together under the unifying considerations of the orbital approach. In many of its topics, the book represents an authoritative, elegant and concise exposition of an interesting area. In other places, it presents new, or at least rarely represented viewpoints, as for instance in the hierarchy of symmetry groups given in Fig. 4.1. In other places, it presents less well-founded opinions and prejudices of the author. Thus, the treatment of equivalent orbitals leaves much to be desired.

The vigorous and extensive use of group theory is very welcome; it loses much of its appeal, however, since not only a rather thorough knowledge of this subject is presupposed, but the standard European notation is used throughout without any connection being made to the notation in common usage in this country. In addition, the use of the written out "even" and "odd" instead of the more convenient subscripts g and u makes the reading awkward. In a similar line, the juxtaposition and connection between Slater-Condon and Racah notation is welcome.

The book is organized in 12 chapters. The first four chapters deal with atoms; the entire treatment reflects clearly the research interests of the author, since the centrosymmetric problem is discussed always in such a manner that subsequent reduction of symmetry to octahedral, tetragonal, etc., is facilitated. Subsequent chapters deal with more chemical problems, such as "systems with large internuclear distances," equivalent orbitals and electronegativity. A chapter on absorption spectra treats a large number of typical individual cases. In a chapter on electrodynamic (relativistic) effects, all matters connected with the non-electrostatic terms of the Hamiltonian operator are lumped together, but amazingly little is said about spin-orbit coupling. Chapters on "energy levels in crystals," the lanthanides, and a very brief one on X-ray spectra complete the work.

The book, in spite of its shortcomings, should prove useful to the critical reader reasonably familiar with both ligand field theory and mathematics, particularly group theory. To the general reader, however, the book will provide greater hurdles than he is likely to be able to overcome, and will risk perpetuating certain misconceptions.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CINCINNATI
CINCINNATI 21, OHIO

H. H. JAFFE

Hyperconjugation. By MICHAEL J. S. DEWAR, F.R.S., University of Chicago. The Ronald Press Company, 15 East 26th Street, New York 10, N.Y. 1962. vi + 184 pp. 14 × 21 cm. Price, \$6.00

The concept of hyperconjugation, introduced into chemical theory about 30 years ago, has always been somewhat controversial, and Professor Dewar has now examined it critically in another timely volume of the "Modern Concepts in Chemistry" series. The issue is whether or not hyperconjugation is a useful and unifying concept, which has validity within the framework of structural organic chemistry and contemporary quantum-mechanical theories. Some believe it does; others deny it. Those who attended the Conference on Hyperconjugation at Indiana University in 1958 will remember that Professor Dewar was not among the former. It is stated on the dust jacket that the material is treated in a "moderately impartial" manner. This is true in that the author discusses at considerable length most of the evidence that is commonly being adduced in support of hyperconjugation, but then he goes on to make use of his right to give this evidence his own interpretation.

He first discusses the theoretical basis of hyperconjugation in terms of MO theory. This is followed by three chapters on physical properties. The chapter on bond lengths, perhaps the best in the book, develops the main argument, which is based on two important published papers of Dewar. It is part of the current controversy over the natural length of single bonds formed by carbon in different states of hybridization, such as the sp^2-sp^2 single bond in butadiene or the sp^2-sp^2 single bond in propene. There is general agreement that part of the shortening in these bonds must be due to changes in hybridization of carbon. The

question is "how much"? Many believe that part of it is due to conjugation or hyperconjugation, but Dewar carefully develops his thesis that all of it is due to changes in hybridization. Once this is done, there is, of course, "no discrepancy left to be explained away in terms of resonance." A similar argument is developed for the heats of formation, and, less quantitatively, for dipole moments, and Dewar's view is that classical molecules, such as butadiene or propene (but not non-classical ones like benzene or the allyl radical), are perfectly well explained in terms of localized bonds. He finds evidence for conjugation and hyperconjugation in n.q.r., n.m.r. and, particularly, e.s.r. spectra but finds it difficult to relate the effect of resonance on these spectra to resonance interactions of chemical significance (such as bond length, etc.). He also argues that properties which depend on individual electrons (light absorption, ionization potentials), rather than on all the electrons taken collectively, cannot be discussed in terms of localized bonds at all, and that such evidence has no bearing on the problem of resonance in the chemical sense.

This leaves only evidence derived from chemical reactivity, an area in which, many believe, hyperconjugation is a more important energy factor than in ground states of molecules. This is developed in the last chapter, which comprises about 40% of the book. Some of the arguments that are used here have been in the literature for some time as alternate explanations to hyperconjugation. Perhaps the two most relevant observations that require explanation are the Baker-Nathan order and the secondary isotope effects. The former is explained by the solvation hypothesis, and non-bonded repulsions are offered as one alternative for the latter. The chapter contains a fine quantitative analysis of substituent effects, including Dewar's recent treatment of sigma constants. Here, it turns out, hyperconjugation may be an important factor, but the conclusions, as in other cases, are not considered definite.

Hyperconjugation is a controversial subject, and the book is a controversial book. Even those who do not agree with the author's arguments—and many surely will not—will probably agree that this is a very stimulating and interesting book, which is a pleasure to read. It is extremely well written and in the lively style which one has come to associate with its author. The arguments are put forth clearly and developed neatly. No one who is interested in hyperconjugation, or for that matter in current organic-chemical theories, can afford to miss it.

DEPARTMENT OF CHEMISTRY
BRYN MAWR COLLEGE
BRYN MAWR, PENNSYLVANIA

ERNST BERLINER

Hydrogen Compounds of the Group IV Elements. By F. G. A. STONE, Department of Chemistry, Harvard University. Prentice-Hall, Inc., Englewood Cliffs, New Jersey. 1962. 112 pp. 16 × 23.5 cm. Price, \$3.95 (Text), \$5.25 (Trade).

Dr. Stone suggests that there are areas of inorganic chemistry which, in view of great advances in recent years, deserve more attention from the reviewers than they have received; such an area of neglect is the chemistry of the hydrogen compounds of the Group IV elements. The emphasis in this short volume is upon recent developments; although not intended to be comprehensive, the work includes references needed for a detailed knowledge of the field.

The first chapter contains a brief review of the bonding of the Group IV elements. Chapter two concerns the silicon and organosilicon hydrides; 51 of the 87 pages of actual text material are devoted to this subject. The discussion of transition states involving sp^d hybrid orbitals and the coverage of compounds possessing silicon-nitrogen $d\pi-p\pi$ bonding are especially recommended.

The remaining three chapters review the hydrides of germanium, tin and lead. As one progresses down Group IV the element-hydrogen bonds become less stable and the volume of reported research noticeably declines. Indeed, the brevity of these three chapters may stimulate research in these areas by making obvious those topics about which more knowledge is needed.

In any field where research is increasing so rapidly it is impossible for a review to be completely up-to-date; Dr. Stone has done an admirable job of including many important recent references. One error has been incorporated by the addition of a late reference. On page 6, a recently reported compound, $(CH_3)_2Si:CHSi(CH_3)_3$, is discussed in some detail; it seems likely that the compound obtained does not contain a silicon-carbon double bond but is the previously reported 1,1,3,3-tetramethyl-1,3-disilacyclobutane.

The length and nature of this book are such that one may ask why it was not published in a review journal. There is an encouraging trend to make available advanced topics in inexpensive paperback form. It is hoped that topics of this nature might be made available at an even lower price than that listed for this volume.

This book is well written and brings together a large amount of interesting information concerning the Group IV hydrides and their derivatives. It is recommended to anyone wishing to expand their knowledge of this increasingly important field.

DEPARTMENT OF CHEMISTRY
OHIO UNIVERSITY
ATHENS, OHIO

ROBERT K. INGHAM

The Mössbauer Effect. A Review—With a Collection of Reprints. By HANS FRAUENFELDER, University of Illinois. W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1962. xiv + 336 pp. 15.5 × 23 cm. Price, \$3.95.

In 1958, Mössbauer published several papers on the resonant fluorescent scattering of nuclear gamma rays, papers in which his discovery of recoilless emission and absorption was described, together with a correct theoretical explanation of the phenomenon, now known as the Mössbauer effect. For more than a year the importance of his work remained virtually unrecognized; then suddenly workers in many laboratories began intensive studies using the effect as a tool for the exploration of various fields of modern physics such as relativity and the solid state. Many theoretical calculations were also made. In other words, after a slow start the subject developed with the speed typical of important modern physical discoveries. For his discovery Rudolph Mössbauer received the 1961 Nobel Prize in physics.

Professor Frauenfelder's book is clearly divided into two parts. The first is an account of the history and the concepts of the subject; the second, comprising two thirds of the volume, is a set of reprints. The first section is written in a clear and interesting style. The reader needs a modest acquaintance with quantum mechanics. At one point it is stated that "In nearly every theory there exist steps that are omitted in theoretical papers and not treated in the textbooks. These steps are obviously designed to keep the experimental physicists in their place." In the present case the first section supplies most of those steps. A ten-page bibliography concludes the first section.

The reprint section contains a wide variety of papers beside the classic three by Mössbauer, including one by Lamb (1939) entitled, "Capture of Neutrons by Atoms in a Crystal," giving the theory later modified by Mössbauer to explain his effect, and one by Dicke (1952) on the possible reduction of the Doppler broadening of lines through the effect of collisions. Also included are the well known paper by Pound and Rebka entitled, "Apparent Weight of Photons," and a number of others describing applications in solid state physics, especially ones trading on the uses of the nuclear Zeeman effect. Both experimental and theoretical subjects are included. For some of the theory the reader will need a good grasp of quantum mechanics.

DEPARTMENT OF PHYSICS AND ASTRONOMY
UNIVERSITY OF ROCHESTER
ROCHESTER 20, NEW YORK

H. W. FULBRIGHT

Comprehensive Biochemistry. Volume 2. Organic and Physical Chemistry. Edited by MARCEL FLORKIN, Professor of Biochemistry, University of Liège (Belgium), and ELMER H. STORZ, Professor of Biochemistry, University of Rochester, School of Medicine and Dentistry, Rochester, N. Y. (U.S.A.). American Elsevier Publishing Company, Inc., 52 Vanderbilt Avenue, New York 17, N. Y. 1962. xii + 328 pp. 16 × 23 cm. Price, \$14.50.

It is now a commonplace observation that, after the extensive progress in the elucidation of metabolic pathways of the last few decades, biochemistry is now advancing in two somewhat divergent directions—toward a more detailed understanding of problems which were previously in the realm of biology, and toward an elementary understanding of the detailed chemical processes involved in biological catalysis and synthesis. The growing interest in the second of these directions is reflected in the recent publication of no less than four books concerned with the application of the mechanistic approach of the physical-organic chemist to enzymic reactions. Some two-thirds of the volume under consideration here represents such an undertaking by two eminently qualified chemists, Myron Bender and Ronald Breslow, who have themselves contributed a good deal of the significant work in this field. The greater part of the text is concerned with a description of the mechanisms of chemical reactions which have a relevance to enzymic reactions, with emphasis on the rates and mechanisms of catalysis of such reactions. Although there is relatively little discussion of enzymic

reactions, the importance of these mechanisms to any consideration of enzymic mechanisms is obvious in many instances even when analogies are not given. It is inevitable that in such a rapidly advancing field there should be some disagreement about the interpretation of certain areas (for example, this reviewer would favor a different interpretation of much of the data on the mechanism of phosphate reactions), but the treatment is generally authoritative and always stimulating. The marked resemblance of much of the material on the mechanism of acyl transfer reactions to Bender's recent review on this subject (*Chem. Rev.*, 60, 53 (1960)) can doubtless be justified by the theorem that if something has been said once in the best possible manner then, if it is restated, it should be said the same way. Certainly, this chapter will be required reading for biochemists who wish to conclude their papers on enzymes with proposals for mechanisms of enzyme action.

The latter third of the book contains two chapters by W. D. Stein on the related topics of "Behavior of Molecules in Solution" and "Diffusion and Osmosis." The reader's reaction to these chapters will depend on his attitude toward the subject. Physical chemists will undoubtedly object to the rather elementary approach to these very difficult topics and to the inaccuracies of the treatment (for example, the signs are incorrect in the various expressions of the Debye-Hückel relationship). On the other hand, it is a fact that many biochemists have only a very limited acquaintance with this important subject, although most have been exposed to the relevant equations, and have difficulty obtaining a non-specialist's knowledge of the field from the available advanced treatments. Stein's discussion has the great virtue of providing an intelligible, non-mathematical exposition of the present state of knowledge in this area and non-specialists should find it a very useful introduction.

This reviewer would like to believe that this volume, along with the three other related recent publications, will mark the beginning of a period of rapid advance in the understanding of the mechanisms of enzyme-catalyzed reactions, as did Hammett's classic work for the mechanisms of organic reactions. It will certainly be an important addition to the libraries of biochemists and of those biochemistry students who can afford it.

DEPARTMENT OF BIOCHEMISTRY
BRANDEIS UNIVERSITY
WALTHAM 54, MASSACHUSETTS

WILLIAM P. JENCKS

Mechanisms of Organic and Enzymic Reactions. By S. G. WALEY. Oxford University Press, 417 Fifth Avenue, New York 16, N. Y. 1962. xiii + 365 pp. 16 × 24 cm. Price, \$11.20.

Too often, mechanisms for enzymic reactions have been proposed by biochemists with little feeling for organic reactions, or by organic chemists with little feeling for the capabilities of enzymes. A critical synthesis of the findings of both fields therefore would be a most welcome contribution. Unfortunately, the present volume does not go very far toward filling this need, though it does have merits in other ways.

The book follows a conventional order for reaction mechanisms texts, starting with chapters on molecular structure and the fundamentals of mechanisms and kinetics. These are followed by treatment of the various reaction types: substitution, addition, elimination, carbonyl additions, reactions of acids and acid derivatives, rearrangements and aromatic substitution. The book concludes with a chapter on polymerization. At the end of each chapter is a discussion of enzymic reactions analogous to the organic reactions treated earlier.

The general level of sophistication of the book is comparable to that of Alexander's "Ionic Organic Reactions." It is clearly written, and will be useful to undergraduate and beginning graduate students seeking a first acquaintance with organic and enzymic mechanisms. The more advanced biochemist or organic chemist is likely to find it too superficial to be of much help. Though there is occasional presentation of kinetic support for organic mechanisms, there is no quantitative discussion at all of enzyme kinetics. Space used merely in listing enzymic reactions whose mechanisms are uninvestigated (though possibly similar to other mechanisms treated in the same chapter) might better be devoted to more thorough discussion of those on which something illuminating can be said. Some topics of great interest are dismissed with bare mention. Enzymic polymerization, for example, receives a page and a half, and this is devoted only to polysaccharides.

To criticize a book for superficiality is perhaps not very fair if the author has obviously not even intended to produce a critical and comprehensive work. It is impossible to avoid the temptation, however, when the book he did not write would have been so much more useful than the one he did.

CHEMISTRY DEPARTMENT
UNIVERSITY OF ROCHESTER
ROCHESTER 20, NEW YORK

WILLIAM H. SAUNDERS, JR.