

BOOK REVIEWS

Orbitals in Atoms and Molecules. By CHR. KLIXBÜLL JØRGENSEN, Cyanamid European Research Institute, Coligny, 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.

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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.

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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.