

Book Reviews

Exposition of a Useful Chemical Theory

The Molecular Orbital Theory of Conjugated Systems. LIONEL SALEM. Benjamin, New York, 1966. 592 pp., illus. \$19.75.

The ideas and techniques of theoretical chemistry have been increasingly used, over the last decade, by physical and organic chemists, and, in particular, the application of molecular orbital methods to the understanding of experimental observations has advanced very rapidly. This is so, perhaps, because it is one of the most useful theories that has been introduced into chemistry, but the experimentalist often finds that dealing with its primary literature is difficult. There has been an outpouring of books in this period, but most have been either qualitative and introductory in nature or too advanced and rigorous. Salem has succeeded in producing a work that will be *used* by the practicing physical and organic chemist.

The Molecular Orbital Theory of Conjugated Systems is a well-written, comprehensive study of the structure and properties of molecules containing π -electrons. Under one cover Salem has discussed clearly a wide variety of topics, each in a reasonably uniform fashion. The chapters follow an admirable plan of beginning at an elementary level and progressing to advanced topics; he gives historical perspective when it is important to do so, and the theoretical development of each topic is usually elaborated concisely. The theoretical background given in the first two chapters, which deal broadly with Hückel and self-consistent field theories, along with the theoretical treatments given throughout the book, should be sufficient to enable the physical organic chemist to follow the later applications, with the exception of the chapters dealing with magnetic phenomena. The strength of the book lies in its timeliness, its up-to-date coverage, and the wealth of examples of applications of modern molecular orbital methods; one is grateful that the examples are worked out in detail. Most of the book is devoted to problems that are of current interest in chemistry, and most of the research cited is more recent

than 1957, much of it from the last five years.

The chapters following the first two deal in turn with properties of the ground state, magnetic properties of closed-shell systems, radicals and open-shell systems, molecular orbital theory of the transition state, electronic spectra, and distortions of conjugated systems. In each of these chapters, I found points of theoretical interest of the kind that are often difficult to uncover in primary sources or elsewhere, and this facet has led to many underscorings in my copy for future reference. Perhaps the greatest value of the book to the experimentalist will be in the several "how to calculate . . ." sections. These sections are followed by clear discussions of recent theoretical developments that for the most part are found only in the original literature.

The chapter on the properties of the ground state contains a detailed description of the Longuet-Higgins and Salem theory of bond alternation and a good qualitative account of the bonding in conjugated rings containing d -electrons. The chapter on magnetic properties of closed-shell systems gives clear, modern accounts of the London theory of aromatic diamagnetism and magnetic anisotropy due to ring currents. This is followed by sections dealing with the calculation of chemical shifts in aromatic structures, carbon-13 chemical shifts, and spin-spin coupling. The chapter on radicals and open-shell systems deals only briefly with the theory of electron-spin-resonance spectra, and most of the chapter is devoted to the calculation of spin densities, including the Pople-Nesbet theory of "different orbitals for different spins."

Chemical reactivity is treated in a straightforward manner, but few new ideas are found in this chapter, primarily because little progress has yet been made in this area. The chapter dealing with the theory of electronic absorption spectra is the longest in the book and one of the most thorough. Configuration interaction methods are clearly developed and applied in detail to benzene. This chapter also has a good

description of Simpson's theory of excitation delocalization, which unfortunately has often been neglected in other texts. The final chapter deals in a comprehensible way with molecular distortions and Jahn-Teller considerations, and the important recent work of Hobey and McLachlan, Liehr, Snyder, and others is described in a very readable manner. Cyclobutadiene and related molecules are discussed in terms of pseudo Jahn-Teller effects. The chapter ends with a lengthy section on bond alternation in the even polyenes, which contains a treatment original with Salem, who regards this phenomenon as a further example of pseudo Jahn-Teller effects.

By now, the reader will recognize that the reviewer welcomes this book to his collection. It has taken up where Streitwieser's *Molecular Orbital Theory for Organic Chemists* (Wiley, 1961) left off, and the two, in fact, make fine companion volumes. I expect that this one will be used to advantage as a text in chemical physics and advanced physical organic courses, but it should be of most value to the modern researcher who is interested in going beyond Hückel theory in understanding his problems.

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Myrmecology

An Introduction to the Behavior of Ants. JOHN H. SUDD. St. Martin's Press, New York, 1967. 208 pp., illus. Cloth, \$8.25; paper, \$3.95.

As a myrmecologist I am often asked to identify the best single general account of ants, and I always give the same rueful reply: the quality of books on ants published during the past several decades is uniformly very poor. D. W. Morley's *The Ant World*, published as a paperback by Penguin Books in 1953 and possibly one of the most widely read works on entomology in the English language, is also one of the most inaccurate and misleading. Two other popular books, Wilhelm Goetsch's *The Ants*, translated from the German by Ralph Manheim for the University of Michigan Press in 1957, and S. H. Skaife's *The Study of Ants* (Longmans, London, 1961), are somewhat more reliable, but nevertheless so provincial in view-