# Molecular Orbital Theory for Organic Chemists. By Andrew Streitwieser, Jr.

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The presence of the metal ion significantly reduced the rate of iodination in all cases (Table II). Moreover, these rates can be attributed almost entirely to the reaction of the uncomplexed ligand formed by the partial dissociation of the metal chelate. This indicates that one important way in which the metal ion affects the reactivity of a ligand is by reducing its effective concentration in solution. Our results show that the rate of iodination of the metal chelate itself (since it is present in much higher concentration than the free ligand) must be very much smaller than that of the free ligand. Hence the metal ion is seen to have a far greater effect on the rate of iodination of the ligand to which it is coördinated, because of its ability to affect the over-all electron distribution in the chelate molecule. Work is now in progress on the measurement of the reaction rates of the undissociated metal chelates.

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# Book Reviews

**Structural Principles in Inorganic Compounds.** By W. E. ADDISON. John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y., 1961. 183 pp. 21.5 × 14 cm. Price, $3.25.

In the preface to this excellent little volume, the author states that the book is based on a lecture course which he has given to first year classes at Nottingham University. The book could be understood and appreciated by the better freshmen students in an American university, but, in general, the subject matter is somewhat more advanced than that in most American courses in general chemistry. It might well be used as a supplement to a standard American text.

Although this book is based on a course of college lectures, it is not written in the form of a textbook, but rather as a general survey of structural principles. It will be useful to students, but even more so to practicing chemists who want to review the modern theories of inorganic chemistry. It is well organized and is written in a clear, interesting manner. Although paper-bound, it is well printed on good paper. The type is a little smaller than in most textbooks, so the book contains more material than the number of pages would lead one to expect.

After a brief review of atomic structure and the different types of chemical bonding, the author describes some of the commoner methods used in the determination of structure, and then discusses the structures of the elements, factors which influence the crystal structure of three dimensional lattices, and the structures of representative covalent compounds. The book closes with a very interesting chapter on the defect solid state. The principles involved and the application of modern theory are stressed throughout, as is the relationship between the structures of inorganic compounds and their properties.

This book is not intended to be an exhaustive or advanced treatise, but rather, a fairly elementary review of a most important subject. As such, it will be useful to a large number of chemists who have fallen behind on their study of basic principles.

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**Molecular Orbital Theory for Organic Chemists.** By ANDREW STREITWIESER, JR. John Wiley and Sons, Inc., 440 Park Avenue South, New York, N. Y., 1961. 460 pp. 6 × 9 cm. Price, $13.00.

It seems, at last, that organic chemistry, even the whole of chemistry, has entered that golden age when chemists in all fields can begin to make effective use of quantum mechanics. That molecular quantum mechanics has provided quantitative correlations between chemical phenomena and simple electronic models is well established. Most chemists also probably would agree that from these correlations there have come some useful insights into microscopic chemical phenomena, and some very challenging new chemistry. Moreover, most of the applications of quantum mechanics in chemistry have been based on methods which are fundamentally straightforward—the Hückel model for organic chemistry and ligand field theory in its varied forms for inorganic chemistry. The general use of Hückel theory is much older than the corresponding wide application of ligand field methods; yet its acceptance among organic chemists has required a very long time, in contrast to the fiery love affair between inorganic chemistry and ligand fields. Finally, the past dozen years have seen $\pi$-electron theory, once the exclusive plaything of physicists and physical chemists, used as a guide for essentially every field of organic chemistry. Hückel theory, with its many refinements, is without question the only approach which has yet come from quantum mechanics that has the simplicity, generality, and semiquantitative validity to become a standard computational tool of the laboratory organic chemist.

Professor Streitwieser has written a book to fulfil exactly this function—to give to the organic chemist the operating tools and a full scale of results, so that he can use the methods and have considerable feeling for the range of their validity. The need for such a book has been very great and has been increasing rapidly. The list of more than a thousand footnotes makes this obvious at once. Moreover, the recent "Quantum Chemistry" of Daudel, Lefebvre, and Moser has a very different function, of presenting the variety and basis of quantum methods for extensive calculations. "Molecular Orbital Theory for Organic Chemists" deals, in three parts, with the mechanics of simple calculations of complicated systems and then, in great detail, with how these have been applied to computation of physical properties of molecules and of the directions and rates of reactions. It is this reviewer's opinion that the book could have been given the alternative title of "Modern Organic Chemistry for Physical Chemists"; the impressive quantity of material covered in its second and third divisions is assembled in a coherent, reasonable way, with careful consideration of the validity of alternative sets of assumptions and occasional skepticism toward data which, in context, seems appropriate.

By and large, the book seems to achieve its objective. The large number of examples worked out must inevitably make the book a pedagogic success. The only section about which I have any misgivings is the discussion of group theory in sections 3.5 and 3.6. I suspected when I read these sections that the discussion might be too brief to give a novice much intuitive feeling for the concepts at the basis of the steps given in the remainder of Chapter 3. Judging from questions I've been asked, I tend to think my misgivings were justified. Such a small thing as the inclusion among the examples of a representation containing a repeated irreducible representation and a two-dimensional irreducible would have helped. Despite this shortcoming, the treatment of the *application* of group-theoretical methods is lucid, and could be handled easily by most first-year graduate students.

This reviewer is sorry that the treatment of $n \rightarrow \pi^*$ transitions is so brief, because of their importance in molecules of biological interest. To discuss these, however, the author would have had to go somewhat deeper into electronic structure theory; perhaps this was his justification for the very short coverage.

It is always possible to find some little points to criticize in a review, like the omission of favorite references of the reviewer. The work of D. Z. Robinson on the dipole moment of HCl as a function of hybridization, the correlation of bond lengths and hybridization carried out by Costain and Stoicheff, and the contribution of Moffitt to the polynuclear aromatic hydrocarbon problem all could have been cited to advantage in the text. Another peccadillo: I object to the use of the expression "non-crossing rule" in the context of aromatic substitutions (p. 347). This expression has a well defined meaning in the treatment of approximate and exact electronic states, but is really out of place in the discussion of early *vs.* late transition states in the substitution reactions of non-alternant hydrocarbons.

I noticed that one level is missing in Fig. 8.11 on p. 224, and to my glee, found a pentavalent carbon atom in the pyracyclene molecule on p. 291. Furthermore, I suspect the author of playing a private joke (and admire him for it) when he uses Fig. XXIII and XXIV on p. 448 to represent a charge transfer-complex and an ion pair, respectively.

This reviewer enjoyed reading the book and, in addition to learning a good bit of physical organic chemistry from it, expects it to be a valuable reference, for the wealth of data as well as the textual content and footnotes. A book like this, appearing when it does, already must give its author some feelings of uneasiness; for, certainly, it will stimulate enough work in a very short time to set the poor man to writing a new edition.

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**Kupfer, Teil B Lieferung 2, System Nummer 60, 8 Auflage, Gmelins Handbuch der Anorganischen Chemie.** [Copper, Part B Section 2, System Number 60, 8th Edition, Gmelins Handbook of Inorganic Chemistry.] Verlag Chemie, G.m.b.h., Weinheim/Bergstrasse, 1961. 352 pp. 17 × 24.5 cm. In German. Price, $58.00.

This volume is a continuation of the discussion of compounds of copper started in Teil B Lieferung 1. It follows the usual pattern established for the Gmelin series.

A short section discussing the copper–boron system is followed by one pertaining to the binary compounds with carbon. In line with the Gmelin practice, the next section presents the ternary and more complex compounds of carbon, major emphasis being given to the copper(II) carboxylates (about 200 pages). The last 100 pages contain the discussion of other binary and ternary compounds of copper and silicon, phosphorus, arsenic, antimony, and bismuth.

The available information, in some cases up to 1958, is presented in the lucid manner for which Gmelin is so famous. Both the physical and chemical data are described in detail and graphs and diagrams are liberally used throughout, resulting in increased effectiveness of this volume. Structural diagrams are included in many places.

One minor drawback, in this reviewer's opinion, is the absence of a special section on complex compounds of copper(II); these are discussed in the usual Gmelin manner when the compounds of particular coördinating agents are described.

A Table of Contents and marginal annotations in English are of great help.

This volume is a most welcome addition to the Gmelin series and adheres to the excellent standard set previously. It should be on the shelf of every chemistry library; it is highly recommended as the most valuable source book for an investigator interested in copper(II) compounds.

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October 1, 1962–December 1, 1962

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