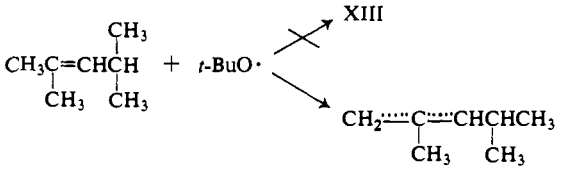
trum is comprised of two septets and is assigned to XIII.[4] This is not an allylic radical since models indicate that the four methyl groups will not allow coplanarity of the carbons.[5] The large CH coupling, indicating that the H is in the antinode of the p orbital, supports this conclusion. Since no rearrangement of the previously discussed radicals to allylic structures is observed even where there is the possibility of gaining resonance energy, it is inferred that abstraction from a ring CH_2 group has occurred.[6] Apparently four methyl groups activate the ring sufficiently to make this the preferred process, but abstraction from side chain CH_3 is becoming competitive at high temperatures.

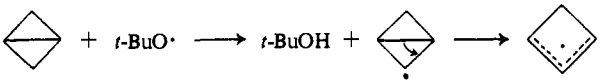
It is not, of course, possible to make unambiguous mechanistic deductions from esr structural data, but there is a rather obvious rationalization of the relationship between radicals VIII and IX. IX is the initial product of hydrogen abstraction, and it requires some activation energy to get to VIII. If the rate of isomerization is less than the reciprocal of the lifetime of the radical (as it could be at low temperatures), VIII will not be observed. The activation process could be associated with rotation about the $R_2\dot{C}$–cyclopropyl bond since a $\pi/2$ rotation will leave the p orbital containing the odd electron in position to interact with the ring antibonding orbital symmetric with respect to the plane of symmetry of the molecule.[7] Strong interaction with this orbital is to be anticipated since it is antibonding between the ring carbon centers adjacent to the substituent, and rearrangement to VIII seems to be a natural consequence.

(4) Attempts to prepare XIII from 2,4-dimethyl-2-pentene and *t*-butoxy radical led only to the isomeric *cis*- and *trans*-2,4-dimethyl-1-penten-2-yl radicals. Hydrogen abstraction from the methyl groups is, thus, preferred to the isopropyl hydrogen in this alkene. The unreactivity of the tertiary isopropyl hydrogen in this alkene is consistent with the nonstabilization of XIII.



(5) A similar nonbonded interaction of methyl groups has recently been discussed relative to rotational barriers in methylated allylic cations [G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, **90**, 6082 (1968)]. These increased steric effects can be reflected in decreased delocalization energy in the allylic radical as well as the cations [*cf.* P. Schleyer, *et al.*, *ibid.*, **88**, 2868 (1966)].

(6) Abstraction of a methylene hydrogen from a cyclopropane ring by *t*-butoxy radical has also been observed in bicyclobutane. The bicyclobutyl radical so formed undergoes spontaneous ring opening to cyclobutenyl radical. The latter process can be retarded only at very low temperatures (to be published).



(7) For discussions related to bonding in these compounds see J. P. Pete, *Bull. Soc. Chim. France*, 357 (1967); C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **90**, 4311 (1968).

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Book Reviews

The Computer and Chemistry. An Introduction to Programming and Numerical Methods. By T. R. Dickson, Orange Coast College. W. H. Freeman and Co., 660 Market St., San Francisco, Calif. 1968. viii + 216 pp. 6 × 24 cm. $5.75.

Though timely in purpose, this book is somewhat less than successful in execution. The treatise promised by the author's ambitious title ("The Computer and Chemistry") is not to be found. Rather, the reader is offered a less than satisfying primer on the Fortran language and a glib discussion of fundamental numerical methods.

Study panels within both the National Academy of Sciences and the National Science Foundation recently recommended the teaching of numerical methods and computer programming during the early stages of undergraduate education. It is viewed that such early training will extend the range of problems with which a developing scientist can deal, will help to acquaint him with an evolving computer environment which is playing a more and more significant role in research, and should serve to encourage more imaginative utilization of computers later in the student's career. In coupling a discussion of the rules of Fortran programming with an introduction to numerical methods, Dickson's book is indeed timely. That it is incomplete may be more a reflection of publishing priorities than the author's judgment. Whatever the case, the book is not strongly recommended. It is intended primarily for second year undergraduate students, according to the author; and despite suggestions to the contrary, researchers are not likely to find the volume valuable for reference. The book relates to chemistry in the choice of problems and applications with which the subject is illustrated.

The book is divided into three sections. The first section is devoted to the Fortran languages (II and IV); the second part, roughly half the volume, treats numerical methods and computer applications; and the last section is composed of four appendices, only one of which is generally useful.

The aware reader may become disappointed early in the text as the author uses an introductory chapter to give the impression that the computer is little more than a replacement for the desk calculator. This is untrue, as many of us appreciate and perhaps more of us should. The computer is an immensely powerful tool with an unbounded range of application. The student should come to appreciate this and make use of it early in his career, for there is little doubt but that the computer is destined to have far-reaching effects upon our execution of science. Dickson offers no assistance toward this end; rather his text reflects a peculiarly narrow outlook.

Although the writing is generally lucid, all too often the author rejects explicit discussion and illustrations, choosing instead to demonstrate concluding variations implicitly, by example. As this produces apparent contradictions, it results in a clumsy presentation

which is likely to be confusing to the novice. The most serious drawbacks in this first part of the book are (1) the author's predisposition to omit elements of Fortran without disclosing these omissions, and (2) his insistence on setting down what appear to be arbitrary rules, some of which are simply incorrect, reflecting his own coding style. The latter would not be so dissatisfying would the author admit the origin of such rules.

The author's discussion of formating is poor. There is little mention of the nAw format and nothing about right adjusting integer data within oversized I fields. The discussion of Fortran IV carriage control is both misleading and incomplete, and use of the comma is not well defined. Further, the complications introduced by variable word length (bytes) on the IBM 360 machines is not at all discussed. There are other problems besides. The author does not tell us that variable subscripts must be positive integers, and there is no mention of standard integer mode library subroutines or built-in functions. The author devotes a sizable section of text to the reading and writing of BCD output tapes but omits all discussion of binary tapes. We read essentially nothing about disc files even though their use is currently quite common. Certain input–output control instructions make no appearance in the text, and COMMON and EQUIVALENCE specifications are mentioned without elaboration. Why the text is so incomplete is not clear. An additional 30 to 40 pages of Fortran syntax would certainly not be out of place. In the very least, the author should have provided an inclusive list of Fortran instructions and specifications, perhaps within an appendix.

What there is of the book has been carefully assembled; a reasonably careful reading turned up only a few obvious errors. These occur on page 26, where a variable is omitted from the statement EKIN = .5*XM**2; page 48, where a continuation number appears in column 5; and page 75, where there is a Hollerith miscount. In addition, on page 29, some confusion arises concerning use of the logical operator OR. On the other hand, the author is especially lucid in describing the arithmetic statement function and in his introduction to variable formats.

Section II begins with simple iterative methods for determining the roots of equations. It continues with illustrations of methods of numerical integration: Trapazoidal Rule, Simpson's Rule, and the Monte Carlo method—the brief discussion of which is very clear. The author then discusses matrix manipulations and the solution of simultaneous equations. He reviews Gauss–Jordan Elimination, matrix inversion, Cramer's Rule, the solution of simultaneous equations by iteration, and the so-called Gauss–Seidel iteration for solving systems of linear equations. For each case he provides little more than formulas. Indeed, he requires only 12 pages to introduce matrix mechanics and to treat the various methods for solving simultaneous equations. The discussion of curve fitting is essentially limited to straight-line correlations, although some general formulas for polynomial fits are also presented.

Chapter 11 (the next to the last) seems inappropriate for a book directed at the second year undergraduate. In 12 pages here Dickson attempts to describe the eigenvalue problem, the secular equation, and simple molecular orbital calculations. This all too brief exposure to a subtle subject might be more harmful than good. To compound matters, the author provides a black box program providing the student with the means to carry out "molecular orbital calculations" for π systems. This fails to square with the fact that only a few chapters earlier the author eases students into the definition of a definite integral, and in Chapter 10, the use of rudimentary differential calculus is carefully avoided.

All examples of Fortran programs in the text are set in type as are ail examples of computer output. I view this as a mistake. It destroys all column registry, it removes a significant factor of authenticity, and it destroys a valuable check on the accuracy of the coding. All illustrative programs should have been keypunched, listed, and photographed. Similarly, examples of computer output should have been just that. Authentic input/output is particularly valuable for teaching purposes. As far as student problems and applications are concerned, numerous are offered, the most interesting of which deal with calculation of the concentrations of ionic species in solutions of weak polyprotic acids. An acceptable index is provided and some useful references are listed in the bibliographies included.

In summary, this is a weak effort. It is suggested only for the student who is willing to fortify himself with a more thorough treatment of mathematical methods and a more complete discussion of the rules of Fortran programming. As the latter are available in splendid variety, this reviewer doubts that the present volume adds very much to or improves very much upon what has already been published. While the book is readable and may appeal to certain weaknesses of the student, I should think it will not be very useful as a pedagogical tool.

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Molecular Complexes. By J. ROSE, M.Sc., Ph.D., F.R.I.C., F.I.L., M.B.I.M., Principal, College of Technology and Design, Blackburn. Pergamon Press Inc., 44–01 21st St., Long Island City, N. Y. 1967. x + 177 pp. 14.5 × 22 cm. $8.00.

There are few books devoted to the subject of molecular complexes. The one by Briegleb, "Elektronen-Donator-Acceptor-Komplexe," 1961, gives a thorough account of the literature on charge-transfer complexes to 1960. The book by Andrews and Keefer, "Molecular Complexes in Organic Chemistry," 1964, is oriented toward a special field.

The present book is not in a class with either of these. It is stated in the Preface that "the work is concerned with a survey of the field of molecular complexes covering a period of about 70 years up to 1966." Probably, then, the book was intended for the person who knows little about molecular complexes and wants to gain some insight into the broad scope of the subject. But covering such areas as (a) charge-transfer complexation, (b) interaction of Lewis acids (group III elements) with Lewis bases (group V and VI elements), and (c) some hydrogen bonding would be a monumental task to do rigorously, so that a survey in a short text is bound to be achieved at the expense of completeness and critical evaluation.

The first chapter defines the class of compounds considered in the text and gives an extremely brief historical account of the field along with a number of general references. The second chapter introduces the Mulliken charge-transfer theory and discusses the energetics of bond formation. The third chapter is the most informative and the largest of all, constituting one-third of the book. Here, methods for studying the complexes, their composition, and stabilities are discussed. In the fourth chapter, there is an account of the properties of molecular complexes, mostly spectral, with mention of magnetic properties, dipole moments, and geometries of a limited number of charge-transfer complexes. The fifth chapter discusses the effects on complex formation of some structural features and substitutions in donors and acceptors. Chapter Six is concerned with the interactions of Lewis acids containing elements in group III with Lewis bases containing elements in groups V and VI. Chapter Seven, the last one, is quite short and gives a few examples where the theory and properties of molecular complexes have been applied.

Most of the material has been compiled from the literature covering the period 1945–1963, and very little beyond that. Therefore, the book does not give an up-to-date account of the subject. Also, pertinent references prior to 1963 have been overlooked which would have modified the discussion in some sections, *e.g.*, the relative strengths of donors and acceptors. In some cases topics are mentioned so briefly that they would not be meaningful except to the person already acquainted with the subject, *e.g.*, p 165, "Molecular orbital calculations lead to factors known as Z-values, which are indices of chemical reactivities"; p 166, in a discussion of carcinogeneity, "This hypothesis has been attacked by the Pullmans, who advocate instead a theory based on the reactivities of the K and L regions in aromatic hydrocarbons." (It is amusing to have a famous husband–wife scientific team referred to as the Pullman brothers.)

In summary, this book is not for the person active in the field. It might be of use to the novice, if the limitations of a survey of a vast subject are kept in mind.

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