

tures given by the author to doctoral students in physical chemistry at the University of Paris. Of its nine chapters, two are devoted to the basic classical and quantum mechanical theory of molecular vibrations, five to symmetry and group theory, one to perturbation treatment of anharmonic vibrations, and one of thirty pages to the theory of infrared absorption spectra. The only molecule considered in this last chapter is carbon dioxide. The treatment is clear throughout but is all familiar to students of "Molecular Vibrations" by Wilson, Decius and Cross (1955).

The last sentence in the book ends with a semicolon. Perhaps this is the author's way of indicating more to follow. In the preface, it is stated that "the second part of this work will discuss the calculation of vibrational frequencies by Wilson's method, the calculation of vibrational frequencies of functional groups, the determination of transitions that are made possible by electrical anharmonicity, and an important chapter on chemical spectroscopy illustrating the possibilities of applying infrared to qualitative and quantitative chemical analysis." It is to be hoped that Part II will discuss the spectra of other molecules in addition to carbon dioxide and that the chapter on chemical applications will justify to the student the mathematical treatment of vibrations by showing him its power and utility in the understanding of infrared spectra.

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Ultra-violet and Visible Spectroscopy. Chemical Applications. By C. N. R. RAO, Ph.D., D. Sc., A.R.I.C., Indian Institute of Science, Bangalore, India, formerly of Purdue University, Lafayette, Indiana, U.S.A. Butterworth Inc., 7235 Wisconsin Avenue, Washington 14, D. C. 1961. xiii + 164 pp. 15.5 × 25 cm. Price, \$5.25.

The years 1949-1950 marked the turning point in our understanding of the electronic spectra of organic molecules. This was when H. Kuhn showed the central role of alternating bonds in conjugated-chain spectra; when Kasha gave the $n-\pi$ -explanation of Burawoy's regularities; when McClure proved the identification of triplets by spin-orbit perturbations; when Clar's regularities in condensed-ring spectra and Stern and Wenderlein's regularities in porphyrin spectra were rationalized; when the Benesi-Hildebrand molecular-complex spectra were published, with Mulliken's charge-transfer interpretation; and when, on the theoretical side, the free-electron and perimeter approximations were developed, and the numerical applicability of the molecular orbital theory to spectral energies, to aza-perturbations and to the general double-bond twisting problem became established.

These advances and their subsequent more quantitative developments all showed the power of a new approach—the "chemical perturbation" approach—which used chemical systematics phenomenologically both as the crucial test and as the prime objective of the proper quantum-mechanical classification of the observed spectra. This approach had been pioneered by Pauling in interpreting Zechmeister's *cis-trans*-polyene changes, by Sklar in explaining substituted-benzene spectra, and by Lewis and Kasha in their triplet interpretations, but it had been neglected for many years and is still not understood by many experimentalists and by many otherwise competent spectroscopic theorists.

The principal reason for this wide lack of understanding has been the lack of any systematic treatise in the last 12 years explaining these new developments and showing how they lead to numerical predictions of organic spectra and their solvent and substituent effects. Two or three such books are said to be in the offing, but in the meantime students are dependent on Brode's "Chemical Spectroscopy" of 20 years ago, or on books such as "Electronic Absorption Spectroscopy" by Gilliam and Stern (1958) or the present little book by Rao and several collaborators (1961), which are still in the early tradition of empirical and analytical emphasis.

For practical organic chemists and students who want such a guide, especially for the smaller chromophores, Rao's book is not a bad one. It has short chapters on the spectra of "simple" molecules, conjugated chains, aromatics,

heterocyclics, steric effects, vacuum ultraviolet spectra, fluorescence, and charge-transfer spectra, with several pages on proteins, ligand-field theory, rotatory dispersion and other subjects, and with a long chapter on "Applications" (though only 11 of its 98 references are later than 1955). It is up-to-date in many ways, notably in its numerous assignments of $n-\pi$ -spectra, and in its treatment of steric twisting effects. And the chapter on charge-transfer spectra, by a collaborating author, Dr. R. M. Mallya, is a good brief introduction to the Mulliken and Orgel theories of molecular complexes.

The most serious flaw in the book is its lack of breadth and balance. The discussion of fluorescence, by another collaborating author, Miss N. Rajalakshmi, is weak; and phosphorescence is essentially ignored. Needless to say, any author's selection of subject matter from the 5000 or so papers on organic spectra in the last 10 years, or from the 10,000 or so papers that must have been published since about 1930, is bound to be highly personal. But in a book with "Visible Spectroscopy" in the title, it is surprising to find 8 pages devoted to dienes and their homologs but only two pages to carotenoids and only one to the condensed-ring aromatics and one to porphyrins and chlorophyll. The Chicago school, I must admit, is treated very well, but the theoretical interpretations of the English Cambridge school are generally neglected as well as the important spectral studies of the Amsterdam group, the Stuttgart group and the Munich group. And out of 500 or so different references, I could find only 4 to Kasha, 3 to Sidman, 2 to Moffitt, 2 to Brooker, 1 to Förster, and none to Sponer. There is no reference to Förster's "Fluoreszenz Organischer Verbindungen" nor to Clar's "Aromatische Kohlenwasserstoffe." (And there are numerous misspellings of proper names.)

All in all, it is a limited little book. But it is readable by any chemistry student and, until some more comprehensive volume comes along describing the new systematic approaches, it may be the best book we have for introducing students to the empirical singlet absorption spectra of the smaller conjugated systems.

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Cahiers de Synthèse Organique. Méthodes et Tableaux d'Application. Volume IX. Cyclisations. By JEAN MATHIEU, ANDRÉ ALLAIS and JACQUES VALLS. Published under the direction of Léon Velluz. Masson et Cie., 120, Boulevard Saint-Germain, Paris 6, France. 1962. 325 pp. 15.5 × 22.5 cm. Price, broché, 90 NF.; cartonné toile, 100 NF.

The increasing importance of heterocyclic compounds in all fields of organic chemistry, particularly those of pharmaceuticals and natural products, has resulted in the production of a voluminous periodical literature on the subject. This has been accompanied by the publication of many books, dealing for the most part with individual ring systems, or with related series of such systems. One might consider the next logical step to be an attempt to systematize, to provide keys to make this mass of information more readily available. The book under review creditably endeavors to provide such systematization in the field of monomolecular heterocyclization.

This ninth in the series of "Cahiers de Synthèse Organique" is the third volume to treat cyclization, Volumes VII and VIII having dealt with carbocyclization of the monomolecular and polymolecular types, respectively. Structurally it is divided into three parts, Texte, Tableaux, and Table des Cycles.

The Texte is in discursive form with a progressive marginal ring index. The structures are codified in terms of substituents split out during cyclization. Syntheses representative of each type structure are described. Reactions and yields are given, with literature references conveniently placed at the bottom of the page.

The Tableaux are indexed by the rings formed in cyclization, progressing from tetraphenylepoxyethane to the complex nine-membered ring 1H-dibenzo[f,h][1,2,4,5]-tetrazonine. Starting materials, final products, condensing agents and solvents, yields and references are provided.

The final section, the Table des Cycles, is a general index by rings to all the *Cahier* series, principally volumes V through IX. It includes carbocyclic as well as heterocyclic compounds. For each ring, the code number of the reaction involved in its formation, the page of the Texte where it is discussed, and the page of the Tableaux where it is to be found, are given. This section would properly constitute the starting point of a search. Except for the Texte, only a minimal knowledge of French would be required for efficient use.

It is to be hoped that this volume will be followed by one on the larger field of polymolecular heterocyclization. Such a book, together with the present one, would constitute a substantial forward step toward the systematization of information on all heterocyclic chemistry.

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Les Triterpenes Tetracycliques. By GUY OURISSON, Professeur a la Faculte des Sciences de Strasbourg, and PIERRE CRABBE, Professeur a l'Institut Meurice-Chimie de Bruxelles. Hermann et Cie., 115, Boulevard Saint-Germain, Paris VI, France. 1961. 194 pp. 17.5 × 24 cm. Price, 30 NF.

This survey of the chemistry of "Tetracyclic Triterpenes" is the first rather complete review on the subject to include the important advances which have been made since 1955.

After an introduction to the general subject, the book gives a description of the methods used for the elucidation of structures. This description is based on the chemistry of various functional groups as they are affected by the environment found in each ring and is probably more valuable than a description of the elucidation of the structures and of the chemical properties of individual tetracyclic triterpenes taken one at a time. Synthetic work in the field is briefly mentioned as well as various biochemical aspects (biogenesis and biological properties) of the tetracyclic triterpenes.

A major contribution of this monograph consists in the tables at the end of the book which report formulas, physical properties and pertinent references for every known triterpene at the time of publication. In a further table, the data on infrared, ultraviolet and rotatory dispersion for each type of function are summarized. These tables alone should make this volume useful in any laboratory interested in the study of natural products.

Although the foreword was written on May 2, 1961, it is obvious, as shown by the list of addenda at the end of the book as well as on the basis of various omissions, that the printing of the book took a rather long time (there is, for instance, no full description of the chemistry of limonin, nomilin and obacunone, no mention of the interesting n.m.r. study of the cucurbitacins made by Noller, *et al.*, etc.). One can also regret a number of printing errors (see pp. 12, 33, 35, 79, 99, 110) and some confusion in the author index (R. N. Jones has been confused with E. R. H. Jones, for instance). Along the same lines the work of Djerassi on the bromination of 4,4-dimethyl 3-ketones (p. 28), is not mentioned while on page 166 the formula gives the wrong absolute configuration for mevalonolactone.

In spite of these criticisms, the book is a very interesting effort at bringing some order into a very difficult field and should be valuable to chemists interested in the natural products.

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Crystallization. Theory and Practice. By ANDREW VAN HOOK, Professor of Chemistry, College of the Holy Cross, Worcester, Massachusetts. Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y. 1961. ix + 325 pp. 16 × 23 cm. Price, \$12.50.

The aim of the American Chemical Society Monographs, of which this book is No. 152, is to make available thorough treatments of selected areas of research for the use of

workers in more or less unrelated fields to assist them in correlating their own work with a larger field of science; also, to stimulate research in the specific field being discussed. To achieve this aim an extensive bibliography is required as a basis for the monograph.

It is fair to say at once that the author has succeeded in realizing the objectives most satisfactorily. The presentation of the material has been organized well. There are but six chapters, each with its own references, plus an appendix in which are listed general references to books, reviews and symposia. The first chapter is intended as a historical review of observations and largely qualitative concepts which have been especially important in the development of the field; Ostwald's influence figures prominently, but recent work is mentioned also and the effect is to provide some orientation in a field whose many different aspects make it very complex. The second chapter, on the basic principles expected to be useful in subsequent discussions, mentions the phase rule, crystallographic principles and X-ray crystallography in such a condensed manner (about four pages each) as to be of limited utility, but then goes on to discuss qualitatively the concepts which have been applied to the growth of external form and habit modification and to outline the development of the Kelvin equation. The chapter concludes with a section on entropy and tables are provided to show the entropy change of various transitions of many different substances; in effect, this chapter is also a survey but of a narrower part of the field.

The third chapter presents, in considerable detail, theories which deal with nucleation-growth phenomena; this is done in two major sections and in each, selected experimental results are given. The first section includes the theories developed for three-dimensional nucleation in liquid-vapor systems and those applying to condensed systems (melts, solutions and solids); two-dimensional nuclei and Frank's screw dislocation theory are also discussed here. The second section of the chapter gives some details of the diffusion and of the adsorption theories of growth.

The fourth chapter contains little theory and serves chiefly to describe methods which have been used to observe the onset of nucleation and the rate of crystallization and to tabulate representative data on nucleation and growth; the collection of references is intended to be sufficiently complete to expedite literature searches for information on specific substances.

The fifth and sixth chapters are devoted to the practical matters of the laboratory preparation of crystals and plant crystallization problems. Crystallization as a unit operation is described rather fully to the point of listing manufacturers of various types of crystallizers and of indicating how a selection might be made. In these two chapters, the author's experience in the sugar industry is the basis for much of the information but, in addition, there is some discussion of heavy chemicals and fertilizers, of single crystals of synthetic gems and of glass and ceramics, the last provided by the Corning Glass Works.

Inevitably, a comparison will be made between this book and the admirable work on crystal growth by H. E. Buckley which appeared in 1951, but actually they are not comparable in detail. Professor Van Hook had first planned a review of the entire subject, but Buckley's book and one by G. Matz in 1954 led him to emphasize more recent theories and crystallization processes. To the extent that there is an overlap in subject matter, the aim has been to make the present book complementary to the others by giving details of matters which appeared in a more condensed form previously and to be brief where former reviews had been fully developed. In addition, the references have been carried through 1959 certainly and apparently through a part of 1960; about 1400 references are given and a casual examination indicates relatively little duplication among chapters. One of the most useful features of the treatment may be the extensive bibliography.

Some regrettable features of the book must be reported. The figures are usually adequate but are rarely excellent and some are crude; there is little uniformity among them. The photographs are good but curiously chosen; for example, it is puzzling that solar salt evaporation should be shown or that bucolic scenes of an old batch sugar process on the island of Mauritius should be included. The number of mistakes in the text is deplorable; without making a line by line search, something like thirty errors were noted in two chapters, including a mis-spelling of Ostwald's name in