

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 Gillam 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.