factor as 0.05, the figure which applies in acetolysis, leads to a K_e value of *ca.* 5×10^{-11}. The standard molar free energy of the [3.2.0] ester I exceeds that of the [2.2.1] isomer III by *ca.* 14,000 cal./mole.

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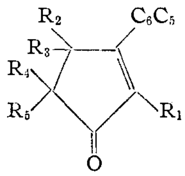
RECEIVED SEPTEMBER 25, 1958

THE ANOMALOUS INFRARED SPECTRA OF SOME CYCLOPENTENONES

Sir:

It has been reported[1] recently that the infrared spectrum of 3,4-diphenyl-2-cyclopenten-1-one (I) in carbon tetrachloride solution is anomalous in that two bands of comparable intensity occur in the carbonyl-stretching region at 5.82 and 5.90 μ; this bifurcation was observed also with solutions in other solvents and with solid state spectra. The spectrum of 2,5-dimethyl-3,4-diphenyl-2-cyclopenten-1-one (II) showed a single band (5.86 μ, CCl_4), as did that of *cis*-3,4-diphenylcyclopentanone (III) (5.74 μ, $CHCl_3$). Since this region is of such extraordinary importance in the application of infrared spectroscopy to structural studies, it was of considerable interest to determine the origin and generality of this phenomenon.

Two possible sources—association or the presence of a mixture of Δ^2 and Δ^3 isomers—already have been eliminated.[1] Further, the perseverance of the double band in the solid state spectra and ultraviolet spectral studies made it most unlikely that the phenomenon is due to the presence of rotational isomers. There remained the possibility of Fermi resonance[2] between the carbonyl vibration and a close-lying overtone. There is in fact a band at 11.63 μ[3] in the spectrum of I which may be tentatively assigned to the out of plane bending vibration of the single ethylenic C-H bond of I.[4] The first overtone of this band should fall very close to the position anticipated for the simple carbonyl stretching frequency of I. That the splitting of the carbonyl band does indeed appear to depend upon the presence of a band at 11.6–11.7 μ has been determined by the examination of the spectra of a series of cyclopentenones. Compounds II, IV and V, all without ethylenic hydrogen, show only very weak or no absorption in this region and have single carbonyl-stretching bands, while compounds I, VI and VII, with single ethylenic hydrogen and bands at 11.6–11.7 μ, have split carbonyl bands. The case of VIII is instructive: the compound possesses a single ethylenic hydrogen but its bending band falls at 11.45 μ and a single carbonyl band is observed.[5]



1, $R_1 = H$, $R_2 = C_6H_5$, $R_3 = R_4 = R_5 = H$
II, $R_1 = CH_3$, $R_2 = C_6H_5$, $R_3 = R_4 = H$, $R_5 = CH_3$
IV, $R_1 = CH_3$, $R_2 = C_6H_5$, $R_3 = R_4 = R_5 = H$
V, $R_1 = CH_3$, $R_2 = R_3 = R_4 = R_5 = H$
VI, $R_1 = R_2 = R_3 = R_4 = R_5 = H$
VII, $R_1 = H$, $R_2 = CH_3$, $R_3 = R_4 = R_5 = H$
VIII, $R_1 = H$, $R_2 = C_6H_5$, $R_3 = H$, $R_4 = R_5 = CH_3$
IX, $R_1 = D$, $R_2 = C_6H_5$, $R_3 = R_4 = R_5 = D$

Confirmation for this view was obtained by the preparation of 3,4-diphenyl-2-cyclopenten-1-one-2,4,5,5-d_4 (IX) by heating I in dioxane with deuterium oxide and sodium carbonate; IX was obtained as colorless needles, m.p. 109.5–110° (*Anal.* Calcd. for $C_{17}H_{10}D_4O$: atom % excess D, 28.57. Found: D, 28.69). The spectrum of IX had no band at 11.63 μ and showed a single carbonyl band at 5.86 μ. Also the deuterated product obtained by similar treatment of VII lacked the band in the 11.6–11.7 μ region and had a single band at 5.86 μ in place of the two bands of VII at 5.81 and 5.89 μ.

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(1) P. Yates, N. Yoda, W. Brown and B. Mann, THIS JOURNAL, **80**, 202 (1958).

(2) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 215; E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955, p. 198.

(3) This and subsequently quoted band positions are for solutions in carbon tetrachloride.

(4) *Cf.* P. Yates, M. I. Ardao and L. F. Fieser, THIS JOURNAL, **78**, 650 (1956); R. N. Jones, F. Herling and E. Katzenellenbogen, *ibid.*, **77**, 651 (1955).

(5) It may be noted that for all of these compounds the first overtones belong to the same symmetry species as the carbonyl-stretching fundamental and thus Fermi resonance is allowed; *cf.* ref. 2.

BOOK REVIEWS

Actualités Biochimiques. No. 20. Aspects Actuels de la Biochimie des Acides Aminés et des Protéines. By J. T. EDSALL, Professeur a l'Université Harvard. Publiées sous la direction de Marcel Florkin et Jean Roche. Masson et Cie., Éditeurs, 120, boulevard Saint-Germain, Paris 6^e^, France. 1958. 156 pp. 16 × 24 cm. 2.000 fr.

Unlike the review of a manuscript that of a book is something like reviewing a TV program—it's too late to do anything about it. In the present instance, however, this reviewer would not have done anything about it even if he had had the opportunity. In this comparatively short monograph the topics for consideration have been carefully selected, are lucidly presented and bring the reader right up to work in progress in the biophysical chemistry of the amino acids, peptides and proteins. In many respects it may be considered a supplement to the earlier ACS monograph on this subject by Cohn and Edsall.

The volume under review is the result of a series of lectures by Professor Edsall at the College of France and at the Sorbonne in late 1955 and early 1956. Translated into easily read French by Professor Jean Roche and associates the material has been published as number 20 in the "Actualites Biochimiques" paperback series. The almost simultaneous appearance of this monograph with volume 1 of Edsall and Wyman's "Biophysical Chemistry" immediately raises the question of the extent to which Professor Edsall's lectures were a preview of the more extended treatise. Actually there is surprisingly little duplication and to this reviewer the topics selected for discussion in the shorter work are the exciting ones in biophysical chemistry.

Opening with a provocative account of the unique properties and role of water as the solvent in biological systems, the acid-base equilibria of amino acids and proteins are next treated, with the recent, definitive work of the author on cysteine serving as a specific example. Those proteins whose primary structure is known, *e.g.*, insulin and ribonuclease, then serve as models for consideration of the secondary and tertiary structure of macromolecules in general, the critical review of the α helix configuration being particularly timely. The formidable problems remaining, especially the configurational details of protein molecules in solution, are not minimized, however. Although the importance of the binding of small particles, other than the proton, by the protein is now clearly recognized, chapter IV, the interpretation of these studies in terms of our rapidly expanding knowledge of the primary structures of proteins, has not yet been fully exploited. In view of the work of the Harvard group on serum albumin and mercaptalbumin, the next two chapters, devoted to the physical chemistry of these proteins in the order mentioned, must be considered authoritative. Is the physical chemist responsible for the uncertainty in the molecular weight of serum albumin or are our fractionating procedures still inadequate for this material? The volume closes with a critical review of denaturation, the complexity of the problem being emphasized by contrasting the behavior of serum albumin and ovalbumin.

This monograph has found a permanent niche on your reviewer's desk and I can certainly recommend it to all biophysical chemists. This includes most biochemists and the many physical chemists with an interest in macromolecules, especially those who will also appreciate the extra dividend of simultaneously reviewing their French.

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Vitamins and Hormones. Advances in Research and Applications. Volume XV. Edited by ROBERT S. HARRIS, Professor of Biochemistry of Nutrition, Massachusetts Institute of Technology, Cambridge, Massachusetts, G. F. MARRIAN, Professor of Medical Chemistry, University of Edinburgh, Edinburgh, Scotland, and KENNETH V. THIMANN, Professor of Biology, Harvard University, Cambridge, Massachusetts. Academic Press, Inc., 115 Fifth Avenue, New York 3, N. Y. 1957. xi + 355 pp. 16 × 23.5 c.m. Price, $9.50.

The present volume of this series contains eight chapters: Chemistry of Vitamin B_{12} by Johnson and Todd, Total Syntheses of Carotenoids by Isler and Zeller, Carnitine by Fraenkel and Friedman, The Biological Synthesis of Cholesterol by Block, Adrenaline and Noradrenaline by Gaddum and Holzbauer, The Metabolic Effects of Growth Hormone and Their Physiological Significance by de Bodo and Altszuler, Steroids in Human Blood by Borth, and Comparison of the Influence of Hormones, Vitamins and Other Dietary Factors upon the Formation of Bone, Dentine and Enamel by Irving.

The chapter on B_{12} by Johnson and Todd covers an area which with a few exceptions is now completely explored. It thus serves nicely to bring up to date the definitive review on B_{12} by Folkers and Wolf (Vitamins and Hormones, Vol. 12). Particular emphasis is laid on the major role which X-ray crystallography played in elucidating the details of molecular structure. Enough data on the biosynthesis of B_{12} analogs was available at the time of writing to provide in addition a good introduction to this field.

Other chapters which summarize relatively mature areas of research are those on synthesis of carotenoids and on biosynthesis of cholesterol, both of them first-rate jobs by pioneers in their respective fields. The latter chapter is carried up to the recent developments on the mechanism of conversion of mevalonic acid into squalene. The authors of the section on growth hormone have plunged into a turbulent biological controversy and have seemingly been successful in presenting the opposing views as to whether this hormone is anabolic or anticatabolic. The literature has been well summarized and the various issues nicely separated. It's a pity that the key to the mystery has not yet come to hand.

The adrenaline chapter is a particularly timely one. The frantic activity touched off in the field of mental disease by the tranquilizers has led to hypotheses involving this hormone in a variety of postulated roles. The biogenesis, metabolic fate, physiological actions and interrelationships of adrenaline and noradrenaline are depicted and provide a lucid background for the still unclear mechanisms of action of reserpine, LSD, adrenochrome and the adrenolytic drugs.

The confusion surrounding carnitine, β-hydroxy-γ-butyro-betaine, is somewhat dispelled, or at least better organized in Fraenkel and Friedman's chapter. The difficulties which the authors and their colleagues have faced in trying to study the distribution and function of carnitine is exemplified by the breakdown of the assay method. The latter was based on the growth response of the larvae of the insect *Tenebrio molitor*. It was not discovered until 1957—some 10 years after its introduction—that this growth response was dependent on variables quite apart from the concentration of carnitine (zinc and potassium). Consequently the present chapter serves to provide a thorough compilation of the literature and background but development of perspective is still to come.

RESEARCH AND DEVELOPMENT DIVISION
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Structure Reports for 1951. Volume 15. General Editor, A. J. C. WILSON. Section Editors, N. C. BAENZIGER (Metals), J. WYART (Inorganic Compounds) and J. MONTEATH ROBERTSON (Organic Compounds). N. V. A. Oosthoek's Uitgevers Mij., Domstraat 1–3, Utrecht, Holland. 1957. viii + 588 pp. 16.5 × 25 cm. Price, $29.00.

The momentous task of bringing Structure Reports up to date and filling the gap left by the war years was planned by the International Union of Crystallography in 1948. In seven years of publication, the editors and committees have been able to analyze and abstract twelve years of literature. Since the very nature of these volumes necessitates two to three years of preparation, these vigorous abstractors are only a few years short of their goal. The series of Structure Reports together with its predecessor, Strukturberichte, now summarizes practically all the structural literature which has been published prior to 1952. It is anticipated that future editions will follow Volume 15 in chronological order so that the continuity which this series now possesses will persist.

Although the volume of structural data continues to increase with each succeeding year, the editors and committee for Volume 15 have not sacrificed any of the quality which has been established in previous years. The summaries are concerned only with work of structural interest and have been extracted from the reported papers in such a manner that it is seldom necessary to refer to the original articles. The arrangement within individual reports is usually name, formula, papers reported, unit cell, space group, atomic positions and parameters, interatomic and intermolecular distances, material, discussion, details of analysis and references. Editorial comments are enclosed in square brackets and are thus readily distinguished. Both prior and subsequent literature references are cited; the subsequent references are quite complete through 1955.

This book is divided into three main parts: Metals (124 pp.), Inorganic Compounds (244 pp.) and Organic Compounds (175 pp.). In the Metals section the arrangement is alphabetical while the Organic and Inorganic Compounds are arranged according to increasing complexity of composition with related structure and substances kept together as much as possible. With this convenient arrangement, a person having reference to a certain compound or structure will automatically find himself reviewing several related compounds.

There are four indexes headed by the subject index which lists the compounds alphabetically by the names as they