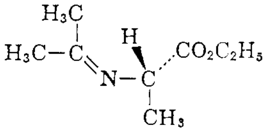
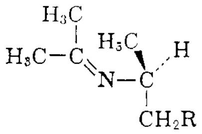
$N{=}C(CH_3)_2 > C_6H_5 > CO_2R > CH_3 > H$.[5] As shown in the projection of the N-isopropylidene derivative of ethyl L-alaninate (IIa), the contribution to the rotatory power due to atomic asymmetry is negative. An additional negative contribution results from the preferred orientation, also shown in projection IIa, of the isopropylideneamino moiety about its attachment bond. For the other derivatives of code II both of these contributions are not as reinforcing, and in IIb at least, the contribution due to atomic asymmetry appears to be the more important. These derivatives all display substantially lower rotatory powers than that of ethyl L-alaninate (*cf.* Table I).[7]


IIa


III

For the derivatives of code III, the preferred conformation of the isopropylideneamino group is as shown in III, and as a result of the flexible chains (CH_2R), additional conformational asymmetry contributions come into play. With the above sequence of polarizabilities, these derivatives are correctly predicted, using only the Conformational Asymmetry Rule, to be dextrorotatory. Similarly for those of codes IV and V, the same atomic and conformational symmetries present in IIa make, except for IVg, reinforcing negative contributions to the rotatory powers, and as in those of code III, the flexible chains give rise to additional conformational contributions. These contributions considered, the derivatives of code IV and V are all correctly predicted to be highly levorotatory, the additional asymmetric centers in those of code V making, as predicted, only small contributions to the rotatory powers.

These same considerations can also be extended to the rotatory powers of similar Schiff bases formed in other ketonic solvents,[2] and we are currently extending this work to include optically active cyclic amines.

(5) This sequence cannot be deduced uniquely from the data in Tables I and II. The priority of the isopropylideneamino group is assigned, however, on the basis of the atomic refraction (polarizability) of nitrogen in Schiff bases of this type.[6]

(6) S. S. Batsanov, "Refractometry and Chemical Structure" Consultants Bureau, New York, N. Y., 1961, p. 22.

(7) Here and in what follows, the somewhat justifiable assumption is made that no significant contributions to the rotatory powers arise from preferred orientations of the carbethoxy, carbomethoxy and carbamoyl groups about their attachment bonds.

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THE CHEMISTRY OF ACTINOSPECTACIN. I. ACTINAMINE

Sir:

Actinospectacin,[1,2,3] a new broad spectrum antibiotic produced by an actinomycete, *Streptomyces spectabilis*, is a basic compound with the molecular formula $C_{14}H_{24}N_2O_7$. Hydrolysis of this antibiotic with boiling 6.0 *N* hydrochloric acid gives actinamine (I) isolated as its dihydrochloride which has the molecular formula $C_8H_{18}N_2O_4 \cdot 2HCl$, m.p. 315° dec., optically inactive. *Anal.* Calcd. for $C_8H_{18}N_2O_4 \cdot 2HCl$: C, 34.41; H, 7.12; N, 10.05; Cl, 25.45; O, 22.93; mol. wt., 279.2. Found: C, 34.46, 34.39; H, 7.12, 7.07; N, 10.02, 9.83; Cl, 25.31; O, 21.23; mol. wt. (electr. titr.), 280. Treatment of the dihydrochloride with an anion exchange resin (Dowex 2) gave the free base, m.p. 129°. *Anal.* Calcd. for $C_8H_{18}N_2O_4$: C, 46.60; H, 8.74; N, 13.59; O, 31.07; mol. wt., 206.2. Found: C, 46.99; H, 8.99; N, 14.06; O, 31.00; mol. wt. (electr. titr.), 204. The free base in water is optically inactive in the range 310 to 589 mμ and shows only end absorption in the ultraviolet region. A strong band at 3200 cm.$^{-1}$ in the infrared spectrum of actinamine is indicative of hydroxyl and/or amino groups, but there are no bands attributable to unsaturation of any type. Both nitrogen atoms are present as methylamino groups as shown by p$K_a{}'$ values of 7.2 and 8.9 and isolation of two moles of methylamine, identified as its *p*-hydroxyazobenzene-*p*′-sulfonic acid salt, from each mole of actinamine dihydrochloride after periodate oxidation. Acetylation of actinamine dihydrochloride with acetic anhydride and sodium acetate gave a hexaacetyl derivative (II), m.p. 196–198°, optically inactive. *Anal.* Calcd. for $C_{20}H_{30}N_2O_{10}(6CH_3C)$: C, 52.40; H, 6.53; N, 6.11; O, 34.93; CH_3C, 19.6. Found: C, 52.34; H, 6.71; N, 6.20; O, 34.46; CH_3C, 18.9. The infrared spectrum of this compound has bands indicative of ester carbonyl (1750 cm.$^{-1}$) and amide carbonyl (1650 cm.$^{-1}$) but no bands in the OH/NH region. The formation of hexaacetylactinamine established that all the oxygen atoms were present as hydroxyl groups.

Actinamine dihydrochloride consumed six moles of periodate per mole with no formation of formaldehyde. The periodate consumption data coupled with analysis and functional group determination point unequivocally to a bis-(methylamino)-tetrahydroxycyclohexane structure for actinamine. There are three possible positional isomers aside from stereoisomers having such a structure. These are 1,2-bis-(methylamino)-, 1,3-bis-(methylamino)- and 1,4-bis-(methylamino)-tetrahydroxycyclohexane. That actinamine is the 1,3-isomer was shown by a study of the periodate oxidation of N,N′-diacetylactinamine (III, prepared by methanolysis of hexaacetylactinamine), m.p. 250–252° dec., infrared absorption bands at 3280 cm.$^{-1}$ and 3180 cm.$^{-1}$ (hydroxyl) and at 1635 cm.$^{-1}$ (amide carbonyl). *Anal.* Calcd. for $C_{12}H_{22}N_2O_6$ $(2CH_3CO)$: C, 49.65; H, 7.58; N, 9.65; CH_3CO, 29.6. Found C, 49.77; H, 7.65; N, 9.47; CH_3CO, 23.3. This diacetyl compound consumed two moles of periodate per mole with formation of one mole of formic acid, conclusively establishing structure I for actinamine.

Actinamine and all of its derivatives are optically inactive, indicating a *meso* compound. There are

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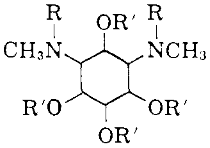
(1) The trade name of The Upjohn Company for actinospectacin is Trobicin.

(2) D. J. Mason, A. Dietz and R. M. Smith, *Antibiotics and Chemotherapy*, **11**, 118 (1961).

(3) M. E. Bergy, T. E. Eble, and R. R. Herr, *ibid.*, **11**, 661 (1961).

eight possible stereoisomers for such a compound. One of these isomers, the all *trans* form which would be N,N′-dimethylstreptamine, has been eliminated as a possibility by comparison of N,N′-dimethylactinamine with N,N′-tetramethylstreptamine. Methylation of actinamine by Witkop's procedure[4] gave N,N′-dimethylactinamine dihydrochloride (the dihydrochloride of IV), m.p. 256–258° dec., optically inactive. *Anal.* Calcd. for $C_{10}H_{22}N_2O_4 \cdot 2HCl$ ($4CH_3N$): C, 39.09; H, 7.82; N, 9.13; CH_3N, 19.4; mol. wt., 307.2. Found: C, 38.91; H, 7.85; N, 9.01; CH_3N, 18.3; mol. wt. (electr. titr.), 318. This compound differed from N,N′-tetramethylstreptamine dihydrochloride[4] in infrared spectrum and melting point and mixture melting points were depressed. The two compounds would be identical if actinamine were the all-*trans* isomer.



I, R = R′ = H
II, R = R′ = CH_3CO
III, R = CH_3CO, R = H
IV, R = CH_3, R′ = H

Acknowledgment—The author is grateful to Dr. Herman Hoeksema for helpful discussion and criticism, to Dr. E. C. Olson and associates for analyses, to Dr. R. W. Rinehart and associates for spectrophotometric data, and to Mr. Dennis J. Weber for titrations.

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[4] G. F. Holland, R. C. Durant, S. L. Friess and B. Witkop, *J. Am. Chem. Soc.*, **80**, 603 (1958).

BOOK REVIEWS

Progress in Reaction Kinetics. Volume 1. Edited by G. PORTER, F.R.S., Professor of Physical Chemistry, University of Sheffield. Assistant Editor, B. STEVENS, M.A., D. Phil., University of Sheffield. Pergamon Press Ltd., Headington Hill Hall, Oxford, England. 1961. viii + 276 pp. 15.5 × 23.5 cm. Price, $12.00.

The appearance of the present volume, the first in a new series, is a sign of the growing importance of chemical kinetics in current research. The stated purpose of this series is to provide authoritative reviews of special topics in reaction kinetics and also to provide a quasi-continuous inventory of "good" rate constants. To this end the editor has drawn on a series of quite diverse experts to prepare the present group of nine articles. The experts are all quite expert and active in their fields and the articles are all clearly written if not always easily readable.

In the field of gas phase reactions, F. Kaufman has prepared a long, comprehensive article on the "Reactions of Oxygen Atoms," while J. A. Kerr and A. F. Trotman-Dickenson have done a somewhat cursory one on "Alkyl Radicals." Both of these are replete with rate constants as well as Arrhenius parameters obtained from more or less conventional studies. In a much more tentative and speculative fashion V. Voevodsky and V. N. Kondratiev present values for rate parameters for steps occurring in branching chain reactions. The reactions considered are the $2H_2+O_2$ explosions as affected by small amounts of additive RH.

The new and growing field of ion-molecule reactions is discussed in considerable detail by F. W. Lampe, J. L. Franklin and F. H. Field. The data here are as yet very crude as are also the energetics. However, the unusual species produced and the very large rate constants involved are sure to presage continued interest and activity.

In the field of solution kinetics, R. M. Noyes has given a very clear and thorough exposition of the intricacies of diffusion-controlled processes and the theory of the establishment of stationary diffusion fields. C. W. Davies reviews the status of the Brönsted–Debye–Hückel treatment of salt effects on ionic reactions and summarizes some of the best data for these systems, in most cases recently obtained. His conclusion, in agreement with Scatchard, is that the theory is in good shape if corrected for ion-pairing. He points out, however, some still unresolved anomalies.

The study of the fast reactions of photochemically excited species in solution by A. Weller is interesting although very specialized in being limited to aromatic systems. Y. Pocker has attempted to clarify the somewhat troubled waters of $S_{N}i$(i = 1,2) in his summary of some of the recent and occasionally conflicting studies of nucleophilic substitution at saturated carbon atoms. Some of the difficulty is here skirted by restricting the discussion to non-hydroxylic solvents.

The final article by L. Peller and R. A. Alberty is an overly short discussion of the conventional physical chemistry of enzyme kinetics. This is perhaps a reflection of the complexity of these systems and the need to bring many points of view to bear on them to obtain even a simple interpretation of the kinetic data.

The present series will be of interest to research workers and students starting work in any of the fields covered. The present articles, however, are not sufficiently detailed to be of great interest to experts already at work in these fields. Particularly in the area of selecting and analyzing data critically, the present series with one or two exceptions is weak. Such a series is in direct competition with *Annual Reviews*, *Chemical Reviews* and a number of other review journals and it is hoped that the editor will in future series sharpen the distinctions between them that will make this a more valuable addition to the field.

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Advances in the Chemistry of the Coordination Compounds. Proceedings of the Sixth International Conference on Coordination Chemistry, held at Wayne State University, Detroit, Michigan, August 27 to September 1, 1961. Edited by STANLEY KIRSCHNER, Professor of Inorganic Chemistry at Wayne State University. The Macmillan Company, 60 Fifth Avenue, New York 11, N. Y. xii + 682 pp. 16.5 × 24.5 cm. Price, $15.00.

The conference was divided into series of eight lectures and sixty-eight papers covering a wide range of interest, not only to coördination chemists but to those on the fringes such as bio, catalytic organic and analytical.

It is, of course, impossible to list the papers, but a review of the lectures may show the scope of the conference. The lecture on bonding by C. T. Ballhausen compares the now familiar crystal field and molecular orbital approaches and in particular reviews methods for, and significance of, the determination of the extent of mixing of metal and ligand orbitals. R. E. Connick reviews some of the data on water exchange with aquo ions, then presents some of his data on rates of interconversion of a series of chloroaquoruthenium-(III) ions. In a particularly lucid and informative lecture