THE PORPHYRINS

Volume III

Physical Chemistry, Part A

Edited by

DAVID DOLPHIN

Department of Chemistry
University of British Columbia
Vancouver, British Columbia, Canada

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Contributors

Fran Adar

J. O. Alben

H. Budzikiewicz

G. W. Canters

David L. Cullen

R. H. Felton

Martin Gouterman

Barton Holmquist

Edgar F. Meyer, Jr.

Yash P. Myer

Ajay Pande

W. Robert Scheidt

John Clark Sutherland

J. H. van der Waals

Charles Weiss

Nai-Teng Yu

List of Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

FRAN ADAR* (167), Department of Biochemistry and Biophysics, University of Pennsylvania, Philadelphia, Pennsylvania 19174

J. O. ALBEN (323), Department of Physiological Chemistry, Ohio State University, College of Medicine, Columbus, Ohio 43210

H. BUDZIKIEWICZ (395), Institute of Organic Chemistry, University of Cologne, Cologne, Germany

G. W. CANTERS (531), Center for the Study of the Excited States of Molecules, Rijks Universiteit, Leiden, The Netherlands

DAVID L. CULLEN (513), Department of Biochemistry and Biophysics, Texas A&M University, Texas Agricultural Experiment Station, College Station, Texas 77843

R. H. FELTON (347), School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

MARTIN GOUTERMAN (1), Department of Chemistry, University of Washington, Seattle, Washington 98195

BARTON HOLMQUIST (249), Biophysics Research Laboratory, Department of Biological Chemistry, Harvard Medical School and the Division of Medical Biology, Peter Bent Brigham Hospital, Boston, Massachusetts 02115

* Present address: Instruments SA, Inc., Metuchen, New Jersey 08840.

EDGAR F. MEYER, JR. (513), Department of Biochemistry and Biophysics, Texas A&M University, Texas Agricultural Experiment Station, College Station, Texas 77843

YASH P. MYER (271), Department of Chemistry, State University of New York at Albany, Albany, New York 12222

AJAY PANDE (271), Department of Chemistry, State University of New York at Albany, Albany, New York 12222

W. ROBERT SCHEIDT (463), Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

JOHN CLARK SUTHERLAND* (225), Department of Physiology, California College of Medicine, The University of California, Irvine, California 92664

J. H. VAN DER WAALS (531), Center for the Study of the Excited States of Molecules, Rijks Universiteit, Leiden, The Netherlands

CHARLES WEISS (211), International Bank for Reconstruction and Development, Washington, D.C. 20433

NAI-TENG YU (347), School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30322

* Present address: Biology Department, Brookhaven National Laboratory, Upton, New York 11973.

General Preface

> Man cannot give a true reason for the grass under his feet why it should be green rather than red or any other color.
>
> Sir Walter Raleigh
> *History of the World: Preface (1614)*

Just over two centuries after these words of Raleigh, Verdeil in 1844 converted chlorophyll to a red pigment which prompted him to suggest a structural relationship between chlorophyll and heme. Shortly thereafter, Hoppe-Seyler, in 1880, strengthened this hypothesis by showing the spectral resemblances between hematoporphyrin and an acid degradation product of chlorophyll. The final steps in these structural elucidations were initiated by Willstätter, and culminated in the heroic work of Hans Fischer who showed that but for two hydrogen atoms grass would indeed be red and that only two more hydrogen atoms would have ensured that Raleigh and his countrymen would indeed have been blue-blooded Englishmen.

The close structural similarity between the porphyrins and chlorins gives little measure of the relationships among and the diversity of their numerous and important biochemical functions. All life on this planet relies directly on the central role of the chlorophylls and cytochromes in photosynthesis by means of which photonic energy is converted and stored as chemical energy. It is likely that long before oxygen was abundant in the Earth's atmosphere the cytochromes were responsible for respiration. With the advent of photosynthesis the oxygen produced is the

terminal electron acceptor for all aerobic respiration. For many organisms the means by which oxygen is transported, stored, reduced, and activated are frequently mediated by heme proteins. In mammals, oxygen is transported by the cooperative tetrameric protein hemoglobin and stored by monomeric myoglobin. When oxygen is reduced to water, in the terminal step of respiration, four electrons are transported via a series of cytochromes to cytochrome oxidase. Cytochrome oxidase contains two iron porphyrins and two copper atoms. In addition, nature also brings about one- and two-electron reductions to superoxide and peroxide. Both the decomposition and further activation of hydrogen peroxide are mediated by the heme proteins catalase and peroxidase. Furthermore, heme proteins function as both mono- and dioxygenases, and recently cytochrome *P*-450, which functions as a monooxygenase by combining properties of both oxygen binding and electron transport, has been shown to be important in a wide variety of biological hydroxylations.

This brief insight into a few of the many central roles played by metalloporphyrins in nature plus the challenges that porphyrins present to the inorganic, organic, physical, and biochemist suggest the wealth of knowledge that is documented in these areas. It is the objective of "The Porphyrins" to present a full and critical coverage of all the major fields relating to porphyrins, their precursors, catabolic derivatives, and related systems in a manner that we trust will be useful to those in physics, chemistry, biochemistry, and medicine.

The treatise consists of seven volumes. Volumes I and II (Structure and Synthesis, Parts A and B) cover nomenclature, history, geochemistry, synthesis, purification, and structural determination of porphyrins, metalloporphyrins, and mono- and polypyrrolic compounds and related systems. Volumes III, IV, and V (Physical Chemistry, Parts A, B, and C) cover electronic structure and spectroscopy including uv-vis, ORD, CD, MCD, mass, ir, resonance Raman, Mössbauer, Zeeman, NMR (diamagnetic, paramagnetic), ESR, and X-ray crystallography. In addition, redox chemistry, electron transfer, aggregation, oxygenation, and solid state phenomena are included. Volumes VI and VII (Biochemistry, Parts A and B) cover the biosynthesis and enzymatic synthesis of porphyrins, chlorophylls, and their precursors, and the chemistry and biochemistry of the bile pigments and the roles of porphyrins and bile pigments in clinical chemistry. The structure and function of the major hemoproteins are also covered.

It remains for me to thank my colleagues and co-workers for their support and assistance. A special debt of gratitude goes to my mentors: Alan Johnson who introduced me to these areas and who taught me why chlorophyll is green, and Bob Woodward who showed the world how to make chlorophyll and taught me why.

DAVID DOLPHIN

Preface

Volume III (Physical Chemistry, Part A) contains chapters on various aspects of porphyrin spectroscopy including circular and magnetic circular dichroism, electronic, infrared, resonance Raman, and Zeeman spectroscopy. Chapters on porphyrin stereochemistry, X-ray crystallography, and mass spectroscopy of porphyrins are also included.

This volume complements Volumes IV and V (Physical Chemistry, Parts B and C), which cover resonance spectroscopies, Mössbauer spectroscopy, redox chemistry, electron transport, and electrochemistry, as well as oxygenation, aggregation, and metallation of porphyrins and chlorophylls (including isolation and characterization) and their solid state phenomena.

The final result is an up-to-date and critical review of the areas described above. This treatise provides, for the first time, a complete and comprehensive review of all of the major aspects of porphyrin chemistry and biochemistry.

I wish to take this opportunity to thank the contributors to this volume. For those who completed their chapters on time, I give my thanks for their patience during the period between submission of their manuscript and the publication of this book. Of those who were not so prompt, I ask that they understand my impatience.

DAVID DOLPHIN

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