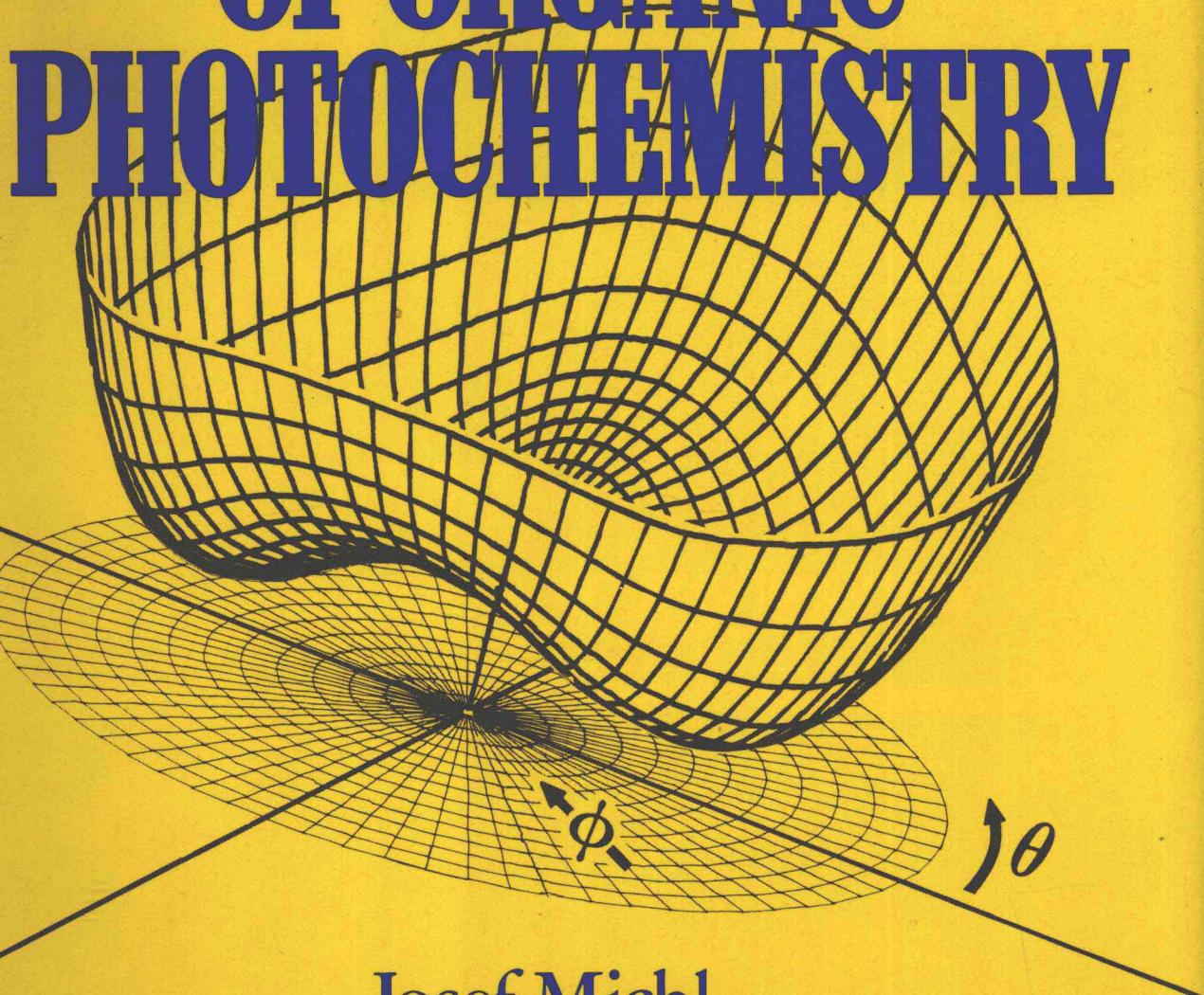
ELECTRONIC ASPECTS OF ORGANIC PHOTOCHEMISTRY



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ELECTRONIC ASPECTS OF ORGANIC PHOTOCHEMISTRY

Vlasta Bonačić-Koutecký: To Jaroslav Koutecký

Josef Michl: To my father, Josef, and to the memory of my mother, Věra

PREFACE

While the experimental, synthetic, and mechanistic aspects of organic photochemistry are well covered in quite a few recent textbooks and monographs, to our knowledge no book has been dedicated to the discussion of its theoretical aspects, that is, to the analysis of the detailed electronic nature of the elementary photochemical reaction steps. Much information on the subject is scattered throughout the journal literature, and the present text represents an attempt to organize it at a level suitable for graduate students. We assume that the reader is already familiar with the phenomenology of organic photochemistry and give little information about experimental results, which can be readily found elsewhere (see Section 1.4 for leading references). While it would have been ideal to combine theory and experiment in a single volume, it would have been of prohibitive size.

Parts of the text have been used in graduate courses for organic chemists at Yale University, Stanford University, California Institute of Technology, the University of Utah, and the University of Texas at Austin in the United States, at the Technion (Haifa) in Israel, and at the University of Münster and the Free University, Berlin in Germany, and we are grateful for the critical comments provided by the students.

It is hoped that in addition to graduate students, the book will also be of interest to practicing photochemists and possibly to physical and theoretical chemists seeking inspiration and looking for problems to which to apply their newly improved tools. Surely, the theory of organic photochemical reactions lags far behind the theory of organic thermal reactions, and a fresh influx of researchers and ideas would be most welcome. If this book helps to bring about such a turn of events, an important goal will have been accomplished.

The origin of the book may be traced back to a series of articles on photochemical mechanisms published in 1972 in *Molecular Photochemistry,* in 1974 in *Topics of Current Chemistry,* and subsequently mostly in the *Journal of the American Chemical Society,* by one of the authors, and to a series of articles on *ab initio* excited state wave functions and their implications for photochemistry, mostly in the *Journal of the American Chemical Society,* by the other author, starting with a 1975 paper on "sudden polarization" in *Angewandte Chemie* with Lionel Salem and several others. Over the years, our views on the subject developed, and the present text represents an outgrowth of several years of collaborative effort, highlighted by a 1987 review article in *Angewandte Chemie.*

The collaboration was made possible by the granting of an Alexander von Humboldt Senior U.S. Scientist award and a J. S. Guggenheim Fellowship award to J.M., and these are gratefully acknowledged. J.M. is grateful to Professor Jaroslav Koutecký at the Free University, Berlin, Professor Albert Weller at the Max-Planck-Institute for Biophysical Chemistry, Göttingen, Professor Horst Kramer at the University of Stuttgart, and Professor Yitzhak Appeloig at the Technion, Haifa,

Israel, for their warm hospitality during work on the manuscript. He is further much obliged to his friends in the following Departments of Chemistry, where much of the text was written during extended visits: at California Institute of Technology, at Stanford University, at the University of Chicago, where he held a Morris S. Kharasch visiting professorship, at Yale University, where he held a Treat B. Johnson visiting professorship, and at the Technion, where he held a Manson visiting professorship. Finally, we are thankful to the U.S. National Science Foundation and to the Deutsche Forschungsgemeinschaft and Fond der Chemischen Industrie, who have supported our work in photochemistry for many years.

The programs used in our computations were originally provided by Professors Robert Buenker and Sigrid Peyerimhoff. Drs. John Downing, Jutta Köhler, Daniella Papierowska-Kaminski, Maurizio Persico, and Klaus Schöffel participated in some of the calculations and computer art production. Professor Piercarlo Fantucci provided advice on valence-bond theory. Numerous authors sent us reprints of their work. Many kindly read parts or all of the text and suggested improvements: Professors Gerhard Closs, Marye-Anne Fox, Karl Jug, Martin Klessinger, Horst Kramer, J. Michael McBride, Lisa McElwee-White, Gabriella Poggi, Lionel Salem, Jack Saltiel, and Jacob Wirz. Dr. Claas Zachariasse has kindly provided unpublished results, and Dr. Regai Makar translated a page from Arabic. We are indebted to all of these, to our illustrator, Mr. Alexis Kelner, for producing art out of the simple sketches we provided, and to Mr. Philip Willden, Ms. Rebecca Cunningham, Ms. Katheryn Clayton, and Ms. Angie Watson for producing a superbly typed manuscript from our dictation and notes.

A special note of thanks goes to Professor Jaroslav Koutecký, from whom we have learned about quantum chemistry and whose constant encouragement over the years of work on this book was essential to its completion.

Finally, we are grateful to our editor, Dr. Theodore Hoffman, for his unfailing patience and kind understanding in the face of seemingly interminable delays in the completion of our work.

JOSEF MICHL
VLASTA BONAČIĆ-KOUTECKÝ

Austin, Texas
Berlin, West Germany
April 1990

NOTATION

Operators:	
one-electron	$\hat{a}$
many-electron	$\hat{A}$
Vectors:	$\mathbf{a}$, $\mathbf{A}$
Matrices:	a, A
Chemical species, structures:	$\mathfrak{A}$
Orbitals:	
general orthogonal	$\mathscr{A}$
most delocalized orthogonal	a
most localized orthogonal	A
most localized nonorthogonal	A
localized on a subunit	a
generalized valence-bond	α
Spinorbitals:	$\mathfrak{a}$

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PART A

BACKGROUND

CHAPTER 1

Introduction

1.1 ORGANIC PHOTOCHEMISTRY

Vitiligo. The following ode on a plant can be found in the Indian sacred book, Atharva Veda (1400 B.C.):

Born by night art thou, O plant,
Dark, black, sable, do thou,
That art rich in color, Stain
This leprosy and white grey spots.
Even color is the name of thy mother,
Even color is the name of thy father,
Thou O plant producest even color
Render this (spot) to even color.

The disease had been dreaded for millenia before the Roman physician Celsus coined the term *vitiligo* for the cosmetic condition that, to this day, disfigures one out of roughly every hundred humans by forming large chalk-white patches on the skin, similar to the white blotches on a spotted calf (*vitelius* is Latin for calf). Throughout history, it made the lives of innumerable victims miserable by turning them into social outcasts.

The ancients had apparently worked at the problem, with some success. Section 877 of the Ebers papyrus (about 1550 B.C.) is believed to refer to the disease and suggests a remedy whose chief components are fly's dirt, powder of wheat, natron, beans, stibium, and oil. Atharva Veda (Book I, Hymns 23 and 24) goes into considerable detail in describing an herbal treatment. The plant whose curative powers are praised in the above ode most likely was Barachee (*Psoralea corylifolia*). Yet another plant, Aatrillal (*Ammi majus*), has been used for centuries in the Nile valley for the same purpose. According to the thirteenth-century author Ibn al Baytar, the medicinal power of the fruits of Aatrillal was discovered by the Berbers, who sold the drug but managed to keep its nature a secret at first (Figure 1.1).

What makes these herbal remedies interesting to a photochemist? All the sources carefully emphasize that the drugs are only potent when combined with sunshine: It is a photochemical reaction of the active principle in the skin that triggers the desired pigmentation.

Lest the power of ancient herbal medicine be idolized, we note that a yellowish-brown powder named Aatrillal was sold by Egyptian native herbalists as a remedy for vitiligo as recently as the first half of this century; this substance was used in much the same way as recommended by Ibn al Baytar: Daily doses of 4–12 grams,

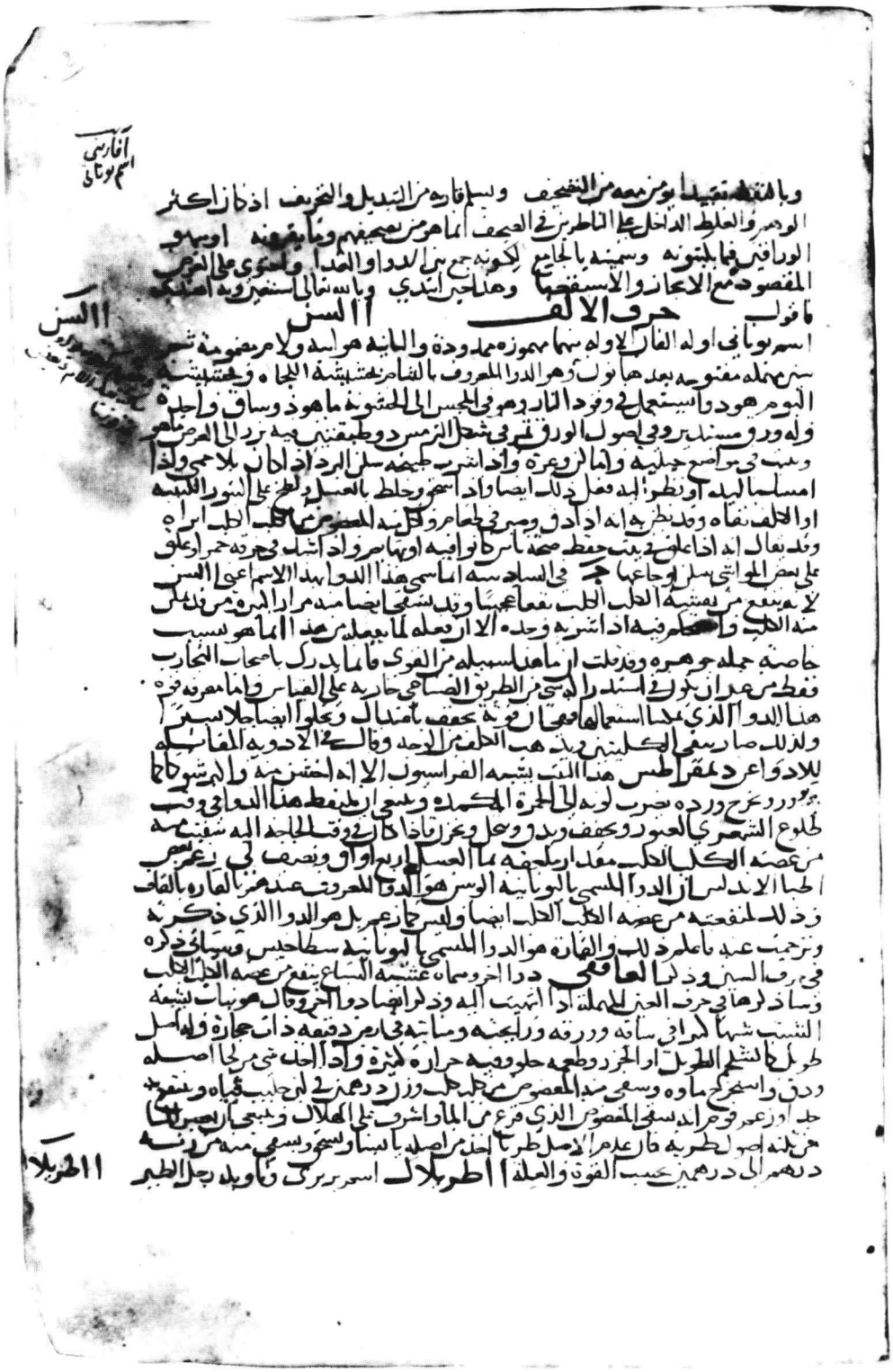

Figure 1.1 A medieval description of the curative powers of Aatrillal. Al-jāmi' li-mufradāt al-adwiya wal-aghdhiya (Materia Medica). By Abdullah Ibn Ahmad al-Andalusi al-Maliqi, known as Ibn al-Baytar [died 646 A.H. (1248 A.D.)]. Photograph purchased from the Chester Beatty Library, Dublin, Ireland.