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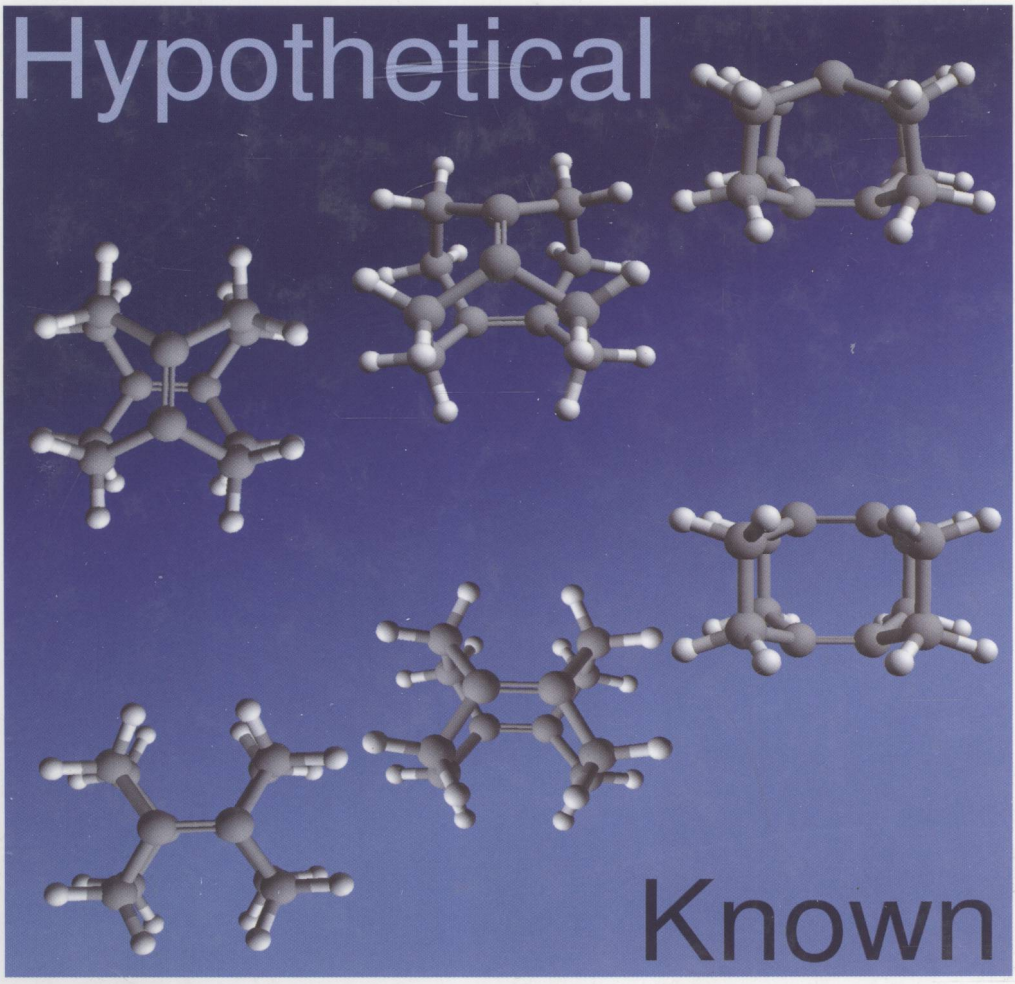
Beyond the van't Hoff and Le Bel Hypothesis
With a Foreword by Roald Hoffmann



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WILEY-VCH Verlag GmbH & Co. KGaA

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Cover illustration
Cover picture kindly provided by
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Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
Die Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.d-nb.de.

Printed in the Federal Republic of Germany
Printed on acid-free paper

Typesetting Manuela Treindl, Laaber
Printing betz-druck GmbH Darmstadt
Bookbinding Litges & Dopf GmbH, Heppenheim

ISBN: 978-3-527-31767-7

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Further Reading

A. V. Demchenko (Ed.)

Handbook of Chemical Glycosylation

2008
ISBN: 978-3-527-31780-6

P. G. Andersson, I. J. Munslow (Eds.)

Modern Reduction Methods

2008
ISBN: 978-3-527-31862-9

L. Kollár (Ed.)

Modern Carbonylation Methods

2008
ISBN: 978-3-527-31896-4

E. M. Carreira, L. Kvaerno (Eds.)

Classics in Stereoselective Synthesis

2008
ISBN: 978-3-527-29966-9

M. M. Haley, R. R. Tykwinski (Eds.)

Carbon-Rich Compounds

From Molecules to Materials

2006
ISBN: 978-3-527-31224-5

Foreword

Chemistry is the truly anthropic science. The molecules we make can heal us, and they can hurt us, because they are on the scale of the molecules that make up our bodies. And our synthetic creations interact, even react, with the molecules that nature – our enzymes, the environment – put into us.

Molecular science is also anthropic (male and female, of course) because it presents a challenge to human intelligence that is just right, commensurate with our intellect. The exciting story this book develops bears testimony on every page to that anthropic cognitive nature of organic chemistry.

Let me explain: our remarkable neural system is steered by a complex brain. That brain has prejudices for sure; it tends to simplify things, falling at every proffered opportunity for beautiful equations, simple mechanisms, Platonic solids and the honeyed simplicities of politicians. But when challenged, we can deal with substantial complexity. Indeed, the brain relishes being stretched: by rich sensual inputs, by patterns, by puzzles.

Along comes a science, our chemistry. It offers in its molecular structures, a game that is at first sight deceptively simple. Take hydrocarbons (most of the molecules in this book are in this category) – what could be simpler? Two elements, C and H, that by a transparent rule of intercombination form four bonds, and one bond, respectively. You are well aware of the manifestation of these rules and combinatorics – a chemical universe of incredible diversity.

These molecules can not only be thought up, they can also be synthesized in a human span – roughly the time it takes for a graduate student to get a Ph.D. We are not making a ladybug, nor a spiral galaxy; we are making a paracyclophane. The complexity of the challenge is on the human scale. And so are the possibilities: What can I do to string eight carbons across the *para* positions of a benzene? Can I reduce the bridging carbons to seven? Will I make it easier if the eight carbons are partially in a benzene ring themselves? The questions just flow one after the other; it takes no talent to ask them, just a normal curious human being, privy to the structural codes of chemistry.

So the game itself, the game of chemical structure, is exciting. Chess pales by comparison. Add to that ludic challenge potential utility, and also the natural human desire to probe limits (just how far can I distort that double bond out of its planar normalcy?), and you have all the makings of intense interaction, part

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intellectual, part emotional, between a human being and an object of his or her creation.

The object of our intense contemplation – a compound macroscopically, a molecule microscopically – is complex enough not to be boring, yet not unpredictably chaotic. The strained molecule is just right for some of us to exercise our creativity in thinking up these strange beasts, others in coming up with ingenious ways of making them (for molecules are real!), all of us admiring the complexity, simplicity and function all rolled into one.

Enjoy reading this book!

Roald Hoffmann

Preface

Strained hydrocarbons represent an amazing domain. About 80 years after the formulation of van't Hoff and Le Bel's hypothesis new, exciting molecules representing in Hoffmann and Hopf formulation (R. Hoffmann, H. Hopf, *Angewandte Chemie*, submitted), what is probably too much of anthropomorphization, 'molecular sadism' were synthesized. Paraphrasing D. J. Cram, one could say that such molecules elicit wonder, stimulate the imagination and challenge both synthetic talents and interpretive instincts. Up to the early 1990s the field of strained hydrocarbons was a kind of elitist area in which only the best synthetic and theoretical chemists were active. It was a playground of few, characterized by vivid interactions between synthetic and theoretical chemistry allowing one to propose plausible synthetic targets on the basis of model calculations. On the other hand, it allowed Bader, Wiberg and their followers to refine the definition of the chemical bond. The situation in the domain of distorted molecules changed after the discovery of fullerenes and nanotubes which attracted numerous researchers. These molecules, having nonplanar systems of conjugated bonds, are not hydrocarbons but their derivatives are numerous. Thus, they have been included into this volume in view of the rapid development of these areas and, still largely unfulfilled, prospects of their applications.

Several researchers helped me in this project. First of all, I would like to thank all contributors to this volume. I would like also to acknowledge the support I have obtained from Professors T. Marek Krygowski, Jay S. Siegel and Henning Hopf in the initial stage. Finding contributors was sometimes a difficult task. The help of Professors A. de Meijere, E. Osawa, F. Diederich, C. Thilgen, W. T. Borden, J. Cioslowski and H. Kuzmany in the search for coauthors is gratefully acknowledged. I am deeply obliged to my colleague, Dr. K. S. Nowinski, for designing the cover picture. On the other hand, I owe a deep apology to the authors of many interesting papers on strained hydrocarbons which could not be presented in this book or were insufficiently covered due to space limitations.

The question: 'To what extent can a bond be distorted without being broken?' is fascinating. This book is devoted to the presentation of distorted hydrocarbons. It is an effort to counteract, in this limited volume, overspecialization by showing not only syntheses, physicochemical studies and theoretical calculations of these molecules, but also the prospects of their applications. Strained molecules are

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exciting objects for studies *per se*. With several novel hypothetical molecules waiting to be synthesized on the one hand, and with the possibility of obtaining fascinating supramolecular complexes with distorted hydrocarbons as building blocks on the other, this domain will remain enthralling.

Warsaw, January 2009 *Helena Dodziuk*

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ISBN: 978-3-527-31767-7

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ISBN: 978-3-527-31767-7