351
Topics in Current Chemistry

Aims and Scope

The series Topics in Current Chemistry presents critical reviews of the present and future trends in modern chemical research. The scope of coverage includes all areas of chemical science including the interfaces with related disciplines such as biology, medicine and materials science.

The goal of each thematic volume is to give the non-specialist reader, whether at the university or in industry, a comprehensive overview of an area where new insights are emerging that are of interest to larger scientific audience.

Thus each review within the volume critically surveys one aspect of that topic and places it within the context of the volume as a whole. The most significant developments of the last 5 to 10 years should be presented. A description of the laboratory procedures involved is often useful to the reader. The coverage should not be exhaustive in data, but should rather be conceptual, concentrating on the methodological thinking that will allow the non-specialist reader to understand the information presented.

Discussion of possible future research directions in the area is welcome.

Review articles for the individual volumes are invited by the volume editors.

Readership: research chemists at universities or in industry, graduate students.

More information about this series at
http://www.springer.com/series/128

Barbara Kirchner
Editor

Electronic Effects in Organic Chemistry

With contributions by

C.B. Aakeröy · K. Ansorg · P.W. Ayers · J. Becker · M. Brehm · M. Brüssel · E. Echegaray · B. Engels · K. Epa · C. Grebner · A. Guevara-García · O. Hollóczki · S. Jenkins · B. Kirchner · S.R. Kirk · W. Lee · S.B.C. Lehmann · L. Nyulászi · A. Paasche · A.S. Pensado · M. Schöppke · T.C. Schmidt · A. Stark · A. Toro-Labbe

Springer

Editor
Barbara Kirchner
Mulliken Center for Theoretical Chemistry
Institut für Physikalische und Theoretische Chemie
Universität Bonn
Bonn
Germany

ISSN 0340-1022 ISSN 1436-5049 (electronic)
ISBN 978-3-662-43581-6 ISBN 978-3-662-43582-3 (eBook)
DOI 10.1007/978-3-662-43582-3
Springer Heidelberg New York Dordrecht London

Library of Congress Control Number: 2014952317

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Preface

A wide range of keywords can be drawn from the topic "electronic effects in organic chemistry" since a lot of topics are connected with this area. While it is simple to define organic chemistry – see any textbooks on general chemistry – it is much more difficult to define electronic effects, especially if we want to avoid simply repeating the terms "effects which are governed by electrons". What can be considered as such electronic effects? All consequences concerning changes caused by the (valence) electrons of organic molecules?

This volume deals with the concepts of electronic structure and associated methods in the context of organic chemistry and provides some answers to the questions above. As all authors are considering some kind of electronic effects, the main emphasis of the book lies in theoretical contributions, because one of the most important sections in theoretical chemistry is electronic structure theory. Nevertheless, important experimental work is highlighted or reviewed at the appropriate position. Hydrogen bonding always plays an important role when it comes to electronic effects, and throughout the book hydrogen bonding always emerges on the surface or plays an indirect role.

The volume begins with a contribution by Oldamur Hollóczki and László Nyulászi on the hot topic of carbenes from ionic liquids, which is also the title of their chapter. It deals with the fact that within ionic liquids–although their direct detection has been impossible so far–carbenes can be accessed by deprotonation of the cation at the appropriate position. This opens the possibility to use ionic liquids as, e.g. organocatalysts, which makes their investigation even more exciting. In the next chapter, Guevara-García et al. elaborate on conceptual density functional theory, which is a very exciting development, in order to describe organic reactivity, and which is thus at the heart of the topic of this book. Instead of considering electron-following, the electron-preceding picture (described by the stress tensor) identifies favourable changes in the electronic structure. Bernd Engels and co-workers review the application of a multi-scale method, namely QM/MM (quantum mechanics/molecular modelling), – which has been mainly applied to biochemical problems – to organic chemistry questions. With regard to organic

reactions, it is important to stress that most of these reactions are carried out in a condensed phase environment, or via complex interactions between the substrate and, for example, a catalyst, which renders the use of such methods – describing the electronic structure at least partly – indispensable. Hydrogen bonding in supramolecular assemblies is one the main origins of the control mechanisms as discussed by Aakeröy and Epa. The authors conclude that p*K*a values are less practical for retaining information whenever different functional groups are involved. They suggest the employment of molecular electrostatic potential surfaces for guiding the synthesis of binary and ternary co-crystals. The same difficulty in the context of ionic liquids and their mixtures, namely the reasonable description of hydrogen bonding, is highlighted in the final chapter by Stark and co-workers.

As editor of the volume, I hope this collection of fine chapters reflects the importance of theoretical methods and conceptual work in this interesting field of "electronic effects in organic chemistry" in a broad review style, while at the same time highlighting possible future directions. I would like to thank Prof. em. Dr. Dr. h.c. Sigrid Doris Peyerimhoff, Prof. Dr. Stefan Grimme and also my group members for fruitful discussions. To all the contributing authors I am indebted for providing this volume with such excellent and thorough chapters, and, finally, I would also like to thank the contributing authors for their patience.

Bonn, Germany
August 2013

Barbara Kirchner

Contents

Carbenes from Ionic Liquids 1
Oldamur Hollóczki and László Nyulászi

QM/MM Investigations Of Organic Chemistry Oriented Questions . . . 25
Thomas C. Schmidt, Alexander Paasche, Christoph Grebner, Kay Ansorg, Johannes Becker, Wook Lee, and Bernd Engels

Electronic Stress as a Guiding Force for Chemical Bonding 103
Alfredo Guevara-García, Paul W. Ayers, Samantha Jenkins, Steven R. Kirk, Eleonora Echegaray, and Alejandro Toro-Labbe

Controlling Supramolecular Assembly Using Electronic Effects 125
Christer B. Aakeröy and Kanishka Epa

A Theoretical and Experimental Chemist's Joint View on Hydrogen Bonding in Ionic Liquids and Their Binary Mixtures 149
Annegret Stark, Martin Brehm, Marc Brüssel, Sebastian B.C. Lehmann, Alfonso S. Pensado, Matthias Schöppke, and Barbara Kirchner

Index 189