Challenges and Advances in Computational Chemistry and Physics

Volume 20

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Boron

The Fifth Element

Springer

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Foreword

One way to bring order into the vast body of knowledge chemists keep accumulating since centuries is to group it neatly by element. Boron, "the fifth element", is one where this approach makes much sense, because its chemistry is rather unique and set apart from that of its neighbours in the periodic table. Boron chemistry is not self-contained; however, there is much potential for cross-fertilisation with other areas, and occasional "spin-offs" can have tremendous impact, as for instance with hydroboration or cross-coupling reactions in synthetic organic chemistry. It is thus useful to have the progress in the field reviewed regularly. The present monograph edited by Drahomír Hnyk and Michael McKee serves precisely this purpose, providing a snapshot of current research in the vibrant area that boron chemistry continues to be.

This chemistry is governed by the electron deficiency of boron. Diborane and its family members, the polyhedral boranes, are the epitomes of multicenter bonding. This type of bonding in turn gives rise to characteristic structural features, exemplified in the preference for clusters with shared polyhedra. In view of the rich and diverse structural chemistry that ensues, it is not surprising that structure and bonding are recurring themes throughout this book.

Another recurring theme is the concert of theory and experiment, teaming up to elucidate the details of structure, bonding and reactivity. Chemistry of boron and the boranes is an ideal playground for quantum-chemical methods. In the absence of heavy elements, a non-relativistic treatment is usually appropriate, so that "off-the-shelf", black-box methods and user-friendly software can be applied rather routinely. It also allows description and interpretation of the results in the language of molecular orbital theory. Many of the basic building blocks in boron chemistry are small enough to be treated with the most sophisticated ab initio methods, which is to say virtually exactly. This in turn allows more approximate methods, such as those mushrooming from the fertile field of density functional theory (DFT), to be reliably calibrated and to be applied to more complex systems such as large metallaboranes. If chosen properly, computational tools can provide answers at a confidence level that rivals those of established experimental techniques. The usefulness and importance of theoretical modelling tends to grow with the ever-increasing

availability of computer power. In fact the largest part of this book is devoted to quantum-chemical applications and the new insights they have provided.

I have been fortunate to start my career in this field, computational boron chemistry, under the guidance of Paul Schleyer. An organic chemist by training and reputation, he did not care about the presence or absence of carbon in a compound as long as its chemistry was interesting. After very fruitful application of the emerging tools to calculate NMR parameters to carbocations in the 1980s, it was only logical for him to have the same methods applied to boron compounds. This has developed into one of the many areas in chemistry where Paul Schleyer has left a lasting mark. He had moved on since then, restlessly working on other topics, but has always kept an interest in boron chemistry. He had agreed to write the introduction to this monograph, but his sudden death in November 2014 prevented him from doing so. I am grateful to the editors for their decision to dedicate this whole book in his memory.

The present monograph is a legacy in many ways. It brings together chapters by some of the towering pioneers in the field, on whose shoulders the coming generations of boron chemists can stand, complemented by contributions from younger scientists eager to carry on the torch. As expected for a vibrant research area, the topics covered are numerous and diverse.

In Chap. 1, Alexander Boldyrev takes us into the wonderful world of boron-based chains, rings, sheets and spheres, where the continuum between localised and delocalised bonding leads to unusual and intriguing phenomena such as fluxionality reminiscent of a "molecular Wankel motor". The mature area of structure elucidation by joint gas-phase electron diffraction and quantum-chemical modelling is reviewed by Drahomír Hnyk in Chap. 2. The vast terrain of metallaborane chemistry is charted by Bruce R. King in Chap. 3 with the help of DFT. Josep Oliva goes beyond ground-state calculations in Chap. 4, exploring absorption and fluorescence properties of octadecaborane and their subtle dependence on configuration ("Dr. Jekyll and Mr. Hyde"-versions of $B_{18}H_{22}$) and on exoskeletal substituents. In Chap. 5, Michael McKee recounts his attempts to elucidate the mechanism of a classical reaction, formation of the *closo*-dodecaborane dianion, through mapping the wonderfully complex potential energy hypersurface with DFT calculations. In Chap. 6, John Kennedy embarks on a journey from the classic *nido* and *arachno* boranes via fused cluster compounds to ever more complex macropolyhedral boron species, all the way to "megaloboranes", that is, big nano-sized globules that are presented as challenging, but potentially rewarding targets for future synthesis. In Chap. 7, Pattath Pancharatna develops an understanding of the bonding in such macropolyhedral boranes based on their electronic structures, as summarised in a set of refined electron-counting rules. Chapter 8 by Narayan Hosmane illustrates how the usefulness of the "classic" hydroboration and Suzuki cross-coupling reactions can be further improved by advances in nanocatalysis. In Chap. 9, Martin Lepšík shares his insights on how seemingly weak intermolecular interactions can open up new avenues in boron chemistry, notably in relation to materials science and biomolecular or medicinal chemistry.

Through this collection of representative snapshots, the monograph conveys a good idea of the recent progress that has been made in the field of boron chemistry.

The book should be appealing and interesting for experimental and computational chemists alike. Providing highlights from the present state-of-the-art in boron chemistry, and an overview of the frontiers that are waiting to be pushed ever further, I am sure it will be a valuable source of information, but also of inspiration for further work in the years to come.

St Andrews, UK Michael Bühl
May 2015

Preface

Professor Paul von Ragué Schleyer, who passed away on November 21, 2014, was a giant among modern scientists. He may be considered as a pioneer of computational chemistry as a whole. His imprint will be felt for generations, undoubtedly also in boron chemistry. Indeed, he won the 1996 IMEBoron Prize for Computational Boron Chemistry. Through the years, his group has been at the forefront in developing tools and applying them to the study of unusual molecules. From the first synthesis of adamantane in 1957, Paul has been on the hunt for usual molecules. His most recent quest has been for planar tetra-coordinate carbon and then later boron in a planar environment. One might argue that his extensive work on the "The Nonclassical Ion Problem" (i.e. the norbornadienyl cation) dovetailed smoothly into his studies of boranes and carbocations since they are isoelectronic. Paul obligingly agreed to write the introduction to this book. Unfortunately he passed away before he could complete the task. We think he would be very much pleased by the diversity and quality of the chapters herein. A fair number of the contributors have collaborated either directly or indirectly with his group. Therefore, we are proud to dedicate this book to his memory.

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May 2015

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