Preface

In the first part of the 20th century chemists were able to produce a wealth of data concerning structure, reactivity and properties of organic molecules. In order to organize these data a number of concepts were introduced such as hybridization, resonance, electronegativity, aromaticity and homoconjugation, to name only a few. These concepts were underpinned by simple one-electron theoretical models on the basis of valence and molecular orbital theory. Although these models had to be based on simplifications such as neglecting the σ system in planar π electron systems or electron−electron interactions, they were very successful in rationalizing the concepts.

The end of the 20th century witnessed fast improvements in computer hardware and the associated development of efficient mathematical algorithms to solve quantum chemical problems. This progress allowed introducing efficient programs to calculate molecular properties in an accurate way, which in turn widened the view of chemists. The achievements in theory were augmented by the development of new spectroscopic techniques, which allowed detecting short-lived species, to investigate radicals and organic ions and to study unstable molecules at low temperatures. The accurate data available by calculations allowed a deeper understanding of long-known concepts and to introduce new ones in order to describe the effects of $\sigma-\pi$ interactions or excited states of molecules. Unfortunately, the high accuracy of data available through calculations frequently led to the habit of not explaining these data in terms of simple concepts but to merely believe them. Thus, the better data has often not been used to gain a deeper understanding of long known concepts or to introduce new ones.

In this book we describe various concepts of bonding by first presenting the experimental results, which led to their postulation, followed by simple MO arguments based on perturbation theory within a one-electron model. The resulting picture is refined by further experimental data and results based on *ab initio* calculations.

The content of the book is based on graduate courses in physical organic chemistry taught at our universities and abroad. The book was written for students at the advanced undergraduate level and the graduate level. A good knowledge of standard first year courses in organic and theoretical chemistry are recommended.

For those readers interested in a more detailed account of theoretical models at different levels of sophistication cited throughout the chapters we refer to Chapter 6. In this section we also briefly discuss qualitative rules for the interactions of localized orbitals, the orbitals

of cyclopropane and cyclobutane as well as ways in which to transform canonical MOs into localized MOs. We also give detailed information about spectroscopic methods such as PE and UV-Vis spectroscopy and the interpretation of those spectra.

The first chapter reaches from simple conjugated olefins and alkynes to complex π electron systems such as graphene, fullerenes and *Möbius* rings. Conjugated rings with $(4n)$ and $(4n+2)\pi$ electron systems and the various criteria for aromaticity are at the center of attention in this chapter.

In the second chapter we present different through-space effects between π electron units or non-bonded electron pairs. Some of these give rise to homoconjugation, spiroconjugation and homoaromaticity.

In Chapter 3 donor-acceptor complexes and various examples of weak non-covalent interactions between aromatic rings are given. These interactions have led to a rich host-guest chemistry resulting in rotaxanes, catenanes and complexes with fullerenes.

In Chapter 4 we demonstrate how the concept of through-bond interaction between π electron units, non-bonded electron pairs and other functional groups is valuable in understanding the PE spectra, electronic absorption spectra, and other properties of molecules.

In Chapter 5 the phenomenon of positive hyperconjugation in neutral molecules, cations, and radicals as well as the concept of negative hyperconjugation in neutral molecules and anions are presented. The manifestation of these effects is discussed mainly on the basis of molecular structures and reactivities. A large part of the chapter is devoted to anomeric effects.

The references at the end of each chapter allow for the reader to quickly get acquainted with the field. Thus, this book should also be of interest to research chemists not yet familiar with the most recent concepts.

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