Aromaticity and Other Conjugation Effects

This is a superb book that covers exactly what the title claims, and it does so in a thorough, highly organized, and readable style. The first author, Professor Rolf Gleiter, at the University of Heidelberg, has been a major contributor to this field for more than 40 years and is intimately familiar with both its historical development and its current state. In each chapter, the authors systematically review landmark advances in the field, generally beginning with key experimental observations and then explaining them by simple molecular orbital arguments based on perturbation theory within a one-electron model, e.g., Hückel MO theory and qualitative orbital interaction diagrams. The overall picture is then further refined by the presentation of additional experimental data and results from ab initio calculations.

The didactic, story-telling nature of the writing derives from Professor Gleiter's many years of teaching this subject to organic chemistry students and makes this an excellent, up-to-date text book for any professors who might like to teach a similar course. For professors who teach broader courses in physical organic chemistry, the book can serve as a gold mine of ready-made lecture notes on a wide range of special topics, with a full complement of literature references for each. All the key papers and virtually every review article and previous book on the topics covered are included in the bibliography, which cites more than 2000 publications. Professional chemists who have already completed their academic training but want to learn more about aromaticity and other conjugation effects will find no better source than this self-contained volume. Experts in the field should consider this book a must for their personal collections.

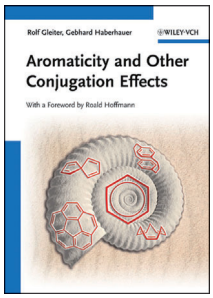
Every chemistry library should own it. Students of organic chemistry who are newcomers to this field and want to know more will find everything they need in this authoritative book. The paperback version is affordable to students at less than half the price of the hard cover book. An appendix with character tables for selected symmetry groups and twelve pages of index are helpful; inclusion of an author index would have made the book even better.

A familiarity with the principles of molecular orbital theory and the Hückel MO method is a prerequisite for readers who want to get the most out of this book. Expertise in quantum mechanics is not essential, but those who have never taken a course in the subject will find themselves disadvantaged. A standard one-year undergraduate course in organic chemistry is the only other background that the authors assume. The final chapter of the book offers a 48-page review of the theoretical methods used throughout the book, starting from the Schrödinger equation, and progressing through the LCAO-MO method, Hückel and extended Hückel theory, ab initio Hartree–Fock procedures, semiempirical SCF methods, and the various ways theoreticians have dealt with the problem of electron correlation, including the popular density functional approach. Readers seeking a refresher will appreciate this section of the book, and experts can skip it, but the uninitiated will find it rough sledding. The chapter ends with a clear discussion about qualitative rules for the interactions of localized orbitals and a primer on spectroscopic methods for detecting conjugation effects. Experimental results from UV/Vis spectroscopy and photoelectron spectroscopy appear again and again throughout the book, and there is no one better qualified than Professor Gleiter, the world's foremost champion of photoelectron spectroscopy, to enlighten those who are unfamiliar with this powerful technique for probing the molecular orbitals of molecules.

The main body of the book begins with simple conjugated polyenes and polyynes, moves on to cyclic conjugation, and spends a long time discussing aromaticity and the various criteria that have been used to try to quantify it. The section on why benzene adopts D_{6h} instead of D_{3h} symmetry is one of the clearest explanations I have ever read. Chapter 1 ends with more than 50 pages on polycyclic aromatic hydrocarbons, graphene sheets, bowl-shaped (geodesic) polyarenes and fullerenes, and, finally, with Heilbronner–Möbius rings and ribbons. As in all the chapters, the presentation is rich in graphics, including many spectra, data tables, and figures reproduced with permission from the original literature. The absence of color graphics is unfortunate.

Abbreviated synthesis schemes are sprinkled here and there, which many readers will appreciate, but the focus is firmly on the relationship between the structure and the electronic properties of molecules.

Chapter 2, on through-space interactions, traces the roots of the homoconjugation concept to classic experiments on the cholesteryl cation in the 1940s and describes how the notion of homoaromaticity subsequently came to be recognized. The treatment of transannular effects is not confined to hydrocarbon systems but also includes fundamental studies on interactions of non-bonding electron pairs on divalent sulfur and tertiary nitrogen atoms with transannular carbonyl groups. Detailed discussions about "proton sponges" and spiroconju-



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gation round out the chapter. The venerable subject of through-space interactions in donor–acceptor (D–A) complexes between planar arenes is treated separately in Chapter 3. First observed as charge-transfer bands in UV/Vis absorption spectroscopy, other consequences of such D–A interactions show up in crystal packing motifs, and they have been exploited with great success for the synthesis of rotaxanes and catenanes. Chapter 3 ends with an excursion into the realm of convex–concave interactions involving ball-, bowl-, and belt-shaped conjugated systems. Biochemists concerned with π-stacking, energy transfer, and electron transfer between aromatic rings will find this chapter particularly useful.

In many cases, through-bond interactions are larger than through-space interactions, even over several bond lengths, on account of direct σ-bonding, and these interactions are discussed in Chapter 4. As in the earlier chapters, the scope of the treatment includes not only hydrocarbon π-systems but also interactions involving heteroatom non-bonding electron pairs. The unique capability of certain rings and cages to electronically connect distant electron pairs is especially intriguing.

Chapter 5 deals with hyperconjugation, an important stereoelectronic effect that has been used to explain various properties and reactivities of molecules since the 1930s. A distinction is made between positive and negative hyperconjugation, and each class is then divided into different types depending on which orbitals are involved in the interaction. Natural Bond Orbital (NBO) analyses reveal trends in the hyperconjugative abilities of various donor and acceptor orbitals.

By compiling decades of lecture notes and transforming them into a published book, the authors have performed a tremendous service to the organic chemistry community. We concur enthusiastically with Professor Roald Hoffmann, who says in the Foreword, "*This volume provides true understanding, which is the best thing one can say of any book*."

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