PREFACE

This volume on *Modern Electronic Structure Theory and Application in Organic Chemistry* focusses on the use of quantum theory to understand and explain experiments in organic chemistry. High level *ab initio* calculations, when properly performed, are useful in making quantitative distinctions between various possible interpretations of structures, reactions and spectra. Chemical reasoning based on simpler quantum models is, however, essential to enumerating the likely possibilities. The simpler models also often suggest the type of wave function likely to be involved in ground and excited states at various points along reaction paths. This preliminary understanding is needed in order to select the appropriate higher level approach since most higher level models are designed to describe improvements to some reasonable zeroth order wave function.

In the first chapter in this volume, Zimmerman discusses a wide variety of thermal and photochemical reactions of organic molecules. Quantum theory is used mostly as a qualitative tool to explain facts taken from experiments. The next two chapters focus in greater depth on two particular classes of reactions. Gronert discusses the use of *ab initio* calculations and experimental facts in deciphering the mechanism of β-elimination reactions in the gas phase. He gives a detailed review of the experimental facts, the important questions they raise, and the answers obtained from high level calculations. Bettinger *et al.* focus on carbene structures and reactions with comparison of the triplet and singlet states. This chapter also contrasts the results found by many of the standard *ab initio* methods with the large body of experiments on carbenes. Next, Hrovat and Borden discuss more general molecules with competitive triplet and singlet contenders for the ground state structure. Again, the focus is on experimental facts, qualitative reasoning and quantitative calculations with the most appropriate *ab initio* methods.

None of the preceding chapters describe the theoretical methods in detail. All of the methods used have already been treated in a more elaborate fashion in the book, *Modern Electronic Structure Theory*, edited by David R. Yarkony. These chapters illustrate the use of these standard *ab initio* methods, coupled with reasoning based on simple quantum models, to treat problems in organic chemistry.

The final three chapters are somewhat different in nature. Treatment of the large variety of possible wave functions for excited states is not a routine problem. Reliable "black-box" methods do not yet exist. Cave explains the difficulties and considerations involved with many of the methods and illustrates the difficulties by comparing with the UV spectra of short polyenes.

Jordan *et al.* discuss long-range electron transfer using model compounds and model Hamiltonians. For compounds of this size, *ab initio* calculations are still not feasible for studying the mechanism of electron transfer. Hence, the approach follows the long tradition of semi-empirical theory applied to organic molecules.

Finally, Hiberty discusses the breathing orbital valence bond model as a different approach to introducing the crucial $\sigma\pi$ correlation that is known to be important in organic reactions (see, e.g. W.T. Borden and E.R. Davidson, *Acc. Chem.* Res. **29**, 67 (1996)). This concept is illustrated by looking at the bond energies of very small inorganic and organic molecules.

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