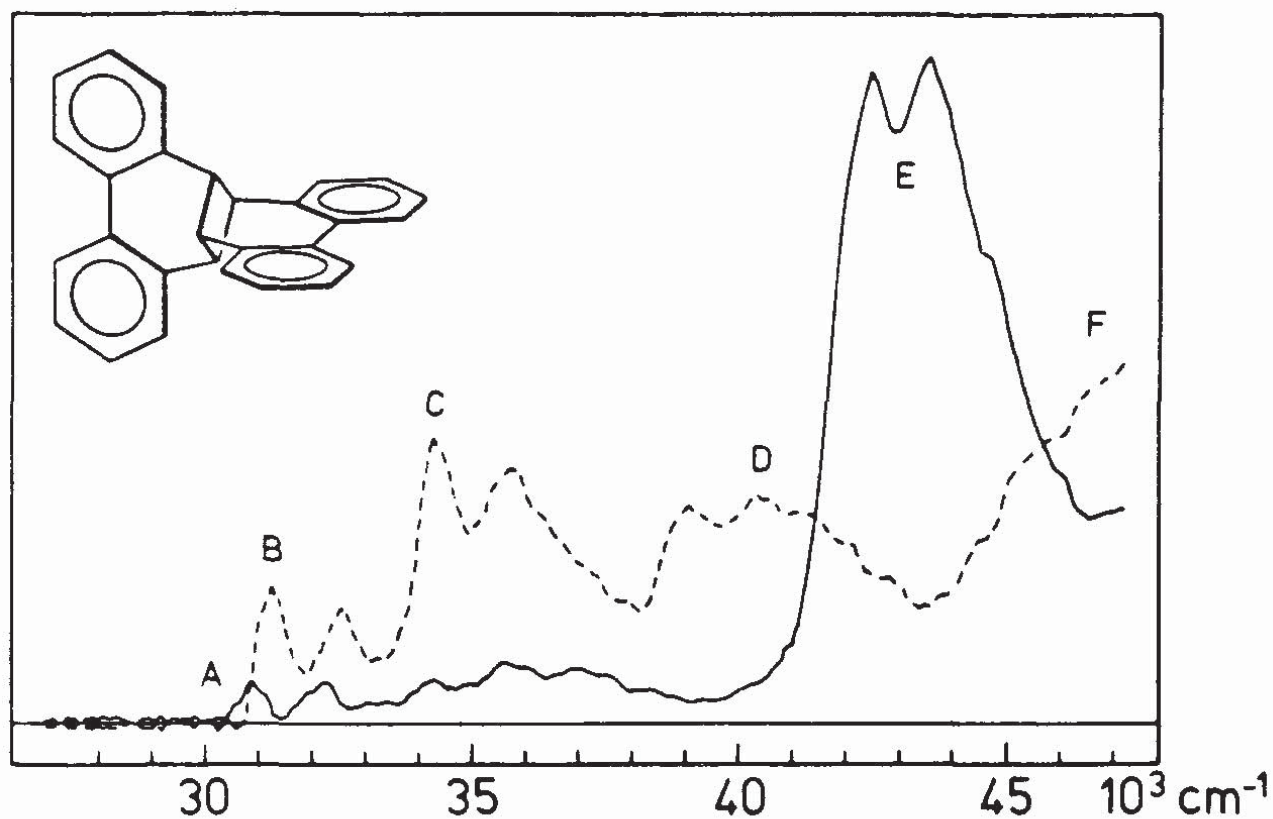


INTRAMOLECULAR INTERACTIONS  
IN  
SOME HYDROCARBON MODEL SYSTEMS



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"Quantum chemistry is faced with two fundamental problems: how to reduce chemistry, in a practical way, to numerics; and how to avoid doing so and still benefit from theory."

(Wittel & McGlynn 1977)

## 1. Introduction

During the last few decades and in particular since the success of the Woodward-Hoffmann rules (1965, 1969) qualitative molecular orbital (MO) theory has become an indispensable tool for the organic chemist. About 20 years ago the following picture of the orbital structure of organic molecules had gradually evolved in the minds of experimentalists (Hoffmann 1971): Assume an underlying framework of localized  $\sigma$  bond orbitals; on top of that place, as needed, delocalized  $\pi$  electron systems and "lone pairs"; if several non-conjugated functional groups or chromophores occur in one molecule think of them as possessing orbitals localized within each such group; these orbitals or groups of orbitals, localized to a group, perhaps delocalized within that group, confer on that functional group its characteristic physical and chemical properties. But in more recent years this simplistic prescription has undergone a number of refinements, in particular with respect to our ways of thinking about the interaction of localized sets of orbitals, or chromophores, or functional groups. For example, two of the most widely accepted notions are those of "through bond" and "through space" interaction (Hoffmann, Imamura & Hehre 1968, Heilbronner & Schmelzer 1975). This development has been reviewed comprehensively by Hoffmann (1971), Gleiter (1974), Wittel & McGlynn (1977), Paddon-Row (1982) and Martin &

Mayer (1983).

The interaction between two identical subunits is of particular interest since it can usually be described in terms of the first order energy splitting between two levels which would have been degenerate in the absence of any interaction. This type of splitting is the primary measure of interaction in quantum mechanics and can frequently be observed directly by spectroscopic methods. In this treatise, we shall study the intramolecular interactions between identical fragments for a number of hydrocarbon model systems, thereby learning not only about the mechanism of the interactions but also gaining new information about the individual functional groups or chromophores.

Five model cases have been selected which demonstrate a variety of interesting hydrocarbon functional groups and interaction mechanisms. In chapter 2 an analysis is presented of the conformation dependent interaction between cyclopropane Walsh type orbitals in bicyclopropyl, while in chapter 3 the interaction between the formally separated double bonds in simple 3,3'-bicyclopropenyls is the main topic. These investigations are supported by the results of photoelectron (PE) spectroscopy, using Koopmans' approximation (1934; for a discussion see, e.g., Wittel & McGlynn 1977, Spanget-Larsen 1984). In chapters 4 and 5 we shall consider the excited states of some benzenoid chromophores, first for  $D_{2d}$  spirobifluorene and the corresponding "phenanthrene dimer", then for a series of [2<sub>n</sub>]cyclophanes. We shall attempt to understand the main features of the electronic absorption spectra of these compounds in terms of the interactions between the non-conjugated half-chromophores, thereby referring (in chapter 4) to polarization data determined in stretched polyethylene by the TEM pro-

cedure (Thulstrup et al. 1970, 1976, 1980, 1982). Finally, in chapter 6, we shall study intramolecular interactions in the recently synthesized syn-sesquinorbornene ring system. In this case, electronic spectroscopy is less revealing; we shall relate our discussion to the controversial structural and chemical properties of norbornene and syn-sesquinorbornene. With few exceptions, the molecular systems and topics outlined here have been the subject of previous investigations; the analysis contained in the following chapters includes a critical discussion of these contributions, with emphasis on those aspects where we arrive at a different point of view.

The size of most of these hydrocarbons makes accurate non-empirical calculations prohibitively expensive. We shall consider the results of approximate semi-empirical procedures such as PPP (Pariser & Parr 1953, Pople 1953), EH (Hoffmann 1963), EWMO (Linderberg & Öhrn 1973, Spanget-Larsen 1973, 1974), MINDO/3 (Bingham et al. 1975, Bischof 1976c) and MNDO (Dewar & Thiel 1977, Bischof & Friedrich 1982). However, the emphasis is put on a conceptual analysis in terms familiar to most organic chemists. The aim of this investigation is to determine the most important factors that influence the spectral, structural and chemical observables and try to construct simple arguments which are transferable from molecule to molecule. The lack of mathematical and physical rigour is compensated for by the application of powerful empirical correlation techniques. Hence, the resulting models are half theory, half experiment.

This approach is not likely to take us to the frontiers of quantum mechanics. Rather, the work presented in this treatise belongs to the field of organic chemistry, which has a strong tradition for characterizing very complex chemic-

al phenomena in terms of a few descriptive parameters (or "effects"). The development of simple conceptual models involves a distinction between those factors which are essential and those which can be left out. This process is intellectually stimulating; in fact, 'conceptual modeling' comes close to whatever we wish to imply by the word 'understanding'.



## 7. Summary

This treatise is concerned with some aspects of the question of how one part of a molecule affects another, a central theme in modern chemistry (see, e.g., Klessinger 1982, Morrison & Boyd 1983). The investigation focuses on the electronic interaction between identical subunits in a number of representative hydrocarbon model systems, which display some important types of functional groups and interaction mechanisms.

Organic compounds of interest are generally so large that the application of accurate quantum chemical methods is too expensive. The aim of this study is to establish useful approximate models which at a simple conceptual level provide an adequate description of the intra-molecular interactions and their most important structural, spectroscopic, or chemical consequences. The most successful general approach in this area is based on the molecular orbital approximation, and qualitative orbital arguments are applied throughout this work. However, it must be emphasized that the 'molecular orbital' is a model concept; it has no physical existence and is no observable (e.g., Spanget-Larsen 1984).

For practical purposes, intra-molecular electronic interactions are traditionally classified as electrostatic, such as exciton and charge-resonance interactions, or conjugative,

i.e., those which within the orbital picture are transmitted via orbital overlap. The conjugative interactions are conveniently subdivided into direct through-space and indirect through-bond varieties. In this investigation, all these model concepts are applied within the framework of simple descriptive or semi-quantitative analyses. The results of these analyses are substantiated by the results of more sophisticated standard calculational procedures, which are critically discussed.

One of the most interesting hydrocarbons is cyclopropane, which can be said to exhibit properties intermediate between those of saturated and unsaturated compounds. An excellent model compound for investigation of the electronic structure of the cyclopropane ring is bicyclopropyl, where important conclusions can be drawn from investigation of the conjugative interaction between the two linked cyclopropyl groups. As discussed in **chapter 2**, the simple tangential Walsh orbital picture for cyclopropane must be modified to incorporate around 20 per cent radial character in order to account for the photoelectron (PE) spectroscopic data for bicyclopropyl and its homologues. The three-membered cyclopropane ring can thus be considered to occupy a natural position between, on one side, the "cycloethane ring" (i.e., the olefinic double bond) where tangential and radial (i.e.,  $\pi$  and  $\sigma$ ) contributions are separated by symmetry, and, on the other side, the cyclobutane and higher cycloalkane rings with complete admixture of tangential and radial components. As a byproduct, the analysis leads to tentative conclusions concerning the preferred conformations of bicyclopropyls in the gas phase and leads to a new interpretation of the observed PE spectrum of bicyclopropyl.

3,3'-Bicyclopropenyl, a tetradehydro derivative of bicyclopropyl and a valence isomer of benzene, is an ideal model

compound for investigation of the interaction between two formally separated ethylenic double bonds. Simple model considerations and the application of PE spectroscopy, as described in **chapter 3**, indicate that through-bond coupling leads to an effective splitting by 1.2-1.5 eV of the two  $\pi$  type orbitals in 3,3'-bicyclopropenyls. This splitting is twice as large as previously assumed (Greenberg & Liebman 1981) and demonstrates the significance of hyperconjugative effects; other cases are discussed in **chapters 5 and 6**. In addition, the analysis of the PE data leads to suggestions concerning the preferred conformation of 3,3'-dimethyl-3,3'-bicyclopropenyl in the gas phase; as in the bicyclopropyl case, the preference of a gauche conformation is indicated.

Further examples of long-range interactions between  $\pi$  systems are presented in **chapters 4 and 5**, in which analyses of the excited electronic states of several compounds containing benzenoid chromophores are given. To a first approximation, 9,9'-spirobifluorene and the corresponding "phenanthrene dimer" discussed in **chapter 4** can be considered as containing weakly conjugated identical half-chromophores, and a description in terms of exciton and charge-resonance contributions is illustrative. In contrast to previous assumptions (e.g., Sagiv et al. 1977), the importance of low energy charge-resonance configurations is indicated. This study is supported by the results of polarized absorption spectroscopy in a stretched polyethylene matrix. In the case of the series of  $[2_n]$ cyclophanes considered in **chapter 5**, transannular interactions are dominated by strong conjugative effects. A systematic analysis indicates that experimental trends can be rationalized under the assumption of a delicate balance between through-space and through-bond effects, leading, e.g., to an explanation of the near-constancy of the onset of the absorption spectra and a reassignment of low energy triplet states.



Finally, in **chapter 6**, intra-molecular interactions in syn-sesquinorbornene are investigated. The exceptional reactivity and stereochemistry of the norbornene ring system have puzzled chemists for decades, but investigation of syn-sesquinorbornene with two co-operating norbornene fragments should help to elucidate the effects prevailing in this system. Particular attention is given to the possible origins of the observed ground and excited state distortions of the syn-sesquinorbornene double bond, leading to a straightforward rationalization in terms of hyperconjugative effects. In the light of these results, a discussion of the norbornene "x" factor is presented. This was introduced by Huisgen et al. (1980, 1981) to account for the spectacular exo reactivity of the norbornene double bond. Recent suggestions by Rondan et al. (1982) and Houk et al. (1983) are also considered.

The examples discussed in this work illustrate the usefulness of simple model approaches to complex problems in organic chemistry and spectroscopy. Essential advantages are obtained by the performance of a basic conceptual analysis, which helps to concentrate the mind on fundamental aspects and to interpret the numbers produced by computers in a form which can be communicated to the practising chemist. Numerous routine computational procedures are now readily available, but in spite of great sophistication many of the most popular of these procedures show serious shortcomings; for example, a number of systematic failures of the so-called NDO methods can be traced to the inadequate representation of orbital overlap effects, as frequently observed in this paper.

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