ORBITAL
INTERACTION
THEORY OF
ORGANIC
CHEMISTRY

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ORBITAL INTERACTION THEORY OF ORGANIC CHEMISTRY

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PREFACE

The premise on which this text is based is that the vast majority of chemical phenomena may be qualitatively understood by the judicious use of simple orbital interaction diagrams. The material borrows heavily from the pioneering work of Fukui [1], [2], Woodward and Hoffmann [3], Klopman [4], Salem [5], Hoffmann [6], and many others whose work will be acknowledged throughout. Parts of the text are modeled most closely on the excellent book by Fleming: *Frontier Orbitals and Organic Chemical Reactions* [7], from which a number of illustrative examples are extracted. If there is uniqueness to the present approach, it lies in the introduction of the α and β of Simple Hückel Molecular Orbital theory as reference energy and energy scale on which to draw the interaction diagrams, mixing σ and σ^* orbitals and nonbonded orbitals with the usual π orbitals of SHMO theory on the same energy scale. This approach is difficult to justify theoretically but it provides a platform on which students can construct their interaction diagrams and is very useful in practice. Numerous illustrations from the recent literature are provided.

The book is intended for students of organic chemistry at the senior undergraduate and postgraduate levels. All reactions of organic compounds are treated within the framework of generalized Lewis acid–Lewis base theory, their reactivity being governed by the characteristics of the frontier orbitals of the two reactants. All compounds have occupied molecular obitals and so can donate electrons, i.e., act as bases in the Lewis sense. All compounds have empty molecular orbitals and so can accept electrons, i.e., act as acids in the Lewis sense. The "basicity" of a compound depends on its ability to donate the electron pair. This depends on the energy of the electrons, the distribution of the electrons (shape of the MO) and also on the ability of the substrate to receive the electrons (on the shape and energy of its empty orbital). The bas-

icity of a compound toward different substrates will be different, hence a distinction between Lowry–Bronsted basicity and nucleophilicity. A parallel definition applies for the ''acidity'' of the compound. The structures of compounds are determined by the energetics of the occupied orbitals. Fine distinctions, such as conformational preferences, can be made on the basis of minimization of repulsive interactions and/or maximization of attractive interactions between the frontier localized group orbitals of a compound. All aspects are examined from the point of view of orbital interaction diagrams from which gross features of reactivity and structure flow naturally. The approach is qualitatively different from, and simpler than, a number of alternative approaches, such as the VBCM (*valence bond configuration mixing*) model [8], and OCAMS (*orbital correlation analysis using maximum symmetry*) approach [9], [10].

The organization of the text follows a logical pedagogical sequence. The first chapter is not primarily about ''orbitals'' at all, but introduces (or recalls) to the student elements of symmetry and stereochemical relationships among molecules and among groups within a molecule. Many of the reactions of organic chemistry follow stereochemically well-defined paths, dictated, it will be argued, by the interactions of the frontier orbitals. The conceptual leap to orbitals as objects anchored to the molecular framework, which have well defined spacial relationships to each other is easier to make as a consequence. Whether or not orbitals interact can often be decided on grounds of symmetry. The chapter concludes with the examination of the symmetry properties of a few orbitals which are familiar to the student.

The second chapter introduces the student to ''orbitals'' proper, and offers a simplified rationalization for why Orbital Interaction theory may be expected to work. It does so by means of a detailed derivation of Hartree–Fock theory making only the simplifying concession that all wavefunctions are real. Some connection is made to the results of *ab initio* quantum chemical calculations. A brief description of how to carry out these calculations using the GAUSSIAN system of codes is provided in Appendix A. Postgraduate students can benefit from carrying out a project based on such calculations on a system related to their own research interests. A few exercises are provided to direct the student. For the purpose of undergraduate instruction, this chapter may be skipped and the essential arguments and conclusions provided to the students in a single lecture as an introduction to Chapter 3.

Orbital Interaction theory proper is introduced in Chapter 3. The independent electron (Hückel) approximation is invoked and the effective one-electron Schrödinger equation is solved for the two-orbital case. The solutions provide the basis for the orbital interaction diagram. The effect of overlap and energy separation on the energies and polarizations of the resulting molecular orbitals are explicitly demonstrated. The consequences of 0–4 electrons are examined and applications are hinted at. Group orbitals are provided as building blocks from which the student may begin to assemble more complex orbital systems.

Chapter 4 provides a brief interlude in the theoretical derivations by examining a specific application of the two-orbital interaction diagrams to the description of σ bonds and their reactions.

In Chapter 5, conventional Simple Hückel Molecular Orbital (SHMO) theory is introduced. The Hückel "α" is suggested as a reference energy, and use of "$|\beta|$" as a unit of energy is advocated. Parameters for heteroatoms and hybridized orbitals are given. Finally, the interactive computer program, SHMO, a copy of which is provided with this book, is described in Appendix B.

Chapters 6–11 describe applications or orbital interaction theory to various chemical systems in order to show how familiar concepts such as acid and base strengths, nucleo- and electrophilicity, stabilization and destabilization, thermodynamic stability, and chemical reactivity may be understood.

Pericyclic reactions are described in Chapter 12 as a special case of frontier orbital interactions, i.e., following Fukui [1]. However, the stereochemical nomenclature, *suprafacial* and *antarafacial*, and the very useful general component analysis of Woodward and Hoffmann [3] are also introduced here.

Chapter 13 deals with orbital correlation diagrams following Woodward and Hoffmann [3]. State wave functions and properties of electronic states are deduced from the orbital picture, and rules for state correlation diagrams are reviewed, as a prelude to an introduction to the field of photochemistry in Chapter 14.

In Chapter 14, the state correlation diagram approach of the previous chapter is applied to a brief discussion of photochemistry in the manner of Dauben, Salem and Turro [11]. A more comprehensive approach to this subject may be found in the text by Michl and Bonacic-Koutecky [12], Turro [13], or Gilbert and Baggott [14].

Sample problems and quizzes, grouped by chapter, are presented in Appendix C. Many are based on examples from the recent literature and references are provided. Detailed answers are worked out for a few. These serve as further examples to the reader of the application of the principles of orbital interaction theory.

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December, 1993

ORBITAL INTERACTION THEORY OF ORGANIC CHEMISTRY

CONTENTS

12 PERICYCLIC REACTIONS 182

13 ORBITAL AND STATE CORRELATION DIAGRAMS 198

CHAPTER 1

SYMMETRY AND STEREOCHEMISTRY

PURPOSE

Symmetry is a concept that we all make use of in an unconscious fashion. We notice it every time we look in our bathroom mirror. We ourselves are (approximately) bilaterally symmetric. A reflected right hand looks like a left hand, a reflected right ear like a left ear, but the mirror image of the face as a whole, or of the toothbrush does not look different from the original. The hand, a *chiral* object, is distinguishable from its mirror image; the toothbrush is not. The toothbrush is *achiral*, and possesses a mirror plane of symmetry which bisects it. It would not surprise us if we were to inspect the two sides of the toothbrush and find them identical in many respects. It *may* surprise us to note that the two sides are distinguishable when held in the hand, i.e., in a chiral environment (the fingers hold one side and the thumb the other). However, the achiral toothbrush fits equally comfortably into either the right or the left hand. Chiral objects do not. They interact differently with other chiral objects and often the different interactions are known by separate words. When you hold someone's right hand in your right hand, you are *shaking* hands; when it is the other person's left hand in your right, you are *holding* hands. Similar properties and interactions exist in the case of molecules as well.

In this chapter we will familiarize ourselves with basic concepts in *molecular* symmetry [15]. The presence or absence of symmetry has consequences on the appearance of spectra, the relative reactivity of groups, and many other aspects of chemistry, including the way we will make use of orbitals and their interactions. We will see that the orbitals that make up the primary description of the electronic structure of molecules or groups within a molecule have a definite relationship to the three-dimensional structure of the molecule as de-

1

fined by the positions of the nuclei. The orientations of the nuclear framework will determine the orientations of the orbitals. The relationships between structural units (groups) of a molecule to each other can often be classified in terms of the symmetry that the molecule as a whole possesses. We will begin by introducing the basic terminology of molecular symmetry. Finally we will apply simple symmetry classification: to local group orbitals to decide whether or not interaction is allowed in the construction of molecular orbitals, to molecular orbitals in order to determine the stereochemical course of electrocyclic reactions and to help determine the principal interactions in bimolecular reactions, and to electronic states, in order to construct state correlation diagrams.

We begin by introducing molecular point groups according to the Schoenflies notation and assigning molecular and group symmetry following Jaffe and Orchin [16] where greater detail may be found.

DEFINITION OF A *GROUP*

A group, $G = \{. , . , . , . g_i , . , . , .\}$, is a set of elements related by an operation which we will call *group multiply* for convenience, and has the following properties:

1. The product of any two elements is in the set, i.e., the set is <u>closed</u> under group multiplication.
2. The associative law holds, e.g., $g_i(g_j g_k) = (g_i g_j)g_k$
3. There is a *unit* element, e, such that $eg_i = g_i e = g_i$.
4. There is an *inverse*, g_i^{-1}, to each element, such that $(g_i^{-1})g_i = g_i(g_i^{-1}) = e$. An element may be its own inverse.

MOLECULAR POINT GROUPS

A molecular point group is a set of symmetry elements. Each symmetry element describes an operation which when carried out on the molecular skeleton, leaves the molecular skeleton unchanged. Elements of point groups may represent any of the following operations:

1. Rotations about axes through the origin.

   C_n = rotation through $2\pi/n$ radians (in solids, n = 1, 2, 3, 4, and 6).

2. Reflections in a plane containing the origin (center of mass)

   σ = reflection in a plane

3. Improper rotations—a rotation about an axis through the origin followed

by a reflection in a plane containing the origin and perpendicular to the axis of rotation.

S_n = rotation through $2\pi/n$ radians followed by σ_h.

SCHOENFLIES NOTATION

E = identity

C_n = rotation about an axis through $2\pi/n$ radians. The *principal* axis is the axis of highest n.

σ_h = reflection in a horizontal plane, i.e., the plane through the origin perpendicular to the axis of highest n.

σ_v = reflection in a vertical plane, i.e., the plane containing the axis of highest n.

σ_d = reflection in a diagonal plane, i.e., the plane containing the axis of highest n and bisecting the angle between the two-fold axes perpendicular to the principal axis. This is a special case of σ_v.

S_n = improper rotation through $2\pi/n$, i.e., C_n followed by σ_h.

$i = S_2$ = inversion through the center of mass, i.e., $\mathbf{r} \rightarrow -\mathbf{r}$.

INTERRELATIONS OF SYMMETRY ELEMENTS

1. (a) The intersection of two reflection planes must be a symmetry axis. If the angle, ϕ, between the planes is π/n, the axis is n-fold.

1. (b) If a reflection plane contains an n-fold axis, there must be n-1 other reflection planes at angles of π/n.

2. (a) Two 2-fold axes separated by an angle π/n require a perpendicular n-fold axis.

2. (b) A 2-fold axis and an n-fold axis perpendicular to it require n-1 additional 2-fold axes separated by angles of π/n.

3. An even-fold axis, a reflection plane perpendicular to it, and an inversion center are interdependent. Any two of these implies the existence of the third.

TYPE CLASSIFICATION

The following classification by types is due to Jaffe and Orchin [16]. Representative examples are given below for a number of types. The reader is challenged to find the rest.

Type 1. No rotation axis; point groups C_1, C_s, C_i.

(a) $C_1 = \{E\}$. This group has no symmetry elements. It is the point group of *asymmetric* compounds.