THE
ORGANIC CHEMIST'S
BOOK OF ORBITALS

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To Alice and Axel

To Catherine

To the people of Vietnam

December 25, 1972

Science sans conscience n'est que ruine de l'âme

RABELAIS, Pantagruel, 1532

Preface

The last decade has witnessed an unprecedented strengthening of the bond between theory and experiment in organic chemistry. Much of this success may be credited to the development of widely applicable, unifying concepts, such as the symmetry rules of Woodward and Hoffmann, and the frontier orbital theory of Fukui. Whereas the theoretical emphasis had historically been on detailed structure and spectroscopy, the new methods are designed to solve problems of special importance to organic chemists: reactivity, stereochemistry, and mechanisms.

These theories are inevitably based upon analyses of the interactions and transformations of molecular orbitals, and consequently the accurate construction and representation of molecular orbitals has become essential. Furthermore, although the forms of molecular orbitals in diatomics and of delocalized π orbitals in conjugated systems are familiar, a general, noncomputational method for determining the qualitative nature of σ and π orbitals in arbitrary molecules has been lacking.

In the present work a theory for the facile construction of complex molecular orbitals from bond and group orbitals is presented and complemented by accurate drawings of the valence molecular orbitals for over one hundred molecules representing a wide range of connectivities and functional groupings. Direct applications to phenomena in organic chemistry are also discussed.

This book is addressed to all those for whom orbitals have ceased to be an abstract concept, but have instead become concrete and useful in the daily practice of chemistry. It is especially directed to the new generation of chemists eager to understand molecular structure at the electronic level.

We are greatly indebted to Professor E. J. Corey for much stimulating advice and for the unswerving encouragement which he gave us. We wish to thank Dr. Donald Barth for consultation on the graphic aspects of the project, and also many friends for their advice. Receipt of numerous unpublished results from Dr. Warren J. Hehre, Prof. J. M. Lehn, and Dr. Georges Wipff was greatly appreciated.

The greater part of the book was written while L. S. was Visiting Professor at Harvard University. He sincerely thanks the Chemistry Department for their kind hospitality.

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I. How Molecular Orbitals Are Built by Delocalization

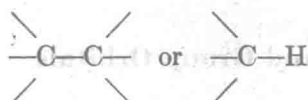## A Unified Approach Based on Bond Orbitals and Group Orbitals

1. Bond Orbitals and Group Orbitals

The delocalization of molecular orbitals lies at the heart of modern chemistry. The concept that the π orbitals of benzene or naphthalene cover the entire carbon skeleton promoted the successful understanding of conjugated molecules. The work of R. Hoffmann and others has proven that in saturated molecules σ orbitals are also delocalized over several bonds, often reaching opposite ends of a sizable molecule. The purpose of this chapter is to provide some enlightenment as to the mechanism by which delocalization of orbitals occurs in organic molecules.

By far the most obvious, but also the most significant characteristic of the molecular orbitals which are pictured in Chapter III is that they are composed almost exclusively of a very small number of typical *group* and *bond* orbitals which recur endlessly from molecular orbital to molecular orbital and from molecule to molecule. Generally, in a given molecular orbital only a given type of group or bond orbital occurs, from which the label of the molecular orbital is derived (see also Chapter II). The reader will soon become proficient at recognizing the basic types of localized orbitals. The following sections are aimed at helping him in this exercise, and at allowing him to go one step further to construct, qualitatively, the delocalized molecular orbitals from the localized group orbitals. The concept which we use is an old one: localized bond orbitals were first introduced by Lennard-Jones and Hall, and the wave-mechanical properties of localized electron pairs have been widely discussed. How-

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ever, for the first time accurate drawings of molecular orbitals show that these localized orbitals subsist as basic units even in large molecules with no symmetry. These drawings allow the reader to recognize and label, in almost every case, the localized building blocks for the molecular orbitals of arbitrary organic molecules. We shall now try and provide in a qualitative manner the theoretical framework for the understanding of these drawings.

Let us take a typical hydrocarbon skeleton (what will be said throughout this chapter on orbitals around carbon is of course equally valid for orbitals around nitrogen or oxygen). In hydrocarbons we can recognize basic bonds, such as

$$\overset{\backslash}{\underset{/}{-C}}-\overset{/}{\underset{\backslash}{C}}- \text{ or } \overset{\backslash}{\underset{/}{-C}}-H$$

and also basic groups such as

$$\text{methylene groups } \overset{H}{\underset{H}{\backslash / }} C \quad \text{ or methyl groups } \overset{H}{\underset{H}{-C}}-H$$
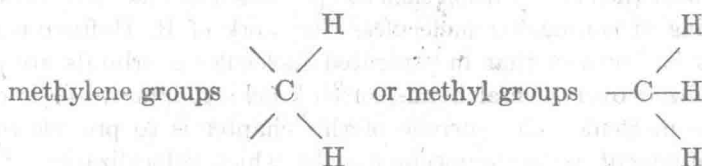
At a given carbon atom we will recognize a CH *bond* if there is only one hydrogen atom attached to it and all other substituents are different from hydrogen; if there are two hydrogen atoms attached to it we recognize a CH_2 *group*; if there are three, a CH_3 *group*. In other words, a given carbon atom carries only one type of CH_n unit. Now we can think of the CC or CH bonds and of the CH_2 or CH_3 groups of a hydrocarbon, not only as the building blocks from which the overall molecular geometry is derived, but also as carrying basic sets of localized orbitals—CC bond orbitals (two for a single bond, four for a double bond), CH bond orbitals (two), CH_2 group orbitals (four), CH_3 group orbitals (six). Again, at a given carbon atom we recognize only one set of CH_n (CH or CH_2 or CH_3) orbitals. And while the molecule is built by linking these bonds or groups together, so are the molecular orbitals constructed by adding, subtracting or combining these bond and group orbitals. Although the basic

orbitals are essentially *localized* on their own group, there is generally sufficient *overlap* between the orbitals of adjacent groups—sometimes even non-adjacent ones—to ensure that these combinations are possible. The three-dimensional "waves" on interacting adjacent groups can interfere to form "standing waves" for the entire molecule.

With respect to a local symmetry plane, the basic orbitals are either σ, *symmetric* or π, *antisymmetric*. This is true not only for the CC and CH bond orbitals but also for the CH_2 and CH_3 group orbitals. If the local symmetry elements are preserved in the full molecule, the π (or σ) local orbitals can combine to give π (or σ) molecular orbitals. The reader should, therefore, not be surprised to find, for instance, π type molecular orbitals in cyclopropane which are delocalized over the CH_2 groups.

Let us now construct in turn the various basic localized orbitals and consider their most significant features.

2. CC Single-Bond Orbitals

The valence atomic orbitals which are available to form the orbitals of a CC single bond, directed along the x axis, are the 2s and $2p_x$ atomic orbitals on each carbon atom. Their admixture—in proportions which depend on the number of neighbors at each carbon and on the subsequent hybridization—creates two (s, p_x) hybrids on each atom. One of these hybrids points away from the other atom and can be used for bonding to additional atoms. The pair of hybrids which point at each other overlap and interact in the conventional fashion [we symbolize the non-interacting orbitals by an interruption of the bond axis (Fig. 1)]. The two bond orbitals which are formed in this manner both have σ symmetry, i.e., rigor-
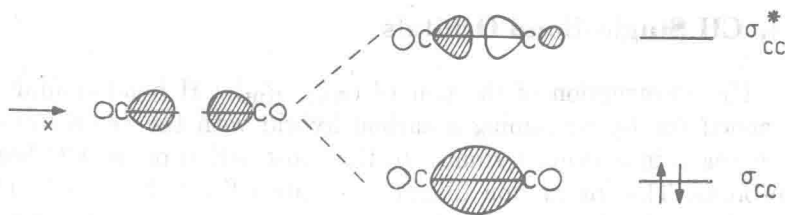

Fig. 1.

ously they are cylindrically symmetric around the bond axis. A *fortiori*, they are symmetric with respect to any plane containing the bonds. The bonding σ_{CC} orbital has two electrons, which form the "Lewis pair" in that bond, while the antibonding σ^*_{CC} orbital is empty.

3. CC Double-Bond Orbitals

If the pair of carbon atoms shown above each have only two neighbors so that they are doubly-bonded in the conventional sense, there is an extra p orbital available on each atom. These p orbitals point along the (z) direction, perpendicular to the plane of the molecular fragment. The interaction of these two atomic orbitals via overlap creates a new pair of bond orbitals with local π symmetry (Fig. 2, where again we have symbolized the non-interacting or-
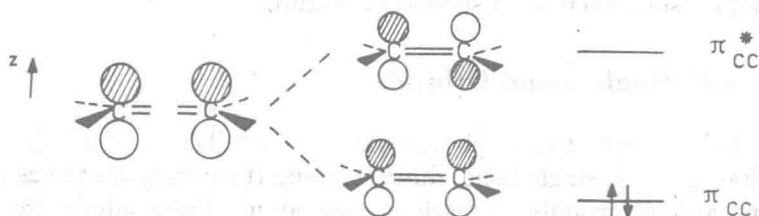

Fig. 2.

bitals by an interruption of the CC axis). Again the bonding combination is full while the other orbital is empty. The reader may wish to compare the schematic, conventional drawings with the actual three-dimensional graphics of the ethylene π orbitals (III.18).

In acetylene or triple-bonded systems, there will be a second pair of (π_{CC}, π^*_{CC}) orbitals with axes parallel to the y direction.

4. CH Single-Bond Orbitals

The construction of the pair of (σ_{CH}, σ^*_{CH}) CH bond orbitals is carried out by combining a carbon hybrid with the 1s orbital on hydrogen in a manner similar to the construction of the CC bond orbitals. The interaction diagram is shown below in Fig. 3. The bonding orbital is occupied by the two bond electrons. These two
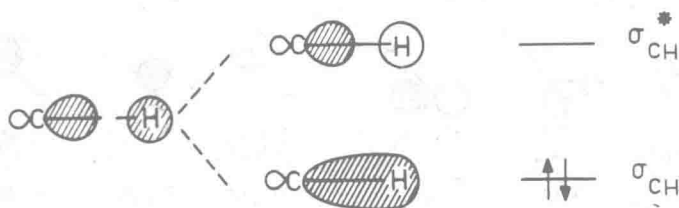
Fig. 3.

CH bond orbitals should be used for building molecular orbitals
only if the other substituents on the carbon atom are not hydrogen
atoms.

5. The Localized Orbitals of a CH_2 Group

Let us now turn to a CH_2 fragment, with two conventional CH
single bonds lying in the xz plane (Fig. 4). The xy plane is a local
symmetry plane for the group and we can, therefore, classify or-
bitals as σ-like (symmetric) or π-like (antisymmetric) with respect
to this plane. In doing so, we are using the same language which
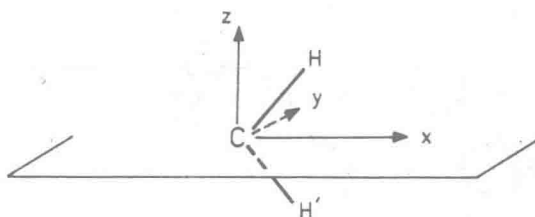presides over the σ, π classification in conjugated molecules.

Fig. 4.

The appropriate valence atomic orbitals which must be considered
are 2s, $2p_x$, $2p_z$ on carbon, and the 1s orbitals $1s_H$ and $1s'_H$. The
orbital $2p_y$ is clearly nonbonding (a) relative to the carbon-hydrogen
interactions and need not be considered further. The hydrogen or-
bitals can be combined into a $(1s_H + 1s'_H)$ combination of σ sym-
metry and a $(1s_H - 1s'_H)$ combination of π symmetry. (Fig. 5).
Although there are three available basic σ orbitals, only two of these
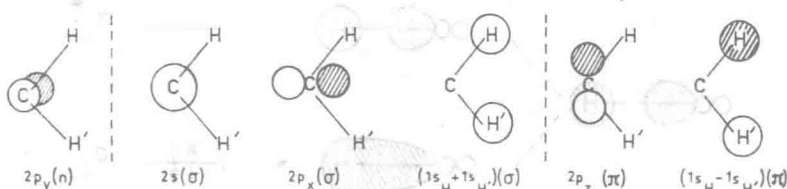belong to the CH_2 group proper. We can first eliminate the ("out")

$2p_y(n)$ $2s(\sigma)$ $2p_x(\sigma)$ $(1s_H + 1s_{H'})(\sigma)$ $2p_z(\pi)$ $(1s_H - 1s_{H'})(\pi)$

Fig. 5.

combination of 2s and $2p_x$ which points away from the hydrogen atoms, along the outer bisector of the CH_2 group, and which serves (together with the n orbital) to bind the CH_2 fragment to the remainder of the molecule. We are left with a $(2s, 2p_x)$ "in" hybrid pointing towards the hydrogens and with the $(1s_H + 1s_{H'})$ combination. Their interaction is shown in Fig. 6, and leads to a bonding σ_{CH_2} group orbital and an antibonding $\sigma^*_{CH_2}$ group orbital. Again these drawings are very schematic: proper σ_{CH_2} and $\sigma^*_{CH_2}$ orbitals can be found in methylene (III.2). For delocalized combinations see cyclopropane (III.56). The σ_{CH_2} bonding orbital has two electrons, while the $\sigma^*_{CH_2}$ orbital is empty.

$\sigma^*_{CH_2}$

σ_{CH_2}
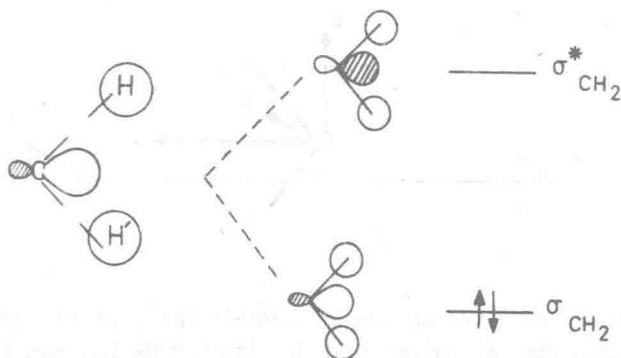
Fig. 6.

Two π-type CH_2 group orbitals can be constructed in a similar manner (Fig. 7). The two electrons in the bonding π_{CH_2} combination bring the total number of CH_2 electrons to four, corresponding to the two electron pairs in the CH bonds. The reader will find π_{CH_2}