70 Topics in Current Chemistry
Fortschritte der Chemischen Forschung

Structural Theory of Organic Chemistry

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Springer-Verlag
Berlin Heidelberg New York 1977

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ISBN 3-540-08099-6 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-08099-6 Springer-Verlag New York Heidelberg Berlin

Library of Congress Cataloging in Publication Data. Main entry under title: Structural theory of organic chemistry. (Topics in current chemistry ; 70). Includes indexes. 1. Molecular orbitals. 2. Chemistry, Physical organic. I. Epiotis, N. D., 1944- II. Series. QD1.F58 vol. 70 [QD461] 540'.8s [547'.1'28] 76-57966

Printed in Germany

Typesetting and printing: Schwetzinger Verlagsdruckerei GmbH, 6830 Schwetzingen. Bookbinding: Konrad Triltsch, Graphischer Betrieb, 8700 Würzburg

Springer-Verlag	Postfach 105 280 · D-6900 Heidelberg 1 Telephone (0 62 21) 4 87-1 · Telex 04-61 723 Heidelberger Platz 3 · D-1000 Berlin 33 Telephone (0 30) 82 20 01 · Telex 01-83319
Springer-Verlag New York Inc.	175, Fifth Avenue · New York, NY 100 10 Telephone 673-26 60

Preface

While MO theory has had a profound impact on the way in which chemists think about reactivity problems, a corresponding influence in the area of structural chemistry has been absent. Typically, "steric effects" provide the basis for rationalizing trends conforming to ordinary intuition and "attractive Van der Waals forces" are invoked to rationalize trends which are opposite to those expected on the basis of the concept of "steric repulsion".

However, molecules which exist preferentially in a "crowded" geometry are not mere aberrations of an order dominated by "steric effects". Indeed, in some classes of molecules, preference for "crowdedness" seems to be the rule rather than the exception. This observation stimulated an initial research of geometric isomerism which later blossomed into a theoretical investigation of structural chemistry. This book constitutes an abbreviated account of our experiences in dealing with such problems during the time period June 1972 – June 1976.

The aim of our work has been to arrive at a *qualitative* understanding of the key factors which determine the preferred geometry of a molecule. The specific procedure involves three principal stages:

a) The *analysis* stage, at which a one electron Hückel-type Molecular Orbital (MO) model is applied to the problem at hand. MO interaction diagrams are the conveyors of the key theoretical deliberations.

b) The *test* stage, at which explicit quantum mechanical computations are carried out to test the validity of the model. It is important to emphasize that the target of attention is not only the final numerical answer but, more importantly, the printout of the MO's and the density matrix. A key electronic effect leaves its mark on the MO's and the density matrix resulting from a calculation while the balance of *all* electronic effects is related to the computed total energy. A *dominant* electronic effect (*e.g.*, a symmetry imposed barrier) is almost always identifiable, regardless of the quality of computation. By contrast, the balance of *all* effects is a more sensitive problem and the answer depends on the quality of computation in a manner which is anything but predictable. This realization constitutes the basis for our preoccupation with *electronic effects* and a *qualitative* understanding of structural chemistry.

c) The *application* stage, at which the predictions of the theoretical model as well as the additional insights provided by the explicit calculations are compared with the available experimental data or form the basis for the design of a new experiment. In short, the triptych espoused in this work is ANALYSIS-TEST-APPLICATION, or, ANALYSIS-COMPUTATION-PREDICTION. In the opinion of the authors, this method constitutes the only *realistic* way of approaching complex problems of chemical structure at this point in time. Related philosophical dispositions are evident in the publications of Gimarc, Hehre, Hoffmann, Lowe, and Salem.

The present work does not answer all questions regarding "why" a given molecule exhibits a geometrical preference. Additional problems, such as the effect of "correlation energy" on structural trends and the related challenge of developing a qualitative understanding of configuration interaction within the context of a model, are currently under investigation. Nonetheless, we believe that the overview of structural chemistry developed herein is sufficiently satisfactory to arouse the interest of theoreticians and experimentalists alike, especially because the vast majority of chemists has been exposed to ways of thinking which are substantially different from those espoused in this work.

June 1976

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Lecture Notes in Chemistry

Volume 1: G.H. Wagnière
Introduction to Elementary Molecular Orbital Theory and to Semiempirical Methods
33 figures. V, 109 pages. 1976

The aim of these notes is to provide a summary and concise introduction to elementary molecular orbital theory, with an emphasis on semiempirical methods. Within the last decade the development and refinement of *ab initio* computations has tended to overshadow the usefulness of semiempirical methods. However, both approaches have their justification. *Ab initio* methods are designed for accurate predictions, at the expense of greater computational labor. The aim of semiempirical methods mainly lies in a semiquantitative classification of electronic properties and in the search for regularities within given classes of larger molecules. Applications to optical activity, concerted reactions and to polymers are included.
(34 references)

Volume 2: E. Clementi
Determination of Liquid Water Structure, Coordination Numbers for Ions and Solvation for Biological Molecules
32 figures, 18 tables. VI, 107 pages. 1976

The structure of liquid water and the solvation of ions and molecules represent an active field of past and current research. The authors have stressed in particular the new quantum mechanical developments that constitute the conceptual base for the recent advancements in this field. They have pointed out, with a variety of examples, the large amount of information embodied in quantum mechanics. The study of solvation represents the ideal field to pass from small chemical systems to large ones, to pass from quantum to statistical mechanics with a first step towards thermodynamics. Particular attention is given to present a unified picture the coherently retains technique and assumption in passing from one type of the description of matter to another. This work is dedicated to Prof. Per-Olov Löwdin, on the occasion of his 60th birthday.
(27 references)

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Reactivity and Structure

Concepts in Organic Chemistry
Editors: K. Hafner, J.-M. Lehn, C.W. Rees, P.v. Ragué Schleyer, B.M. Trost,
R. Zahradník

Volume 1: J. Tsuji
Organic Synthesis
by Means of Transition Metal Complexes
A Systematic Approach
4 tables. IX, 199 pages. 1975

This book is the first in a new series, Reactivity and Structure: Concepts in Organic Chemistry, designed to treat topical themes in organic chemistry in a critical manner. A high standard is assured by the compositon of the editorial board, which consists of scientists of international repute. This volume deals with the currently fashionable theme of complexes of transition-metal compounds. Not only are these intermediates becoming increasingly important in the synthesis of substances of scientific appeal, but they have already acquired great significance in large-scale chemical manufacturing. The new potentialities for synthesis are discussed with examples. The 618 references bear witness to the author's extensive coverage of the literature. This book is intended to stimulate organic chemists to undertake further research and to make coordination chemists aware of the unforeseen development of this research field.

Volume 2: K. Fukui
Theory of Orientation and Stereoselection
72 figures, 2 tables. VII, 134 pages. 1975

The 'electronic theory' has long been insufficient interpret various modern organic chemical facts, in particular those of reactivity. The time has come for a book making one realize what is within, and what is beyond, the reach of quantum-chemical methods. Graduate students and young researchers in chemistry both theoretical and experimental, will find this book useful in getting accustomed to the quantum-chemical way of thinking. Theory produces new experimental ideas, and, conversely, a host of experimental data opens new theoretical fields. A book such as the present one will constantly keep its value, although the quantum-chemical approach to the theory of reactivity is, of course, still in the developmental stage.

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Contents

Introduction

In the past four years, we published various papers with the purpose of drawing the attention of chemists to the following possibilities:

a) Nonbonded interactions and their influence on torsional isomerism can be understood within the context of simple one electron MO theory$^{1-8)}$. These ideas are discussed in Parts I and II.

b) Sigma interactions, designated geminal interactions, may affect the shape of molecules and associated shape-related properties in a manner which is also understandable within the context of one electron MO theory$^{9)}$. These concepts are presented in Part III.

c) Chemical reactivity can be understood in terms of donor-acceptor interactions with definite trends being expected as one reactant becomes an increasingly better donor and the other an increasingly better acceptor$^{10-14)}$. These ideas have now been applied in an explicit manner to problems of molecular structure and are discussed in Part IV under the heading of conjugative interactions.

d) Bond ionicity effects can be best understood by means of an effective one electron configuration interaction approach in a way which is suitable for the formulation of general predictive rules$^{15)}$. These ideas are discussed in Part V.

These sense in which terms like conjugative interactions, nonbonded interactions, etc., are meant will become clear when we discuss each individual type of interaction or effect. Suffice to say that, in many instances, conjugative interactions as well as geminal interactions or bond ionicity effects contain implicitly the idea of nonbonded interactions. Thus, it should be emphasized that the labels of the basic types of interactions proposed here reflect the way in which the problem is formulated rather than different electronic principles.

In Parts I and II, a molecule is viewed as a composite of submolecular fragments each described by delocalized MO's. Nonbonded and geminal interactions can be simply formulated in this manner. In Part IV, a molecule is viewed as a composite of submolecular fragments each described by hybrid bond MO's. Conjugative interactions are best understood in this fashion. Finally, in Part V a one electron configuration interaction approach involving a Linear Combination of Fragment Configurations (LCFC) is used to reveal bond ionicity effects. Indeed, this book can be titled "The Chemist's Handbook of MO Interactions and Their Implications for Molecular Architecture".

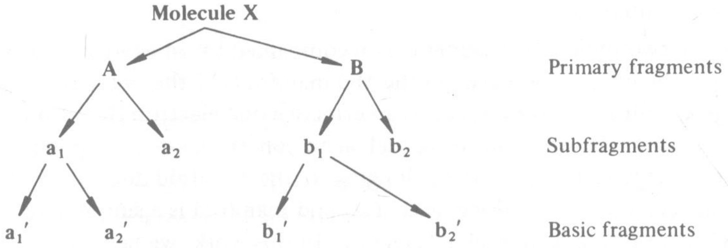
Throughout the entire work, we have tried to present experimental as well as computational results pertinent to cases under scrutiny. The calculation results are especially significant since they provide tests for the proposed theoretical models.

It is our hope that the reader will be stimulated to delve deeper into the world of orbital interactions and, hopefully, find a chance to apply the key concepts to problems of direct interest.

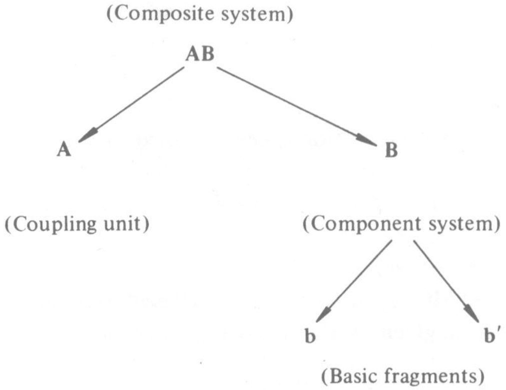
Part I. Theory

1. General Theory

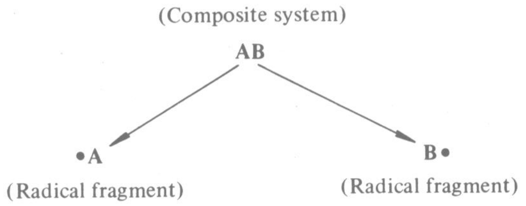
The theoretical analysis to be employed throughout Part I of this work is based upon One-Electron Molecular Orbital (OEMO) theory. In our approach, a given molecule in a specified geometry is constructed by a sequential union of molecular fragments. A typical construction is illustrated below:



In certain problems of torsional isomerism we shall employ the dissection of a molecule **A–B** into two closed shell fragments **A** and **B**. On the other hand, most problems of torsional isomerism which we shall be dealing with in the first part of this work can be treated by employing the dissection shown below. The appropriate definitions are specified in parenthesis.



Finally, an alternative approach employs a dissection into two radical fragments as shown below:



The delocalized group MO's of each fragment can be constructed by means of perturbation theory[16–19] or explicit calculations. Once one knows the MO's of basic fragments, he can construct the MO's of any molecule by means of relatively simple operations. Here, we note that a recent publication of Salem and Jørgensen[20] is a welcome addition to the library of any organic chemist since it includes an extensive compilation of basic fragments and their MO's and provides illustrative examples of the theoretical manipulations involved in the construction of a total system from subunits.

The union of any two molecular fragments is accompanied by an energy change which depends upon the interaction between the MO manifolds of the two fragments. This energy change is evaluated with respect to an effective one-electron Hamiltonian operator, the choice of the operator being such as to confer maximal simplicity to the analysis. The energy change of a MO belonging to one manifold due to its interaction with a number of MO's belonging to a second manifold is a simple sum of the energy changes resulting from each interaction. In this work, we need to distinguish between two types of MO interactions:

(a) The interaction of a doubly occupied MO, ϕ_i, with a vacant nondegenerate MO, ϕ_j, leads to two electron stabilization, ΔE_i^2, which is inversely proportional to the energy separation of the two MO's, $\epsilon_i - \epsilon_j$, and directly proportional to the square of their interaction matrix element, H_{ij}. This is a well known result of perturbation theory and the assumptions involved in its derivation are valid for most systems studied in this work. The algebraic expression for the two electron stabilization is given below:

$$\Delta E_i^2 = \frac{2(H_{ij} - \epsilon_i S_{ij})^2}{\epsilon_i - \epsilon_j} \tag{1}$$

If overlap is neglected, *i.e.* $S_{ij} = 0$, the above expression takes the form shown below.

$$\Delta E_i^2 = \frac{2H_{ij}^2}{\epsilon_i - \epsilon_j} \tag{2}$$

The interaction of a singly occupied MO, ϕ_i, with a singly occupied degenerate MO, ϕ_j, leads to two electron stabilization given by the following equation:

$$\Delta E_i^2 = \frac{2(H_{ij} - \epsilon_i S_{ij})}{1 + S_{ij}} \tag{3}$$

The corresponding expression where overlap is neglected is shown below.

$$\Delta E_i^2 = 2H_{ij} \tag{4}$$

(b) The interaction of two doubly occupied nondegenerate MO's, ϕ_i and ϕ_j, leads to net four electron destabilization, ΔE_{ij}^4, which increases as the overlap integral of the two MO's, S_{ij}, and the mean of their energies, ϵ_0, increase. This result is obtained by application of the variational method to the case of a two orbital-four electron interaction and involves no special assumptions[6, 21, 22]. The four electron destabilization energy is given by the equation:

$$\Delta E_{ij}^4 = \frac{4(\epsilon_i S_{ij}^2 - H_{ij} S_{ij})}{1 - S_{ij}^2} \tag{5}$$

If the doubly occupied MO's, ϕ_i and ϕ_j, are degenerate the four electron destabilization energy is given by the equation:

$$\Delta E_{ij}^4 = \frac{4(\epsilon_i S_{ij}^2 - H_{ij} S_{ij})}{1 - S_{ij}^2} \tag{6}$$

It is clear that when overlap is neglected the four electron destabilizing interaction becomes zero, *i.e.* $\Delta E_{ij}^4 = 0$.

At this point a discussion of the approximation of the interaction matrix element H_{ij}, where i and j are MO's, is appropriate. In general, we distinguish two situations:

a) In problems which involve comparisons of two systems having identical atomic constitution, the interaction matrix element can be simply approximated as indicated below[23].

$$H_{ij} = k\,S_{ij},\ k = -39.7\ \text{eV} \tag{7}$$

Here, S_{ij} is the overlap integral of the two interacting MO's, i and j.

b) In problems which involve comparisons of two systems which differ in atomic constitution, the interaction matrix element, H_{ij}, is expanded in terms of interaction matrix elements between AO's, h_{mn}, which are approximated as indicated below:

$$h_{mn} = \frac{1}{2}(\beta_A + \beta_B)\,S_{mn} = \beta_{AB}^0\,S_{mn} \tag{8}$$

The above equation is the one employed in the CNDO parametrization developed by Pople and co-workers[24]. Here, β_A and β_B are specific to the atoms A and B and S_{mn} is the overlap integral between two AO's m and n of A and B. The interaction matrix element between AO's, h_{mn}, is frequently called the resonance integral of the m and n AO's[a].

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[a] The terms resonance integral, h_{mn}, and coulomb integral, h_{mm}, conform to the nomenclature pertinent to Hückel theory. It should be pointed out that the parametrization suggested in Table 1 is not neccessarily the best one but is adequate for illustrating qualitative principles. Obviously, when a given trend arises from conflicting variations of energy gaps and interaction matrix elements, a prudent choice of the β_{AB}^0 parameters is essential for obtaining reliable results.

Table 1. Two center interaction matrix elements

A_m, B_n	r_{mn}	S_{mn} [a)]	β^0_{AB} (eV) [b)]	h_{mn}(eV)
F2s-C2s	1.381	.2473	−30.00	−7.419
O2s-C2s	1.430	.2713	−26.00	−7.054
Cl3s-C2s	1.767	.2670	−21.62	−5.783
F2p-C2p, σ	1.381	.2571	−30.00	−7.713
O2p-C2p, σ	1.430	.2855	−26.00	−7.423
Cl3p-C2p, σ	1.767	.3255	−21.66	−7.050
F2p-C2s, σ	1.381	.2053	−30.00	−6.159
O2p-C2s, σ	1.430	.2455	−26.00	−6.383
Cl3p-C2s, σ	1.767	.3124	−21.66	−6.766
F2s-C2p, σ	1.381	.3443	−30.00	−10.329
O2s-C2p, σ	1.430	.3568	−26.00	−9.277
Cl3s-C2p, σ	1.767	.3064	−21.66	−6.637
F2p-C2p, π	1.381	.1206	−30.00	−3.620
O2p-C2p, π	1.430	.1392	−26.00	−3.620
Cl3p-C2p, π	1.767	.1392	−21.66	−3.015
Csp^3-Osp^3, σ	1.430	.5427	−26.00	−14.110
Csp^3-Ssp^3, σ	1.820	.6017	−19.57	−11.775
Csp^3-Fsp, σ	1.381	.5431	−30.00	−16.293
Csp^3-Clsp, σ	1.767	.5841	−21.66	−12.652
Csp^2-Fp, σ	1.381	.5670	−30.00	−17.010
Csp^2-Clp, σ	1.767	.6510	−21.66	−14.101

a) Overlap integrals were calculated with a CNDO/2 program.
b) β^0_{AB} values were taken from Ref.[24].

Representative values of β^0_{AB}, S_{mn} and h_{mn} are provided in Table 1. An examination of these data leads to the formulation of the following qualitative rules:

a) With only one exception, the resonance integral, h_{mn}, decreases in absolute magnitude as X varies *down* a column of the Periodic Table, *i.e.* as X becomes less electronegative along a column.

b) With only one exception, the resonance integral h_{mn} decreases in absolute magnitude as X varies *to the left* of a row of the Periodic Table, *i.e.* as X becomes less electronegative along a row. It should be noted, however, that in the cases of overlap of pure AO's the differences are very small.

At various points, we shall be interested in the effect of substitution on the strength of a given orbital interaction. In general, a substituent will alter the energy gap and the interaction matrix element of two levels and produce a change in the strength of the interaction. Hence, we would like to know how fast the strength of an interaction changes as a result of a change in $\epsilon_i - \epsilon_j$ and H_{ij} introduced by the substituent. The following differential forms of the equations for two electron stabilization, neglecting overlap, will be useful in our future discussions.

$$\frac{d(\Delta E_i^2)}{d(H_{ij})} = \frac{4H_{ij}}{\epsilon_i - \epsilon_j} \tag{9}$$

$$\frac{d(\Delta E_i^2)}{d(H_{ij})} = 2 \qquad \text{(degenerate MO's)} \tag{10}$$

$$\frac{d(\Delta E_i^2)}{d(\epsilon_i - \epsilon_j)} = \frac{-2H_{ij}^2}{(\epsilon_i - \epsilon_j)^2} \tag{11}$$

$$\frac{d(\Delta E_i^2)}{d(\epsilon_i - \epsilon_j)} = 0 \qquad \text{(degenerate MO's)} \tag{12}$$

1.1. Orbital Energies and Interaction Matrix Elements

At this point, we have completed the presentation of the key equations which will be crucial to the development of a predictive theory of molecular structure. These equations will form the basis for determining the *relative* stability of isomers, the *relative* stabilization of a cationic, radical or anionic center by substituents, etc. On the other hand, the differential expressions (9) to (12) will form the basis for determining how substitution affects the *relative* stability of isomers, the *relative* stabilization of cationic, radical and anionic centers, etc. It is then obvious that a working knowledge of Eqs. (1) to (6) presupposes a great familiarity with the key quantities involved in these equations, namely, orbital energies and interaction matrix elements.

We shall first consider the effect of atomic replacement on sigma or pi orbital energies.

$$CH_3{-}F \xrightarrow[\text{Replacement}]{\text{Atomic}} CH_3{-}Cl$$

$$CH_2{=}CH_2 \xrightarrow[\text{Replacement}]{\text{Atomic}} CH_2{=}SiH_2$$

Here, we shall inquire as to how the energy of a given MO is related to features like atom electronegativity and/or bond distance. In quantum mechanical terms, the problem amounts to determining how the energy of a ith MO is altered if we change one (or more) atomic coulomb integral, h_{mm}, and/or one (or more) resonance integral, h_{mn}, by a small amount. The pertinent expression, derived on the basis of simple perturbation theory, is the following:

$$\delta\epsilon_i = \sum_m a_{im}^2\, \delta h_{mm} + 2 \sum\sum_{m<n} a_{im} \cdot a_{in}\, \delta h_{mn} \tag{13}$$

On the basis of Eq. (13), we distinguish the following cases:

a) Replacement of an atom is accompanied by a greater change in the first term of Eq. (13). In such a case, the energy of the ith MO will be reduced if $\delta\, h_{mm} < 0$

and increased if $\delta h_{mm} > 0$. The former situation obtains when an atom is replaced by a more electronegative one and the latter when an atom is replaced by a more electropositive one. In general, experience shows that the coulomb integral term variation dominates the resonance integral term variation whenever an atom is replaced by another atom of the same row of the Periodic Table. Thus, for example, the energy of a given MO will progressively decrease as carbon is replaced by a more electronegative atom of the same row, *i.e.* the MO energy depression will increase in the order F > O > N.

b) Replacement of an atom is accompanied by a greater change in the second term of Eq. (13). In such a case, the energy of the ith MO will be raised or lowered depending upon the sign of the coefficient product $a_{im}\, a_{in}$ as well as the sign of δh_{mn}. The various possibilities are summarized below:

δh_{mn}	$a_{im}\, a_{in}$	$\delta \epsilon_i$
+	+	+
+	–	–
–	+	–
–	–	+

Experience shows that, in most cases, the resonance integral term variation dominates the coulomb integral term variation whenever an atom is replaced by another atom of the same column of the Periodic Table. Thus, for example, the energy of the σ^* antibonding MO of HX, where X is a halogen, will progressively decrease as fluorine is substituted by a less electronegative atom of the same column, *i.e.* the MO energy will increase in the order $\sigma^*_{HF} > \sigma^*_{HCl} > \sigma^*_{HBr} > \sigma^*_{HI}$.

An interesting and important corollary of the above analysis is that in systems where the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) have identical or similar electron densities, replacement of an atom so that h_{mn} becomes less negative results in shrinkage of the HOMO-LUMO energy gap while replacement of an atom so that h_{mn} becomes more negative has the opposite effect. These results are valid regardless of the direction in which the coulomb integral of the variable atom changes and may have wide applicability to ultraviolet spectroscopy$^{25)}$.

	Calculated HOMO-LUMO Gap (eV)
$CH_2{=}CH_2$	15.22
$CH_2{=}O$	17.90

The HOMO-LUMO gap calculated by an *ab initio* method using an STO-3G basis set$^{26)}$ seems to support these ideas. A more definitive test will be possible after the nature of the lowest excited state in carbon unsaturated systems is understood$^{27)}$.

We shall next consider the effect of substitution on sigma and pi orbital energies.

$$CH_3{-}F \xrightarrow{\text{Substitution}} NC{-}CH_2{-}F$$

$$CH_2{=}CH_2 \xrightarrow{\text{Substitution}} NC{-}CH{=}CH_2$$