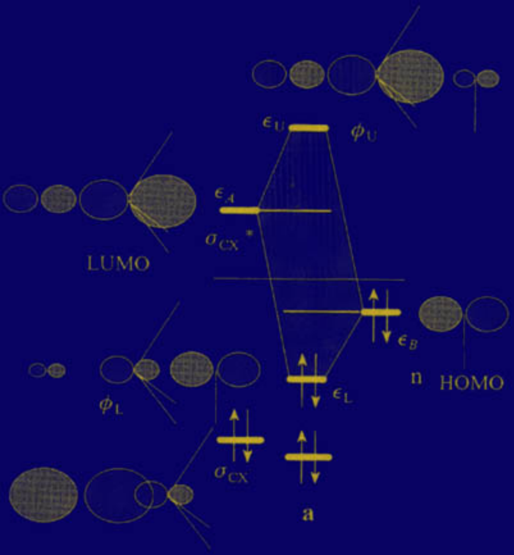
WWW.
LINK AVAILABLE

Orbital Interaction Theory of Organic Chemistry

SECOND EDITION


ϵ_U
ϕ_U
ϵ_A
$\sigma_{CX}{}^*$
LUMO
ϵ_B
n HOMO
ϕ_L
ϵ_L
σ_{CX}
a

ARVI RAUK

ORBITAL INTERACTION THEORY OF ORGANIC CHEMISTRY

Second Edition

This page intentionally left blank

ORBITAL INTERACTION THEORY OF ORGANIC CHEMISTRY

Second Edition

ARVI RAUK
Professor Emeritus
University of Calgary, Canada

WILEY-
INTERSCIENCE

A John Wiley & Sons, Inc., Publication
New York • Chichester • Weinheim • Brisbane • Singapore • Toronto

This book is printed on acid-free paper.♾

Copyright © 2001 by John Wiley & Sons, Inc. All rights reserved.

Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning or otherwise, except as permitted under Sections 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4744. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 605 Third Avenue, New York, NY 10158-0012, (212) 850-6011, fax (212) 850-6008, E-Mail: PERMREQ@WILEY.COM.

For ordering and customer service, call 1-800-CALL-WILEY.

Library of Congress Cataloging-in-Publication Data:

Rauk, Arvi, 1942–
Orbital interaction theory of organic chemistry / by Arvi Rauk.—2nd ed.
p. cm.
"A Wiley-Interscience publication."
Includes bibliographical references and index.
ISBN 0-471-35833-9 (acid-free paper)
1. Molecular orbitals. 2. Chemistry, Physical organic. I. Title.
QD461 .R33 2001
547′.128—dc21 00-033010

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

CONTENTS

PREFACE xiii

1 SYMMETRY AND STEREOCHEMISTRY 1

Purpose / 1
Definition of a Group / 2
Molecular Point Groups / 2
Schoenflies Notation / 2
Interrelations of Symmetry Elements / 3
Type Classification / 3
Isomerism and Measurements / 6
Stereoisomerism of Molecules / 8
Stereotopic Relationships of Groups in Molecules / 9
Asymmetric Synthesis and Stereochemistry / 10
NMR and Stereochemistry / 12
Symmetry and Structural Parameters / 14
Note on Hybridization / 15
Symmetry and Orbitals / 16
    Atomic Orbitals / 16
    Molecular and Group Orbitals / 17
In What Combination? / 19

2 MOLECULAR ORBITAL THEORY 20

Introduction / 20
Electronic Schrödinger Equation (A.1) / 21

Fock Equations (A.42) / 23
The Basis Set (STO-3G, 6-31G*, and All That) / 24
Orbital Energies and Orbitals / 25
Representation of MOs / 27
Total Energies and the Hartree–Fock Limit / 29
Successes and Failures of Hartree–Fock Theory / 29
Beyond Hartree–Fock / 30
Density Functional Theory / 31
Geometry Optimization / 31
Normal Coordinates and Harmonic Frequency Analysis / 32
Zero Point Vibrational Energies / 33

3 ORBITAL INTERACTION THEORY **34**

Relationship to Hartree–Fock Equations / 34
Hückel Approximation / 34
    Orbital Energies and Total Electronic Energy / 34
Case Study of a Two-Orbital Interaction / 35
    Case 1: $\varepsilon_A = \varepsilon_B$, $S_{AB} = 0$ / 38
    Case 2: $\varepsilon_A = \varepsilon_B$, $S_{AB} > 0$, $S_{AB} \ll 1$ / 39
    Case 3: $\varepsilon_A > \varepsilon_B$, $S_{AB} = 0$ / 40
    Case 4: $\varepsilon_A > \varepsilon_B$, $S_{AB} > 0$ / 42
Effect of Overlap / 44
Energetic Effect of Overlap / 44
Orbital Effect of Overlap / 44
First Look at Bonding / 45
Relationship to Perturbation Theory / 45
Generalizations for Intermolecular Interactions / 46
Energy and Charge Distribution Changes from Orbital Interaction / 47
    Four-Electron, Two-Orbital Interaction / 47
    Three-Electron, Two-Orbital Interaction / 48
    Two-Electron, Two-Orbital Interaction / 49
    One-Electron, Two-Orbital Interaction / 51
    Zero-Electron, Two-Orbital Interaction / 51
Interactions between Molecules: Many Electrons, Many Orbitals / 52
    General Principles Governing the Magnitude of h_{AB} and S_{AB} / 52
    Interactions of MOs / 52
Electrostatic Effects / 55
Group Orbitals / 56
    Zero-Coordinated Atoms / 56
    Monocoordinated Atoms / 57
    Dicoordinated Atoms / 58
    Tricoordinated Atoms / 59
    Tetracoordinated Atoms / 59

Assumptions for Application of Qualitative MO Theory / 61
Example: Carbonyl Group / 62
Construction of Interaction Diagram / 62
Interpretation of Interaction Diagram / 65
Chemical Reactivity / 66
Why Does It Work and When Might it Not? / 69

4 SIGMA BONDS AND ORBITAL INTERACTION THEORY 72

C—X σ Bonds: X = C, N, O, F and X = F, Cl, Br, I / 72
σ Bonds: Homolytic versus Heterolytic Cleavage / 74
    Heterolytic Cleavage of σ Bonds Involving C or H / 74
    Homolytic Cleavage of σ Bonds Involving C or H / 75
    Homonuclear σ Bonds C—C, N—N, O—O, F—F, Cl—Cl, Br—Br, and I—I / 76
Interactions of σ Bonds / 77
σ Bonds as Electron Donors or Acceptors / 81
σ Bonds as Electron Acceptors / 81
    As a σ Acceptor / 81
    As a π Acceptor / 82
σ Bonds as Electron Donors / 83
    As a σ Donor / 83
    As a π Donor / 84
Bonding in Cyclopropane / 84

5 SIMPLE HÜCKEL MOLECULAR ORBITAL THEORY 86

Simple Hückel Assumptions / 86
Charge and Bond Order in SHMO Theory: ($S_{AB} = 0$, One Orbital per Atom) / 91
    Electron Population and Net Charge of Center A / 91
    Bond Order between Centers A and B / 92
Factors Governing Energies of MOs: SHMO Theory / 92
    Reference Energy and Energy Scale / 92
Heteroatoms in SHMO Theory / 93
    Effect of Coordination Number on α and β / 93
    Hybridization at C in Terms of α and β / 96
Gross Classification of Molecules on the Basis of MO Energies / 96

6 REACTIONS AND PROPERTIES OF π BONDS 98

Reactions of Olefins (Alkenes) / 98
Effect of X: Substituents / 99
Effect of Z Substituents / 101
Effect of "C" Substituents / 101
Effect of Distortion of Molecular Skeleton / 102

Alkynes / 103
π Bonds to and between Higher Row Elements / 103
π Bonds to Silicon, Phosphorus, and Sulfur / 103

7 REACTIVE INTERMEDIATES **105**

Reactive Intermediates $[CH_3]^+$, $[CH_3]^-$, $[CH_3]^\bullet$, and $[:CH_2]$ / 105
  Carbocations / 105
  Intermolecular Reactions of Carbocations / 106
  Intramolecular Reactions of Carbocations / 107
  Silyl Cations / 108
  Carbanions / 108
  Carbon Free Radicals / 110
  Carbenes / 114
Nitrenes and Nitrenium Ions / 116
  Nitrenes / 116
  Nitrenium Ions / 118

8 CARBONYL COMPOUNDS **121**

Reactions of Carbonyl Compounds / 121
  Electrophilic Attack on a Carbonyl Group / 121
  Basicity and Nucleophilicity of the Oxygen Atom / 122
  Nucleophilic Attack on a Carbonyl Group / 124
  Amide Group / 126
Thermodynamic Stability of Substituted Carbonyl Groups / 127

9 NUCLEOPHILIC SUBSTITUTION REACTIONS **129**

Nucleophilic Substitution at Saturated Carbon / 129
  Unimolecular Nucleophilic Substitution S_N1 / 129
  Bimolecular Nucleophilic Substitution S_N2 / 130
  Another Description of the S_N2 Reaction: VBCM Model / 134

10 BONDS TO HYDROGEN **137**

Hydrogen Bonds and Proton Abstraction Reactions / 137
  Hydrogen Bonds / 137
  Symmetrical and Bifurcated Hydrogen Bonds / 139
  Proton Abstraction Reactions / 141
  E2 Elimination Reaction / 143
  E1cB Mechanism Reaction / 144
  E1 Elimination Reaction / 144
Reaction with Electrophiles: Hydride Abstraction and Hydride Bridging / 145
  Activation by π Donors (X: and "C" Substituents) / 145

Hydride Abstraction / 145
Hydride Bridges / 147
Reaction with Free Radicals: Hydrogen Atom Abstraction and One- or Three-Electron Bonding / 147
Hydrogen-Bridged Radicals / 147
Hydrogen Atom Transfer / 148

11 AROMATIC COMPOUNDS 150

Reactions of Aromatic Compounds / 150
Cyclic π Systems by Simple Hückel MO Theory / 150
Aromaticity in σ-Bonded Arrays? / 151
Reactions of Substituted Benzenes / 152
Electrophilic Substitutions / 152
Effect of Substituents on Substrate Reactivity / 153
Electrophilic Attack on X:-Substituted Benzenes / 153
Electrophilic Attack on Z-Substituted Benzenes / 154
Electrophilic Attack on "C"-Substituted Benzenes / 155
Electrophilic Attack on N Aromatics: Pyrrole and Pyridine / 155
Nucleophilic Substitutions / 157
Effect of Substituents on Substrate Reactivity / 158
Nucleophilic Attack on Z-Substituted Benzenes / 158
Nucleophilic Attack on N Aromatics: Pyrrole and Pyridine / 158
Nucleophilic Substitution by Proton Abstraction / 159

12 PERICYCLIC REACTIONS 161

General Considerations / 161
Cycloadditions and Cycloreversions / 162
Stereochemical Considerations / 162
Electrocyclic Reactions / 165
Stereochemical Considerations / 165
Cheletropic Reactions / 165
Stereochemical Considerations / 165
Sigmatropic Rearrangements / 166
Stereochemical Considerations / 166
Component Analysis (Allowed or Forbidden?) / 167
Rule for Component Analysis / 168
Diels–Alder Reaction / 169
Cope Rearrangement / 170
1,3-Dipolar Cycloaddition Reactions / 171

13 ORGANOMETALLIC COMPOUNDS 175

Transition Metals / 175

Ligands in Transition Metal Complexes / 176
Orbitals in Transition Metal Bonding / 176
Orbital Energies / 178
Valence Orbitals of Reactive Metal Complexes / 179
Six Valence Orbitals of Tricoordinated Metal / 182
Five Valence Orbitals of Tetracoordinated Metal / 182
Four Valence Orbitals of Pentacoordinated Structure / 185
Transition Metals and C—H or H—H Sigma Bonds / 186
More About C Ligands in Transition Metal Complexes / 186
Chelating Ligands / 187
Organic π-Bonded Molecules as Ligands / 187
Transition Metal Bonding to Alkenes: Zeise's Salt / 187
Agostic Interaction / 191
Ziegler–Natta Polymerization / 192
Oxidative Addition to H—H and C—H Bonds / 194

14 ORBITAL AND STATE CORRELATION DIAGRAMS 196

General Principles / 196
Woodward–Hoffman Orbital Correlation Diagrams / 197
    Cycloaddition Reactions / 197
    Electrocyclic Reactions / 198
    Cheletropic Reactions / 201
    Photochemistry from Orbital Correlation Diagrams / 201
Limitations of Orbital Correlation Diagrams / 203
State Correlation Diagrams / 203
    Electronic States from MOs / 205
    Rules for Correlation of Electronic States / 206
    Example: Carbene Addition to an Olefin / 206

15 PHOTOCHEMISTRY 209

Photoexcitation / 209
Jablonski Diagram / 210
Fate of Excited Molecule in Solution / 211
Dauben–Salem–Turro Analysis / 212
Norrish Type II Reaction of Carbonyl Compounds / 213
Norrish Type I Cleavage Reaction of Carbonyl Compounds / 215

APPENDIX A: DERIVATION OF HARTREE–FOCK THEORY 218

Electronic Hamiltonian Operator / 218
Electronic Schrödinger Equation / 220
Expectation Values / 221
Many-Electron Wave Function / 221

Electronic Hartree–Fock Energy / 222
Variation of E_{HF} / 226
LCAO Solution of Fock Equations / 229
Integrals / 231
The Basis Set (STO-3G, 6-31G*, and All That) / 232
Interpretation of Solutions of HF Equations / 233
    Orbital Energies and Total Electronic Energy / 233
Restricted Hartree–Fock Theory / 234
Mulliken Population Analysis / 236
Dipole Moments / 236
Total Energies / 237
Configuration Energies / 237
Post-Hartree–Fock Methods / 239
Configuration Interaction Theory / 239
Excited States from CI Calculations / 241
Many-Body Perturbation Theory / 241
Rayleigh–Schrödinger Perturbation Theory / 241
Møller–Plesset Perturbation Theory / 244
Density Functional Theory / 245

APPENDIX B: EXERCISES 247

Chapter 1 / 247
Chapter 2 and Appendix A / 249
Chapter 3 / 252
Chapter 4 / 262
Chapter 5 / 264
Chapter 6 / 272
Chapter 7 / 273
Chapter 8 / 278
Chapter 9 / 281
Chapter 10 / 281
Chapter 11 / 284
Chapter 12 / 288
Chapter 13 / 292
Chapter 14 / 296
Chapter 15 / 298
Miscellaneous / 301

REFERENCES AND NOTES 313

INDEX 325

This page intentionally left blank

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 including 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 the reader can construct his or her 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 and for chemists in general seeking qualitative understanding of the (often) quantitative data produced by modern computational chemists [8]. 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 orbitals and so can donate electrons, that is, act as bases in the Lewis sense. All compounds have empty molecular orbitals and so can accept electrons, that is, 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 molecular orbital), and also on the ability of the substrate to receive the electrons (on the shape and energy of its empty orbital). The basicity 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 maximization of attractive interactions and/or minimization of repulsive 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 [9] and OCAMS (orbital correlation analysis using maximum symmetry) approach [10, 11].

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 reader 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 spatial 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 qualitative discussion of Hartree–Fock theory. A detailed derivation of Hartree–Fock theory making only the simplifying concession that all wave functions are real is provided in Appendix A. Some connection is made to the results of ab initio quantum chemical calculations. 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 and Appendix A may be skipped, and the essential arguments and conclusions are provided to the students in a single lecture as the 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 zero to four 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 specific applications 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. An interactive computer program, SHMO, which uses the conventions introduced in this chapter, is available on the Web [12].

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

Pericyclic reactions are described in Chapter 12 as a special case of frontier orbital interactions, that is, 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.

The bonding in organometallic compounds between the metal and C and H atoms is briefly described in Chapter 13.

Chapter 14 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 organic photochemistry in Chapter 15.

In Chapter 15, 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 [13]. A more comprehensive approach to this subject may be found in the text by Michl and Bonacic-Koutecky [14], Turro [15], or Gilbert and Baggott [16].

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

Arvi Rauk
Calgary, Canada

This page intentionally left blank

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, that is, 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 [17]. 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 defined 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 to determine the stereochemical course of electrocyclic reactions and to help determine the principal interactions in bimolecular reactions; and to electronic states 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 [18] where greater detail may be found.

DEFINITION OF A GROUP

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

1. The product of any two elements is in the set; that is, the set is *closed* under group multiplication.
2. The associative law holds: for example, $g_i(g_j g_k) = (g_i g_j) g_k$.
3. There is a *unit* element, e, such that $e g_i = g_i e = g_i$.
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:

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

2. Reflections in planes containing the origin (center of mass):

$$\sigma = \text{reflection in a plane}$$

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:

$$S_n = \text{rotation through } 2\pi/n \text{ radians followed by } \sigma_h \text{ (see below)}$$

SCHOENFLIES NOTATION

The symbols used to designate the elements of molecular point groups in the Schoenflies notation and their descriptions are as follows:

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, that is, the plane through the origin perpendicular to the axis of highest n

σ_v = reflection in a vertical plane, that is, the plane containing the axis of highest n

σ_d = reflection in a diagonal plane, that is, the plane containing the axis of highest n and bisecting the angle between the twofold axes perpendicular to the principal axis. This is just a special case of σ_v

S_n = improper rotation through $2\pi/n$, that is, C_n followed by σ_h

i = inversion through the center of mass, that is, $\mathbf{r} \to -\mathbf{r}$, $=S_2$

INTERRELATIONS OF SYMMETRY ELEMENTS

A number of relationships exist between the elements of symmetry of a point group which are a consequence of the closure property of groups. They may be used to identify difficult-to-locate 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.
   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 twofold axes separated by an angle π/n require a perpendicular n-fold axis.
   b. A twofold axis and an n-fold axis perpendicular to it require $n-1$ additional twofold 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 [18]. 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.

(b) $C_s = \{E, \sigma\}$. This group has only a single plane of symmetry. Methanol (CH_3OH) is an example.

(c) $C_i = \{E, i\}$. This group has only a center of inversion. Two examples are shown in Figure 1.1.

Type 2. Only one axis of rotation; point groups C_n, S_n, C_{nv}, C_{nh}.

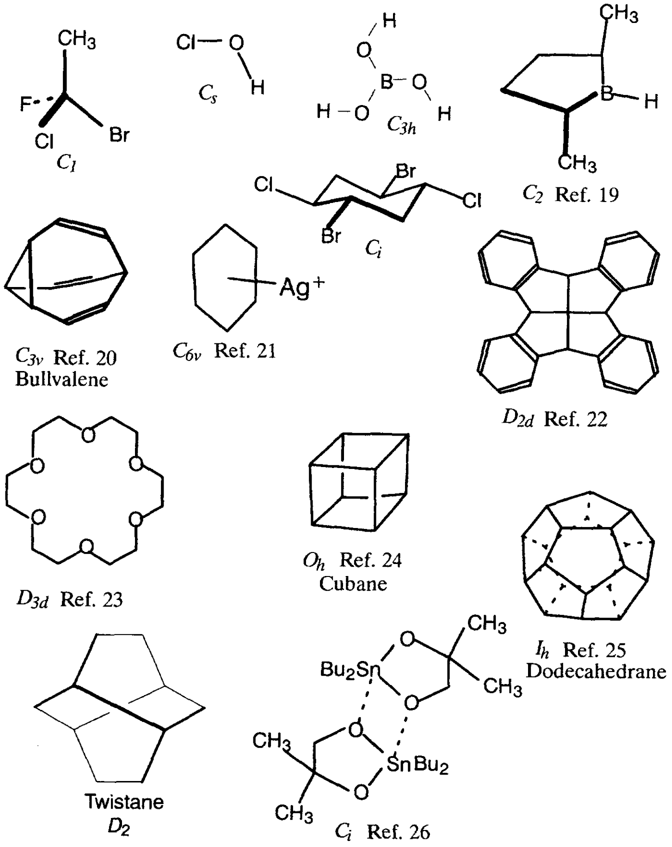

CH3
F
Cl
Br
C_1
Cl—O
H
C_s
H
O
B–O
H–O
H
C_{3h}
CH3
B–H
CH3
C_2 Ref. 19
Cl
Br
Cl
Br
C_i
C_{3v} Ref. 20
Bullvalene
Ag+
C_{6v} Ref. 21
D_{2d} Ref. 22
O
O
O
O
O
O
D_{3d} Ref. 23
O_h Ref. 24
Cubane
I_h Ref. 25
Dodecahedrane
CH3
O
Bu2Sn
CH3
O
O
CH3
SnBu2
O
CH3
C_i Ref. 26
Twistane
D_2

Figure 1.1. Examples of molecules belonging to various point groups.

(a) C_n. This group has only a single rotational axis of order greater than 1. These molecules are *dissymmetric* (chiral) and can be made optically active unless the enantiomeric forms are readily interconvertible.

$C_2 = \{E, C_2\}$. Hydrogen peroxide (HOOH) and *gauche*-1,2-dichloroethane are examples.

$C_3 = \{E, C_3, C_3^2\}$

$C_4 = \{E, 2C_4, C_2(= C_4^2)\}$

(b) S_n

$S_4 = \{E, C_2, S_4, S_4^3\}$. The D_{2d} structure in Figure 1.1 actually belongs to S_4 since the five-membered rings are not planar.

$S_6 = \{E, C_3, C_3^2, i, S_6, S_6^5\}$

(c) C_{nv}. This group has symmetry elements C_n and n σ_v:

$C_{2v} = \{E, C_2, \sigma_v, \sigma_{v'}\}$. Water, formaldehyde, and methylene chloride (CH_2Cl_2) are common examples.

$C_{3v} = \{E, 2C_3, 3\sigma_v\}$. Chloroform ($CHCl_3$) and ammonia are typical examples. See also bullvalene in Figure 1.1.

$C_{4v} = \{E, 2C_4, C_2, 2\sigma_v, 2\sigma_d\}$

$C_{5v} = \{E, 2C_5, C_5^2, 5\sigma_v\}$

$C_{6v} = \{E, 2C_6, 2C_3, C_2, 3\sigma_v, 3\sigma_d\}$

$C_{\infty v}$. HCl and CO and other linear polyatomic molecules without a center of inversion.

(d) C_{nh}. This group has the symmetry element C_n and a horizontal mirror plane σ_h. When n is even, a σ_h implies an i:

$C_{2h} = \{E, C_2, i, \sigma_h\}$, e.g., (*E*)-1,2-dichloroethene

$C_{3h} = \{E, 2C_3, \sigma_h, 2S_3\}$, e.g., boric acid [$B(OH)_3$, see Figure 1.1]

$C_{4h} = \{E, 2C_4, C_2, i, \sigma_h, 2S_4\}$

Type 3. One n-fold axis and n twofold axes; point groups D_n, D_{nh}, D_{nd}.

(a) D_n. This group has only a single rotational axis of order $n > 1$ and n twofold axes perpendicular to the principal axis. These molecules are dissymmetric and can be made optically active unless enantiomeric conformations are readily interconvertible:

$D_2 = \{E, 3C_2\}$, e.g., twisted ethylene, twistane (Figure 1.1)

$D_3 = \{E, 2C_3, 3C_2\}$, e.g., trisethylenediamine complexes of transition metals

(b) D_{nh}. This group has only a single rotational axis of order $n > 1$, n twofold axes perpendicular to the principal axis, and a σ_h (which also results in n σ_v):

$D_{2h} = \{E, 3C_2, 3\sigma_v, i\}$, e.g., ethylene, diborane, and naphthalene

$D_{3h} = \{E, 2C_3, 3C_2, 3\sigma_v, \sigma_h, 2S_3\}$, e.g., cyclopropane

$D_{4h} = \{E, 2C_4, C_2, 2C_2', 2C_2'', i, 2S_4, \sigma_h, 2\sigma_v, 2\sigma_d\}$, e.g., the point group of the square or planar cyclobutane. What about cyclobutadiene?

$D_{5h} = \{E, 2C_5, 2C_5^2, 5C_2, 2S_5, 2S_5^2, \sigma_h, 5\sigma_v\}$, e.g., cyclopentadienyl anion

$D_{6h} = \{E, 2C_6, 2C_3, C_2, 3C_2', 3C_2'', i, 2S_6, 2S_3, \sigma_h, 3\sigma_v, 3\sigma_d\}$, e.g., benzene

$D_{\infty h}$. The other point group of linear molecules, e.g., carbon dioxide and acetylene.

(c) D_{nd}. This group has only a single rotational axis of order $n > 1$, n twofold axes perpendicular to the principal axis, and n diagonal planes σ_d which bisect the angles made by successive twofold axes. In general, D_{nd} contains an S_{2n}, and if n is odd, it contains i:

$D_{2d} = \{E, 3C_2, 2\sigma_d, 2S_4\}$. Allene has this symmetry, as do puckered cyclobutane and cyclooctatetraene.

$D_{3d} = \{E, 2C_3, 3C_2, i, 3\sigma_d, 2S_6\}$, e.g., cyclohexane and ethane. See also Figure 1.1.

$$D_{4d} = \{E, 2C_4, C_2, 2C_2', 2C_2'', 2S_8, 2S_8^3, 4\sigma_d\}$$

$$D_{5d} = \{E, 2C_5, 2C_5^2, 5C_2, i, 2S_{10}, 2S_{10}^3, 5\sigma_d\}$$

Type 4. More than one axis higher than twofold; point groups T_d, O_h, I_h, K_h (*also* T_h, T, O, I). Methane (T_d), cubane (O_h, Figure 1.1), dodecahedrane (I_h, Figure 1.1), and buckminsterfullerene, C_{60} (I_h, Chapter 11). The symbol K_h denotes the point group of the sphere.

Exercise 1.1. As an exercise, let us locate all of the symmetry elements of the D_{3d} point group as they pertain to cyclohexane. The effect of these on the cyclohexane skeleton are shown in Figure 1.2.

Exercise 1.2. A number of molecules representative of some of the point groups discussed are shown in Figure 1.1. Locate all of the elements of symmetry for each.

ISOMERISM AND MEASUREMENTS

The molecular point group describes the symmetry characteristics of a particular static arrangement of the nuclei. In fact, the nuclei are not static but in constant motion, oscillating about their equilibrium positions even at 0 K! In the classical sense, we determine the symmetry on the basis of a time-averaged structure or, equivalently, a spatially averaged structure. This works because our human time scale (about 0.1 s) and the time scale of most of our measurement techniques are long compared to the time scales of molecular vibrations. The implicit conclusion is that the symmetry of a molecule may depend on the method of measurement [17]. We may therefore define *isomers* as molecules having the same molecular formula but differing in structure *and separated by energy barriers*. If isomers convert at immeasurably fast rates, they are *not* considered isomers. Therefore, the method of measurement used to distinguish isomers must be faster than the rate of interconversion.

Table 1.1 lists minimum lifetimes for observation of separate species and the appropriate spectroscopic methods. The time scale of nuclear magnetic resonance (NMR) experiments is particularly long, and many conformational isomers and some constitutional isomers (see below) interconvert rapidly within the time of observation and appear to be more symmetric than simple bonding considerations would imply. We will expand on these ideas after the next two sections.

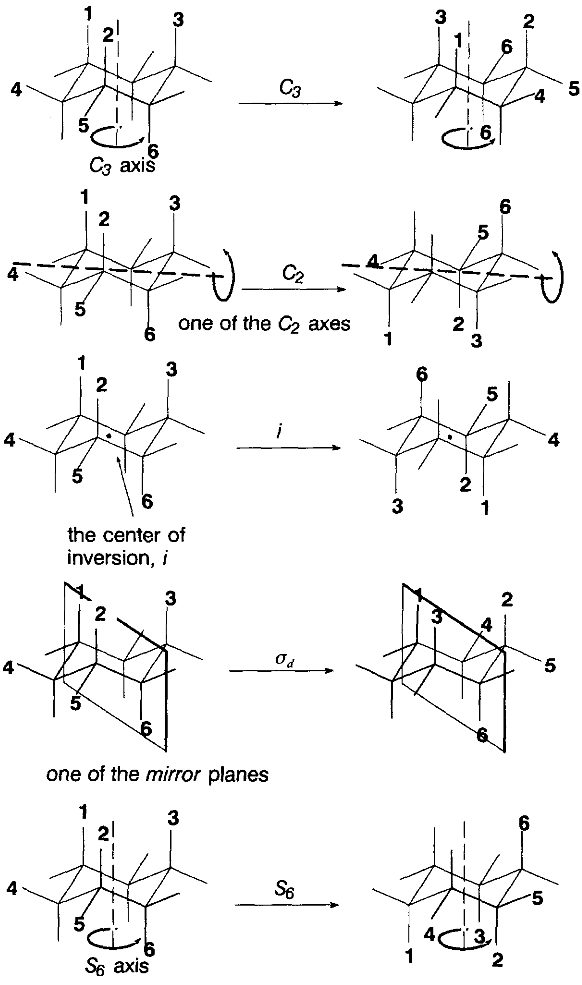

C3
C3 axis
C2
one of the C2 axes
i
the center of inversion, i
σd
one of the mirror planes
S6
S6 axis

Figure 1.2. Symmetry elements of D_{3d} in cyclohexane.

TABLE 1.1. Minimum Lifetimes for Observation of Separate Species

Type of Observation	Lifetime (s)
Electron diffraction	10^{-20}
Neutron, X-ray diffraction	10^{-18}
Ultraviolet (UV) visible	10^{-15}
Infrared (IR) Raman	10^{-13}
Microwave	10^{-4}–10^{-10}
Electron spin resonance (ESR)	10^{-4}–10^{-8}
NMR	10^{-1}–10^{-9}
Mössbauer (iron)	10^{-7}
Molecular beam	10^{-6}
Physical isolation and separation $>10^2$	

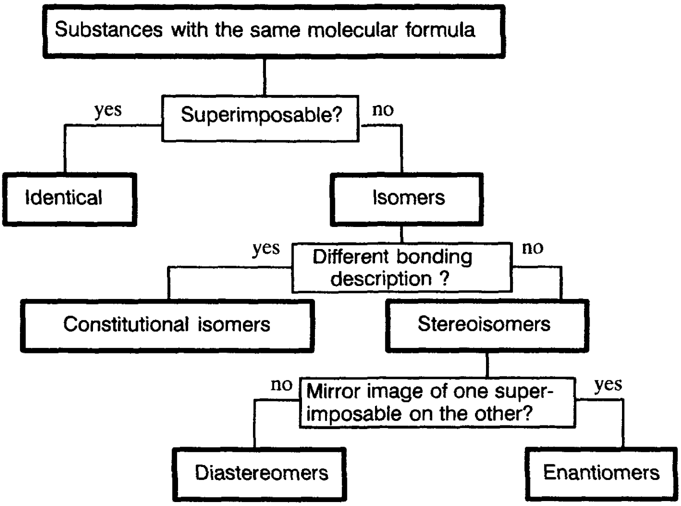

Substances with the same molecular formula
Superimposable?
yes
no
Identical
Isomers
Different bonding description ?
yes
no
Constitutional isomers
Stereoisomers
Mirror image of one superimposable on the other?
no
yes
Diastereomers
Enantiomers

Figure 1.3. Flow chart for deciding stereomeric relationships between pairs of substances.

STEREOISOMERISM OF MOLECULES

The stereomeric relationship between pairs of substances may be derived through the sequence of questions and answers represented by the flow diagram [17] in Figure 1.3. In terms of properties, three broad categorizations arise:

1. **Identical Molecules** Not distinguishable under any conditions, *chiral or achiral.*
2. **Enantiomers** The same in all scalar properties and distinguishable only under chiral conditions. Only molecules of which the point groups are C_n ($n \geq 1$), D_n ($n > 1$), T, O, or I are chiral and can exist in enantiomeric forms.
3. **Constitutional Isomers and Diastereomers** Differ in all scalar properties and are distinguishable in principle under any conditions, chiral or achiral. Geometric isomers, which are related by the orientation of groups around a double bond, are a special case of diastereomers.

Molecules are *chiral* if their molecular point groups do *not* include any S_n ($n \geq 1$) symmetry elements. Otherwise they are *achiral.* An achiral molecule is not distinguishable from its own mirror image. This is often phrased as "an achiral molecule is superimposable on its own mirror image." A chiral molecule is *not* superimposable on its mirror image. A molecule which is identical to the mirror image of another molecule is the enantiomer of that molecule. According to the definitions above, an object is either chiral or it is not, it belongs to a particular point group or it does not. However, efforts have been made to define *degrees* of chirality [27] and continuous measures of symmetry [28].

The concepts of *chirality* and *isomerism* may readily be extended to pairs or larger assemblages of molecules, hence the reference to chiral and achiral *environments* above.

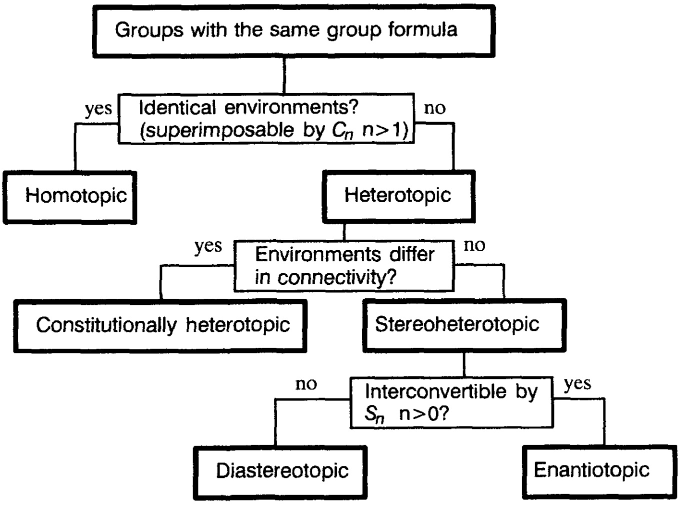

Groups with the same group formula
yes
Identical environments? (superimposable by C_n n>1)
no
Homotopic
Heterotopic
yes
Environments differ in connectivity?
no
Constitutionally heterotopic
Stereoheterotopic
no
Interconvertible by S_n n>0?
yes
Diastereotopic
Enantiotopic

Figure 1.4. Flow chart for deciding stereotopic relationships between pairs of groups.

STEREOTOPIC RELATIONSHIPS OF GROUPS IN MOLECULES

Many of the ideas espoused in this and the next section are due to the work of Mislow [29]. For an alternative discussion of the concepts introduced in this section, see reference 30. The reader is also directed to excellent texts by Juaristi [31] and by Eliel and Wilen [32].

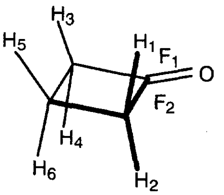
The concepts used to describe relationships between pairs of molecules may readily be extended also to pairs of groups within a molecule [17]. This is particularly useful in determining the appearance of an NMR spectrum or the possibility of selective reaction at similar functional groups. Regions (such as faces of planar portions) around molecules may be similarly classified. The same relationships could also be applied to (groups of) atomic orbitals within the molecule. These are collectively referred to as "groups" for the purpose of the flow chart in Figure 1.4. From the analysis of Figure 1.3, three broad groupings of properties emerge:

1. **Homotopic Groups** Not distinguishable under any conditions, *chiral or achiral.* To have homotopic groups, a molecule must have a finite axis of rotation. Thus the only molecules which *cannot* have homotopic groups are those whose point groups are C_1, C_s, C_i, and $C_{\infty v}$.
2. **Enantiotopic Groups** The same in all scalar properties, distinguishable only under chiral conditions.
3. **Constitutionally Heterotopic and Diastereotopic Groups** Differ in all scalar properties and are distinguishable under any conditions, chiral or achiral. Asymmetric molecules cannot contain homotopic or enantiotopic groups, only diastereotopic or constitutionally heterotopic groups.

Groups may be compared by *internal comparison* (groups in the same molecule) or by *external comparison* (groups in different molecules).

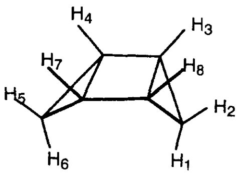
One can also compare *faces* of a molecule in the same way as groups, since the comparison actually applies to environments. Thus, the two faces of the carbonyl groups of aldehydes, unsymmetrical ketones, esters, and other acid derivatives are enantiotopic. Reaction at the two faces by a chiral nucleophile will take place at different rates, resulting in asymmetric induction.

Exercise 1.3. Verify the following group designations:



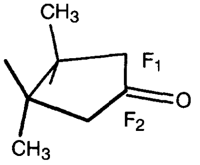
Homotopic groups—(H_1, H_4), (H_2, H_3), (H_5, H_6)
Enantiotopic groups—(H_1, H_2), (H_3, H_4), (H_1, H_3), (H_2, H_4)
Constitutionally heterotopic groups—any of $H_1, \ldots, H_4$ with H_5 or H_6
F_1 and F_2 are homotopic faces.
There are no diastereotopic groups in this molecule.

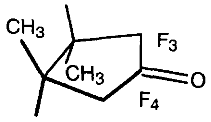
Exercise 1.4. Verify the classification of the pairs of groups in tricyclo[$3.1.0.0^{2,4}$]hexane.



Homotopic—(H_1, H_6), (H_2, H_5), (H_3, H_7), (H_4, H_8)
Enantiotopic—(H_3, H_4), (H_3, H_8), (H_4, H_7), (H_7, H_8)
Diastereotopic—(H_1, H_2), (H_1, H_5), (H_2, H_6), (H_5, H_6)
Constitutionally heterotopic—(H_1, H_3), (H_1, H_4), (H_2, H_8), . . .

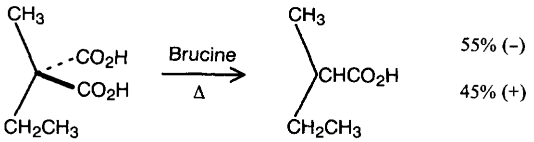
Exercise 1.5. Compare all of the groups and faces of the *trans*-3,4-dimethylcyclopentanones below, by both internal comparison and external comparison.

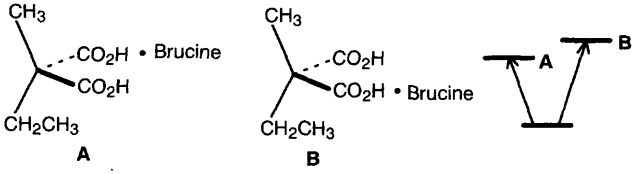




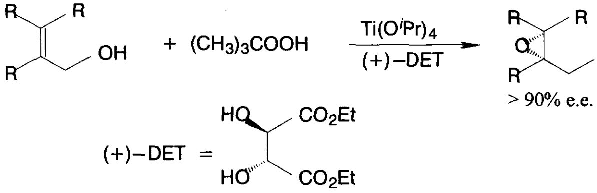
ASYMMETRIC SYNTHESIS AND STEREOCHEMISTRY

Asymmetric synthesis is any synthesis that produces enantiomerically or diastereomerically enriched products. This is the expected result if enantiomerically enriched chiral substrates are employed. Of interest here are asymmetric syntheses where the reactants are either achiral or chiral but racemic. Many examples of this type are collected in volumes edited by Morrison [33]. The first example of an asymmetric synthesis involved use of the *chiral, optically pure* base brucine in a stereoselective decarboxylation of a diacid with enantiotopic carboxyl groups [34]:


CH3
CO2H
CO2H
CH2CH3
Brucine
Δ
CH3
CHCO2H
CH2CH3
55% (-)
45% (+)

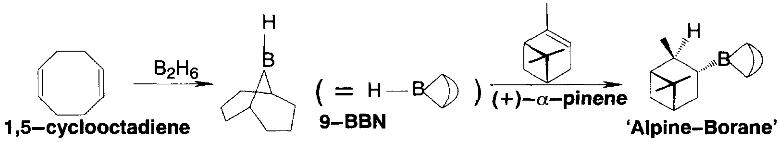

CH3
CO2H • Brucine
CO2H
CH2CH3
A
CH3
CO2H
CO2H • Brucine
CH2CH3
B
A
B

The monobrucine salts **A** and **B** are diastereomeric and therefore different in all properties, including activation energy for decarboxylation. A carbon atom which contains two enantiotopic groups is prochiral. Efficient stereoselection or asymmetric induction requires tight binding of the chiral reagent to the achiral substrate. In addition, there should be a large steric or stereoelectronic distinction between the groups in both substrate and the chiral reagent. For this purpose, the distinction between methyl and ethyl groups in Markwald's experiment shown above is less than ideal. The tight binding requirement can be satisfied by the use of transition metals to which chiral auxiliaries are attached as ligands. One example, the Katsuki–Sharpless epoxidation of allylic alcohols [35], serves to illustrate the principles:

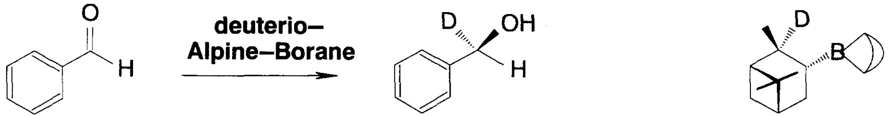

R
R
R
OH
+ (CH3)3COOH
Ti(O^iPr)4
(+)–DET
R
R
O
R
OH
> 90% e.e.
(+)–DET =
HO
CO2Et
HO
CO2Et

Both the allylic alcohol and *tert*-butyl hydroperoxide are achiral, but the product epoxide is formed in high optical purity. This is possible because the catalyst, titanium tetraisopropoxide, forms a chiral (possibly dimeric [36]) complex with resolved diethyl tartrate [(+)-DET] which binds the two achiral reagents together in the reactive complex. The two enantiotopic faces of the allylic double bond become diastereotopic in the chiral complex and react at different rates with the *tert*-butyl hydroperoxide. Many other examples may be found in recent reviews [31, 37–39].

The field of organoboron chemistry pioneered by Brown [40] also provides a wealth of excellent transformations. Consider the asymmetric reduction of carbonyl compounds by Alpine-Borane [41]. Alpine-Borane is prepared by the following sequence:

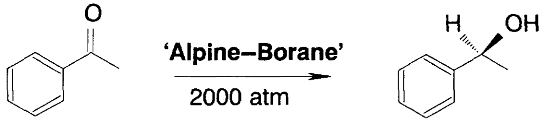

1,5–cyclooctadiene
B2H6
H
B
(= H–B)
9–BBN
(+)–α–pinene
H
B
'Alpine–Borane'

In the second step, achiral 9-borabicyclo[3.3.1]nonane (9-BBN) adds to the less hindered diastereotopic face of α-pinene to yield the chiral reducing agent Alpine-Borane. Aldehydes are rapidly reduced to alcohols. The reaction with deuterio-Alpine-Borane, which yields (*R*)-α-*d*-benzyl alcohol in 98% enantiomeric excess (ee) reveals a very high degree of selectivity of the enantiotopic faces of the aldehyde group in a crowded transition state:



benzaldehyde **(*R*)–α–*d*–benzyl alcohol** 98% e.e. **deuterio– Alpine–Borane**

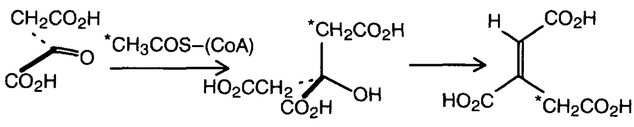
As a consequence of steric congestion in the transition state, ketones generally require high pressures to increase the reaction rate but yield optically active secondary alcohols in high ee. Thus, acetophenone yields 100% ee. of (*S*)-1-phenylethanol at 2000 atm:



acetophenone **(*S*)–1–phenylethanol** 100% e. e.

Many instances of stereospecific selection of enantiotopic groups or faces may be found in nature. One such is extracted from the tricarboxylic acid cycle and is shown in Exercise 1.6. At each step, achiral reactants are transformed to achiral products with high stereospecificity!

Exercise 1.6. Analyze the following sequence from the tricarboxylic acid cycle (*C denotes isotopically labeled carbon):



oxaloacetic acid citric acid aconitic acid

NMR AND STEREOCHEMISTRY

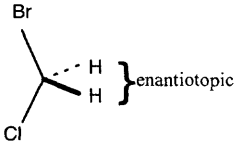
Nuclear magnetic resonance chemical shift differences can serve as an indicator of molecular symmetry. If two groups have the same chemical shift, they are *isochronous*. Isochrony is a property of homotopic groups and of enantiotopic groups under achiral conditions. Diastereotopic or constitutionally heterotopic groups will have different chemical shifts (be *anisochronous*), except by accidental equivalence and/or lack of sufficient resolution.

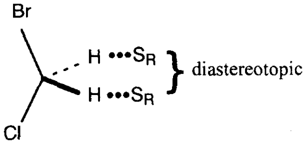
To be anisochronous, (1) groups may not be related by symmetry, taking into consideration internal motions which are rapid on the NMR time scale, and (2) there must be sufficient field gradient so that the difference is observable.

For homotopic groups, chemical shifts are indistinguishable in chiral or achiral solvents, that is, the groups are isochronous.

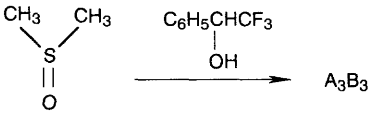
Enantiotopic groups are isochronous in achiral solvents and distinguishable (anisochronous) in chiral solvents.

In principle, the enantiotopic protons of bromochloromethane will be anisochronous in a chiral solvent. However, it requires a fair degree of association to make the chemical shift difference visible. This requirement may be satisfied in hydrogen-bonding solvents:





Thus the enantiotopic methyl groups of dimethylsulfoxide form an A_3B_3 spin system in 1-phenyl-2,2,2-trifluoroethanol; Figure 1.5 [42]:



The hydrogen-bonding association of amino acid esters with 1-phenyl-2,2,2-trifluoroethanol is sufficient to permit NMR to be used as a method for determining the optical purities of α-amino acids [43].

The same principle is involved in the use of chiral lanthanide chemical shift reagents for the determination of enantiotopic purity [44].

Figure 1.6 illustrates the expected observations when a chiral solute is dissolved in a chiral solvent and optical purities of both vary from zero (racemic) to 100%. When the optical purity of the solvent is increased, the separation of the enantiomer (actually diastereomer in the chiral solvent) signals increases. When the signal separation is sufficient, the optical purity of the solute may be determined by integration of the paired signals. When the solute optical purity is 100%, only a single signal is observed at all solvent optical purities. Recognition of the solute optical purity in the absence of the second

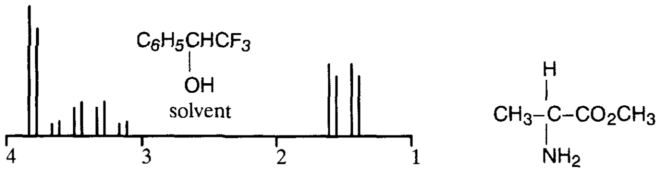


Figure 1.5. Simulated NMR spectrum of methyl alanine in a chiral solvent.

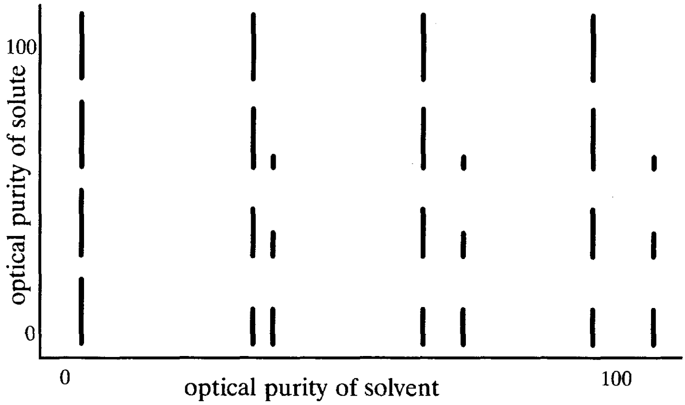


Figure 1.6. Effect of solvent and solute optical purity on the appearance of NMR signals of enantiomers or enantiotopic groups (bottom row).

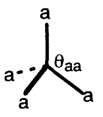
signal requires prior knowledge of the expected pure enantiomer chemical shift under the conditions of the experiment.

Enantiomeric purity is often determined by derivatization with an optically pure chiral agent. For alcohols and amines, α-methoxy-α-trifluoromethylphenylacetic acid (MTPA) and α-cyano-α-fluorophenylacetic acid (CFPA) [45] work well.

SYMMETRY AND STRUCTURAL PARAMETERS

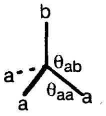
Structural parameters (bond lengths, bond angles, dihedral angles) *must* be the same in a molecule when they are interconvertible by a symmetry operation, that is, congruent. Conversely, structural parameters *cannot* be the same in a molecule when they are not congruent. If the structural parameters are not congruent, it is not possible to use symmetry arguments to predict the magnitude of the difference.

Some relationships between the bond lengths and angles of nominally tetrahedral molecules are shown below. The notation a and b denote groups which are different in some way. The point groups shown denote the *molecular* point group. For the relationships to hold *exactly*, the structures of a and b must be such as to preserve the overall symmetry. The relationships may be *approximately* obeyed if the denoted point groups are a fair representation of the *local* symmetry. For example, the first structure will have exactly T_d symmetry if a is H, Cl, or Me but not if a is Et, since the ethyl group does not have a threefold axis of symmetry. Equation (1.1) defines the tetrahedral angle. Equation (1.2) may be handy for relating the internal bond angle of a threefold symmetric species, such as ammonia, to the out-of-plane angle of the bonds. Equation (1.3) applies to molecules like methylene chloride (CH_2Cl_2) or cyclopropane.



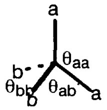
T_d

$$\cos\theta_{\mathrm{aa}} = -\tfrac{1}{3} \tag{1.1}$$



C_{3v}

$$3\sin^2\theta_{\mathrm{ab}} = 2(1 - \cos\theta_{\mathrm{aa}}) \tag{1.2}$$



C_{2v}

$$\cos\theta_{\mathrm{ab}} = -\cos(\tfrac{1}{2}\theta_{\mathrm{aa}})\cos(\tfrac{1}{2}\theta_{\mathrm{bb}}) \tag{1.3}$$

Exercise 1.7. What point groups are available for different orientations of the ethyl groups in the 'T_d' structure with a = Et?

NOTE ON HYBRIDIZATION

The concept of hybridization was introduced to provide a mechanism for achieving directionality in bonding, recognizing implicitly that linear combinations of the $2s$ and some of the three $2p$ orbitals point in well-defined directions relative to other such combinations. Thus if one takes a 1 : 1 linear combination of the $2s$ orbitals and *one* of the $2p$ orbitals (leaving the other two $2p$ orbitals alone), one obtains two *sp* hybrid orbitals which are directed at an angle of 180° to each other. As we shall see later, orbitals mix (or hybridize) so as to provide the best overlap for bonding. Mixing the $2s$ orbital with *two* of the three $2p$ orbitals yields three equivalent sp^2 hybrid orbitals which are exactly arranged at 120° relative to each other, yielding the familiar trigonal planar pattern of bonds when each sp^2 hybrid orbital forms a sigma bond to a different but identical atom or group. Likewise, four equivalent sp^3 hybrid orbitals directed toward the corners of a tetrahedron with equal interorbital angles of 109.47° are obtained when the $2s$ and all *three* $2p$ orbitals are mixed. The *one, two* and *three* refer to the "weights" of the $2p$ orbitals relative to the $2s$ orbital in the *sp*, sp^2, and sp^3 hybrid orbitals, respectively. The angles between two equivalent hybrid orbitals are determined by the weights of the $2p{:}2s$ mixture. Conversely, observation of interbond angles of 180°, 120°, and 109.47° between two equivalent (by symmetry) geminal C—X bonds implies that the carbon atom is using *sp*, sp^2, and sp^3 hybrid orbitals, respectively, to form those bonds. Hybridization can be inferred from the observed angles. Since the observed interbond angles are rarely the idealized values 180°, 120°, and 109.47°, it follows that the orbitals are not the idealized hybrids but rather hybrids where the weight of the $2p$ orbital relative to the $2s$ orbital is a positive real number, say λ^2. In this case, a general hybrid orbital, h_i, will thave the composition $s + \lambda_i p$, which is equivalent to $sp^{\lambda_i^2}$ hybridization. The weight λ_i^2 may range from zero to infinity (pure s to pure p). Normalization of the hybrid orbitals requires that the following relationships hold:

$$\sum_i \frac{1}{1+\lambda_i^2} = 1 \qquad \frac{1}{1+\lambda_i^2} = s \text{ character of hybrid orbital } h_i \tag{1.4}$$

$$\sum_i \frac{\lambda_i^2}{1+\lambda_i^2} = 1,2,3 \qquad \frac{\lambda_i^2}{1+\lambda_i^2} = p \text{ character of hybrid orbital } h_i \tag{1.5}$$

In equations (1.4) and (1.5), the sums run over the number of *hybridized* orbitals. For any pair of hybrid orbitals, h_i and h_j, the following relationship exists:

$$1 + \lambda_i \lambda_j \cos \theta_{ij} = 0 \tag{1.6}$$

where θ_{ij} is the angle between two *hybridized* orbitals.

Exercise 1.8. What is the hybridization of the carbon orbitals which form the C—H and C—C bonds of cyclopropane (HCH = 114°)? Verify that if the carbon hybrids which are used for the C—H bonds are exactly sp^2, then the two equivalent hybrids for the C—C bonds must be sp^5 and the interorbital angle is 101.5°!

Empirically, C^{13}—H spin–spin coupling constants are proportional to the "*s* character" of the hybrid orbital used in the σ bond to H:

$$J_{\mathrm{CH}}\ (\mathrm{cps}) \approx \frac{500}{1+\lambda_i^2} \tag{1.7}$$

SYMMETRY AND ORBITALS

Symmetry properties of atomic and molecular orbitals will prove useful in a variety of contexts. We will familiarize ourselves with the characteristics of the basic types of orbitals which will be used throughout the remainder of this book. It is not proper to assign a point group label to orbitals because of the phase characteristics, but rather to the charge distribution which would result upon squaring the orbital. The orbital may then be characterized by designating the label of the *irreducible representation* according to which it transforms within the context of the local or global molecular point group. These attributes are specifically described for atomic *s*, *p*, and sp^n (hybrid) atomic orbitals and for molecular orbitals below.

Atomic Orbitals

The symmetry characteristics of *s*, *p*, and sp^n (hybrid) atomic orbitals are illustrated in Figure 1.7. Thus the charge distribution due to an electron in an atomic *s* orbital is spherically symmetric (point group K_h) and the *s* orbital itself will transform as the totally symmetric irreducible representation. Alternatively, one may assign a label, *S* or *A*, which describes the behavior of the orbital under any relevant symmetry operations. For instance, the *s* orbital does not change sign (phase) upon reflection in any plane containing its center or upon rotation through any angle about any axis of symmetry. It is *symmetric* with respect to any symmetry operation, and this characteristic is conveniently assigned the label *S* for whichever symmetry operation is considered. On the other hand, the charge distribution due to an electron in an atomic *p* orbital is dumbbell

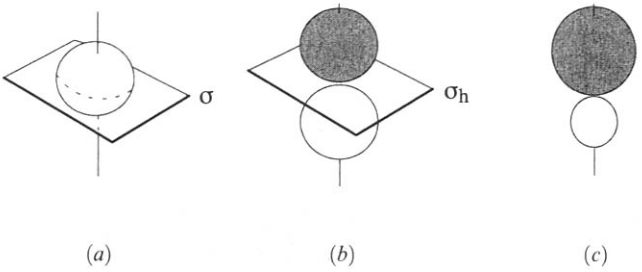
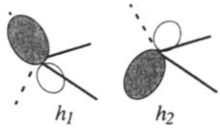


Figure 1.7. The symmetry characteristics of (*a*) *s*, (*b*) *p*, and (*c*) sp^n (hybrid) atomic orbitals. The shapes of the electron distributions are similar if one ignores the phases.

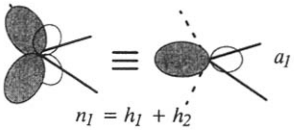
shaped (axially symmetric with a horizontal mirror plane, point group $D_{\infty h}$). The *p* orbital itself will transform as the irreducible representation Σ_u^+; that is, the *p* orbital does not change sign (phase) upon reflection in any plane containing its principal axis or upon rotation through any angle about the principal axis but *does* change sign (phase) upon reflection across the horizontal mirror plane (its own nodal plane) and rotation about any axis of symmetry (necessarily twofold) contained in that plane. It is symmetric (*S*) with respect to any of the first set of symmetry operations. It is *antisymmetric* with respect to any of the second set of symmetry operations, and is assigned the label *A* for these. Hybrid atomic orbitals sp^n retain only the axial symmetry of the pure *s* and *p* orbitals. The node (boundary separating the two phases of the orbital) is now a curved surface and no longer a symmetry element. The charge distribution belongs to the point group $C_{\infty v}$, and the hybrid orbital transforms as the a_1 irreducible representation of $C_{\infty v}$.

Molecular and Group Orbitals

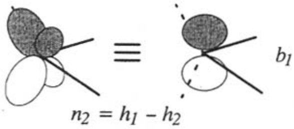
Let us accept that molecular orbitals (MOs) and group orbitals are both described as linear combinations of atomic orbitals. Exactly how and why this is the case will be seen in Chapter 2 and Appendix A. For the purpose of the present section, *proper* MOs are those linear combinations which transform as irreducible representations of the *molecular* point group, that is, are *symmetry adapted. Group* orbitals are linear combinations which are symmetric or antisymmetric with respect to any *local* symmetry operations of that part of the molecule which constitutes the group (e.g., a methyl group). At an intermediate level of description, MOs may be thought of as linear combinations of group orbitals. We shall frequently use the term *localized orbital.* This term has a formal definition in the literature of electronic structure theory, but we shall use it in a loose sense to describe a characteristic piece of a true MO or a group MO such as a sigma bond between a particular pair of atoms or an atomic orbital describing a nonbonded pair of electrons. A localized MO may indeed be a proper MO or a group MO which happens to be concentrated in one region of the molecule. More likely, however, a proper MO or a group MO would be described as a linear combination of localized MOs. Some examples of proper MOs and group MOs are shown in Figure 1.8. Notice that the "proper" MOs of water which describe the "lone pairs" of electrons are in- and out-of-phase combinations of the "rabbit ears" often pictured in elementary texts. The out-of-phase combination has no *s* character at all. It is a pure *p* orbital on the oxygen atom. The same is true of the proper MOs which describe the O—H bonds.



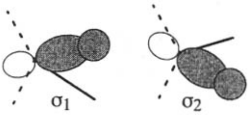
The two *localized* nonbonding orbitals, h_1 and h_2, of H_2O. These are sp^n hybrids ($n \approx 3$).



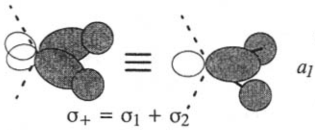
n_1 –A proper MO – a linear combination of the two localized orbitals which is *S* with respect to all symmetry operations of the C_{2v} point group of H_2O.



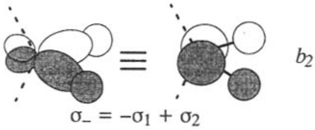
n_2 –A proper MO – a linear combination of the two localized orbitals which is *A* with respect to reflection in the plane of the molecule, *A* w.r.t rotation about the C_2 axis and *S* w.r.t. reflection in the bisecting mirror plane of symmetry.



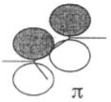
The two *localized* sigma bonding orbitals, σ_1 and σ_2, of H_2O. These are linear combinations of a sp^n hybrid ($n \approx 3$) of O and an *s* orbital of H.



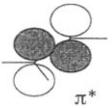
σ_+ –A proper MO – a linear combination of the two localized bond orbitals which is *S* with respect to all symmetry operations of the C_{2v} point group of H_2O.



σ_- –A proper MO – a linear combination of the two localized bond orbitals which is *S* with respect to reflection in the plane of the molecule, *A* w.r.t rotation about the C_2 axis, and *A* w.r.t. reflection in the bisecting mirror plane of symmetry.



The π bond of ethylene (and other olefins) is a proper MO, highly localized to the two carbon atoms. It is the linear combination of the two *2p* orbitals which is *S* with respect to reflection in the bisecting plane and *A* w.r.t. a 180° rotation about the C_2 axis which contains that plane. All 'π'-type orbitals are *A* w.r.t. reflection in the nodal plane of the *p* orbitals themselves.



The π* antibonding orbital of ethylene (and other olefins) is a also a proper MO, highly localized to the two carbon atoms. It is the linear combination of the two *2p* orbitals which is *A* with respect to reflection in the bisecting plane and *S* w.r.t. a 180° rotation about the C_2 axis which contains that plane.

Figure 1.8. Examples of symmetry-adapted (proper) MOs and their constituent atomic or localized orbitals.

IN WHAT COMBINATION?

While it is easy to make sketches of hybrid, group, and molecular orbitals such as used for illustrative purposes in Figure 1.8, the criteria for choosing the *degree* of hybridization or the specific *amount* of mixing of orbitals from different atoms to make MOs are not obvious. As we have seen, if the molecule has nontrivial symmetry (i.e., is not asymmetric, point group C_1), then the charge distribution must have the same symmetry as the molecular framework and proper MOs should also reflect the symmetry. Elements of symmetry can serve as a guide for the amount of mixing. The π bonding MO of ethylene (Figure 1.8) is partly determined by the symmetry. The $2p$ orbitals of each C must mix with equal weights. But why is the in-phase combination occupied and not the out-of-phase combination? The answer lies in the quantum mechanical theory of electronic structure (MO theory).

In Chapter 2, the physical and mathematical basis of the most familiar version of MO theory is presented in a qualitative way using a two-electron "molecule" as an example (a more rigorous treatment is given in Appendix A). It is argued that the chemical and physical properties of molecules arise in large part from the distribution of the electrons in the molecule. This has been taken as an article of faith for many years and ultimately proved in the case of the energy [46]. It will be seen that the simplest form of function which correctly describes the simultaneous distribution of all the electrons in a molecule is a product of functions (MOs) which individually describe the distribution of one electron at a time. Actually one must take a linear combination of such products to allow for the fact that any electron may have any of the one-electron distributions and to recognize the *fermion* character of electrons. In other words, a many-electron wave function is expressed as an antisymmetrized sum of products of one-electron wave functions or MOs. An optimum set of MOs is derived by *minimizing the energy* of the assemblage of electrons and atoms with respect to variations in the MOs. Since the MOs are expanded in terms of atomic orbitals (strictly speaking, atomic orbital–like functions), the process involves variation of the amount of mixing of the atomic orbitals until a mixing combination is found which yields the lowest possible energy. Indeed, a prescription for finding this optimum combination falls out of the theory. The treatment in Chapter 2 is within the grasp of any senior undergraduate student and is worth pursuing. The theory is presented in a mathematically rigorous fashion in Appendix A and concludes with a brief description of ways to improve the theory as well as a practical guide to one of the current computer programs, the GAUSSIAN package of programs, which implements the theory for solving chemical problems.

The level of treatment in Appendix A is most suitable for graduate students. Undergraduates with inadequate mathematical preparation may skip to Chapter 3 and pick up the story at the stage where the orbital interaction diagram is derived.