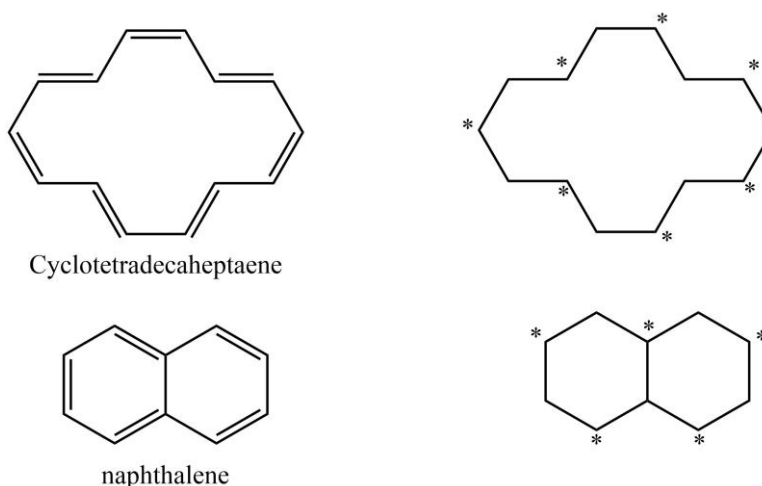


❖ Alternant and Non-Alternant Hydrocarbons

Besides benzenoid and non-benzenoid grouping, all aromatic hydrocarbons can also be classified as alternant and non-alternant hydrocarbons. A general discussion on the two types is given below.

➤ Alternant Hydrocarbons

An alternant hydrocarbon is any conjugated hydrocarbon system that doesn't possess an odd-membered cycle. In such cases, it is quite plausible to follow a starring route, where all the C atoms are divided into two groups; in one group, all the carbons are marked with a star in such a way that no two-starred or unstarred atoms are mutually bonded.



In alternate hydrocarbons, the secular determinant in the Hückel approximation has a simpler form, since cross-diagonal elements between atoms in the same set are necessarily 0.

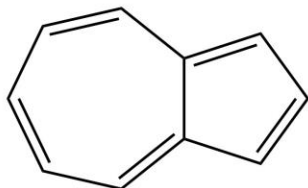
Important properties of alternant hydrocarbons:

- i) The coefficients of two paired MOs are the same at the same position, except for a change of sign in the unstarred group.
- ii) The electron density or population at all sites is equal to 1 in the ground electronic state, so that the distribution of π -electron density is uniform across the entire molecular structure.
- iii) The energies of molecular orbitals for the π system are paired, that is for an orbital of energy $E = \alpha + x\beta$ there is one of energy $E = \alpha - x\beta$.

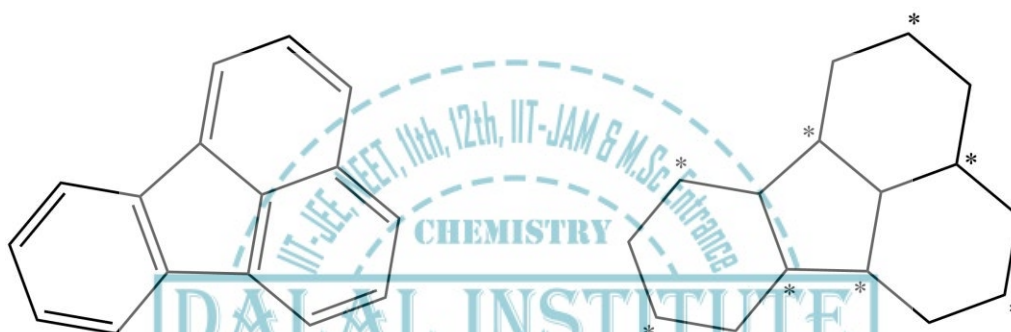
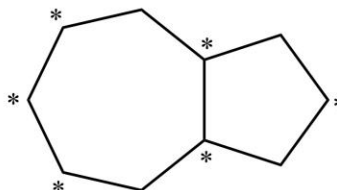
Furthermore, if the alternant hydrocarbon has an odd number of carbon atoms then there must be an unpaired orbital with no bonding energy (i.e., a non-bonding wave function). For this wavefunction, the coefficients on the atomic sites can be given without calculation; the coefficients on all the orbitals belonging to the smaller set are 0, and the sum of the coefficients of the orbitals around them should also be zero. Modest calculations allow the assignment of different coefficients with normalization. This route allows the prediction of patterns of reactivity and can be employed to find Dewar's reactivity numbers for all positions.

➤ **Non-Alternant Hydrocarbons**

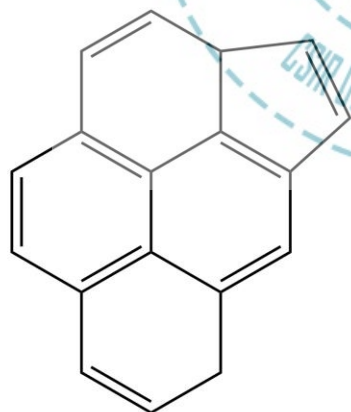
A non-alternant hydrocarbon is any conjugated hydrocarbon system in which it is not possible to mark all the carbon atoms in a complete alternate fashion.



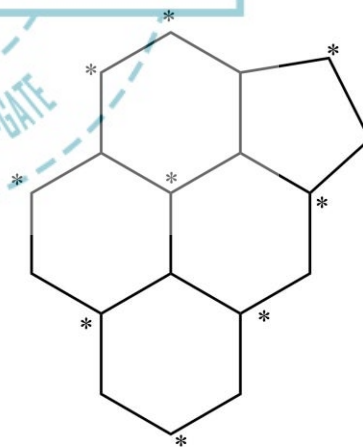
Azulene



Fluoranthene



2a,6-dihydrocyclopenta[cd]pyrene



In non-alternate hydrocarbons, the energies of the antibonding and bonding molecular orbitals are not the same and opposite. Furthermore, it is also worthy to note that the charge distributions in non-alternate hydrocarbons also are not the same in the anions cations and in radical species.

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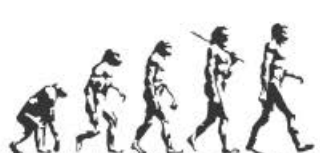
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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Table of Contents

CHAPTER 1	11
Nature of Bonding in Organic Molecules	11
❖ Delocalized Chemical Bonding	11
❖ Conjugation	14
❖ Cross Conjugation	16
❖ Resonance	18
❖ Hyperconjugation	27
❖ Tautomerism	31
❖ Aromaticity in Benzenoid and Nonbenzenoid Compounds	33
❖ Alternant and Non-Alternant Hydrocarbons	35
❖ Huckel's Rule: Energy Level of π -Molecular Orbitals	37
❖ Annulenes	44
❖ Antiaromaticity	46
❖ Homoaromaticity	48
❖ PMO Approach	50
❖ Bonds Weaker Than Covalent	58
❖ Addition Compounds: Crown Ether Complexes and Cryptands, Inclusion Compounds, Cyclodextrins	65
❖ Catenanes and Rotaxanes	75
❖ Problems	79
❖ Bibliography	80
CHAPTER 2	81
Stereochemistry	81
❖ Chirality	81
❖ Elements of Symmetry	86
❖ Molecules with More Than One Chiral Centre: Diastereomerism	90
❖ Determination of Relative and Absolute Configuration (Octant Rule Excluded) with Special Reference to Lactic Acid, Alanine & Mandelic Acid	92
❖ Methods of Resolution	102
❖ Optical Purity	104
❖ Prochirality	105
❖ Enantiotopic and Diastereotopic Atoms, Groups and Faces	107
❖ Asymmetric Synthesis: Cram's Rule and Its Modifications, Prelog's Rule	113
❖ Conformational Analysis of Cycloalkanes (Upto Six Membered Rings)	116
❖ Decalins	122
❖ Conformations of Sugars	126
❖ Optical Activity in Absence of Chiral Carbon (Biphenyls, Allenes and Spiranes)	132
❖ Chirality Due to Helical Shape	137
❖ Geometrical Isomerism in Alkenes and Oximes	140
❖ Methods of Determining the Configuration	146

❖ Problems.....	151
❖ Bibliography.....	152
CHAPTER 3.....	153
Reaction Mechanism: Structure and Reactivity	153
❖ Types of Mechanisms.....	153
❖ Types of Reactions	156
❖ Thermodynamic and Kinetic Requirements.....	159
❖ Kinetic and Thermodynamic Control	161
❖ Hammond's Postulate.....	163
❖ Curtin-Hammett Principle	164
❖ Potential Energy Diagrams: Transition States and Intermediates	166
❖ Methods of Determining Mechanisms.....	168
❖ Isotope Effects	172
❖ Hard and Soft Acids and Bases.....	174
❖ Generation, Structure, Stability and Reactivity of Carbocations, Carbanions, Free Radicals, Carbenes and Nitrenes.....	176
❖ Effect of Structure on Reactivity	200
❖ The Hammett Equation and Linear Free Energy Relationship.....	203
❖ Substituent and Reaction Constants.....	209
❖ Taft Equation.....	215
❖ Problems.....	219
❖ Bibliography.....	220
CHAPTER 4.....	221
Carbohydrates	221
❖ Types of Naturally Occurring Sugars	221
❖ Deoxy Sugars	227
❖ Amino Sugars.....	229
❖ Branch Chain Sugars	230
❖ General Methods of Determination of Structure and Ring Size of Sugars with Particular Reference to Maltose, Lactose, Sucrose, Starch and Cellulose.....	231
❖ Problems.....	239
❖ Bibliography.....	240
CHAPTER 5.....	241
Natural and Synthetic Dyes	241
❖ Various Classes of Synthetic Dyes Including Heterocyclic Dyes	241
❖ Interaction Between Dyes and Fibers	245
❖ Structure Elucidation of Indigo and Alizarin	247
❖ Problems.....	252
❖ Bibliography.....	253
CHAPTER 6.....	254
Aliphatic Nucleophilic Substitution	254
❖ The S_N2 , S_N1 , Mixed S_N1 and S_N2 , S_Ni , S_N1' , S_N2' , S_Ni' and SET Mechanisms.....	254

❖ The Neighbouring Group Mechanisms.....	263
❖ Neighbouring Group Participation by π and σ Bonds	265
❖ Anchimeric Assistance	269
❖ Classical and Nonclassical Carbocations	272
❖ Phenonium Ions	283
❖ Common Carbocation Rearrangements.....	284
❖ Applications of NMR Spectroscopy in the Detection of Carbocations	286
❖ Reactivity – Effects of Substrate Structure, Attacking Nucleophile, Leaving Group and Reaction Medium	288
❖ Ambident Nucleophiles and Regioselectivity	294
❖ Phase Transfer Catalysis.....	297
❖ Problems.....	300
❖ Bibliography	301
CHAPTER 7	302
Aliphatic Electrophilic Substitution	302
❖ Bimolecular Mechanisms – SE_2 and SE_i	302
❖ The SE_1 Mechanism	305
❖ Electrophilic Substitution Accompanied by Double Bond Shifts	307
❖ Effect of Substrates, Leaving Group and the Solvent Polarity on the Reactivity	308
❖ Problems.....	310
❖ Bibliography	311
CHAPTER 8	312
Aromatic Electrophilic Substitution	312
❖ The Arenium Ion Mechanism	312
❖ Orientation and Reactivity	314
❖ Energy Profile Diagrams	316
❖ The Ortho/Para Ratio.....	317
❖ <i>ipso</i> -Attack	319
❖ Orientation in Other Ring Systems	320
❖ Quantitative Treatment of Reactivity in Substrates and Electrophiles	321
❖ Diazonium Coupling.....	325
❖ Vilsmeier Reaction	326
❖ Gattermann-Koch Reaction	327
❖ Problems.....	329
❖ Bibliography	330
CHAPTER 9	331
Aromatic Nucleophilic Substitution	331
❖ The $ArSN_1$, $ArSN_2$, Benzyne and S_RN_1 Mechanisms.....	331
❖ Reactivity – Effect of Substrate Structure, Leaving Group and Attacking Nucleophile.....	336
❖ The von Richter, Sommelet-Hauser, and Smiles Rearrangements	339
❖ Problems.....	343
❖ Bibliography	344

CHAPTER 10	345
Elimination Reactions	345
❖ The E ₂ , E ₁ and E ₁ CB Mechanisms	345
❖ Orientation of the Double Bond.....	348
❖ Reactivity – Effects of Substrate Structures, Attacking Base, the Leaving Group and The Medium	352
❖ Mechanism and Orientation in Pyrolytic Elimination.....	355
❖ Problems.....	358
❖ Bibliography.....	359
CHAPTER 11	360
Addition to Carbon-Carbon Multiple Bonds	360
❖ Mechanistic and Stereochemical Aspects of Addition Reactions Involving Electrophiles, Nucleophiles and Free Radicals.....	360
❖ Regio- and Chemoselectivity: Orientation and Reactivity	370
❖ Addition to Cyclopropane Ring	374
❖ Hydrogenation of Double and Triple Bonds	375
❖ Hydrogenation of Aromatic Rings.....	377
❖ Hydroboration	378
❖ Michael Reaction.....	379
❖ Sharpless Asymmetric Epoxidation	380
❖ Problems.....	382
❖ Bibliography	383
CHAPTER 12	384
Addition to Carbon-Hetero Multiple Bonds	384
❖ Mechanism of Metal Hydride Reduction of Saturated and Unsaturated Carbonyl Compounds, Acids, Esters and Nitriles	384
❖ Addition of Grignard Reagents, Organozinc and Organolithium Reagents to Carbonyl and Unsaturated Carbonyl Compounds.....	400
❖ Wittig Reaction.....	406
❖ Mechanism of Condensation Reactions Involving Enolates: Aldol, Knoevenagel, Claisen, Mannich, Benzoin, Perkin and Stobbe Reactions	411
❖ Hydrolysis of Esters and Amides.....	433
❖ Ammonolysis of Esters.....	437
❖ Problems.....	439
❖ Bibliography.....	440
INDEX	441



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