

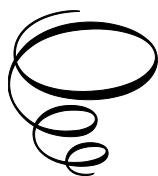
Fundamentals of Stereochemistry

Fundamentals of Stereochemistry

By

Sudhir Chandra Pal

**Cambridge
Scholars
Publishing**



Fundamentals of Stereochemistry

By Sudhir Chandra Pal

This book first published 2025

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

Copyright © 2025 by Sudhir Chandra Pal

All rights for this book reserved. No part of this book may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the copyright owner.

ISBN: 978-1-0364-4253-8

ISBN (Ebook): 978-1-0364-4254-5

In memory of
my Brother-in-law
Dr. Sankar K Saha

Table of Contents

Foreword	xv
Acknowledgements	xvii
Preface	xix
CHAPTER 1: M.F., bonding, structure and naming of molecules	1-24
1.1 Introduction	1
1.2 Molecular formula	1
1.2.1 Cyclic and multiple-bonded compounds	2
1.2.2 D.B.E. or I.H.D.	3
1.3 Hybridisation of carbon orbitals and structure of molecules	4
1.3.1 Hybridisation of tri- and tetra-coordinated N, P, As	7
1.3.2 Polyenes	8
1.4 Bond angle	9
1.5 Bond length	10
1.6 Bond energy and bond dissociation energy	10
1.7 Intramolecular and intermolecular H-bonding	12
1.8 Naming organic compounds	14
1.8.1 Parent selection	15
1.8.2 The characteristic groups to be named as suffix	17
1.8.3 Characteristic groups to be written as prefix only	17
1.8.4 Numbering the parent chain	17
1.8.5 Some illustrative examples	19
Exercise 1	21
CHAPTER 2: Symmetry and chirality	25-82
2.1 Introduction	25
2.1.1 Applications of symmetry	26
2.1.2 Symmetry and stereochemistry	26
2.2 Symmetry elements and operations	27
2.2.1 Axis of symmetry	27
2.2.2 Plane of symmetry	29
2.2.3 Alternating axis of symmetry	30
2.2.4 Centre of symmetry	32
2.3 Classification of molecules into point Groups	33

2.4 Order and symmetry number for different point groups	42
2.5 To investigate symmetry elements in molecules	42
2.5.1 Symmetry with the Fischer projection formula	49
2.6 Symmetry and chirality	51
2.7 Local symmetry and chirotopicity	52
2.7.1 Stereocentre and chiral centre	54
2.8 Factorisation of stereo models into stereogenic units	56
2.8.1 1D and 2D Chirality	56
2.8.2 Chirality in 3-dimension (chirality elements)	57
2.8.3 Pseudoasymmetric stereogenic units	60
2.9 Dipole moment	60
2.9.1 Dipole moment and symmetry	67
Exercise 2	71

CHAPTER 3: Stereoisomerism, configuration and terminologies

83-144

3.1 Introduction	83
3.2 Tetracoordinated carbon: stereogenic centre	83
3.3 Configuration of chiral centre: Fischer projection formulae	86
3.4 Compounds: two stereocentres (constitutionally different)	88
3.5 Newman, sawhorse and flying wedge projections	88
3.6 Relative configuration (threo, erythro)	89
3.6.1 Relative configuration: pref-parf naming	91
3.7 Absolute configuration of a stereocentre and its naming	91
3.7.1 D,L system	92
3.7.2 <i>R,S</i> – notation (the Cahn-Ingold-Prelog system)	93
3.8 Some naming systems for relative nomenclature	102
3.8.1 Syn-anti nomenclature	102
3.8.2 <i>R*S*</i> - system (Chemical abstract)	103
3.8.3 <i>l,u</i> - naming (Brewster)	103
3.9 Specific rotation and molar rotation	104
3.9.1 Optical purity and enantiomeric excess	106
3.9.2 Specific rotation of a mixture of chiral isomers	106
3.10 Stereoisomers with constitutional structure having all stereocentres in single chain	107
3.10.1 Meso-isomers	111
3.10.2 Epimers	112
3.11 Stereoisomerism of compounds having stereocentres in branched chain	112
3.12 Stereogenicity, chirotopicity and pseudoasymmetry	115

3.13 Determination of configuration	118
3.13.1 Chemical correlations	118
3.13.2 Chemical correlation involving diastereomers	121
3.13.3 Experimental determination of absolute configuration	122
3.14 Stereoisomers: classification	122
Exercise 3	125

CHAPTER 4: Prostereoisomerism: topicity of ligands and faces **145-202**

4.1 Introduction	145
4.2 Prochirality and prostereoisomerism	146
4.3 Topic relationship of Ligands	147
4.3.1 Substitution approach	148
4.3.2 Symmetry criterion	149
4.3.3 Homotopic ligands	149
4.3.4 Enantiotopic ligands	154
4.3.5 Diastereotopic ligands	160
4.4 Topicity of faces of planar centres / planar molecules	163
4.4.1 Homotopic, Enantiotopic and diastereotopic faces	163
4.5 External comparison	166
4.6 Nomenclature of stereoheterotopic ligands and faces	167
4.6.1 pro- <i>R</i> /pro- <i>S</i> designation for ligands	167
4.6.2 pro- <i>Z</i> /pro- <i>E</i> (pro- <i>cis</i> /pro- <i>trans</i>), nomenclature of diastereotopic ligands	171
4.6.3 Naming of stereoheterotopic faces: <i>Re</i> / <i>Si</i> symbols	172
4.6.4 <i>Re</i> / <i>Si</i> notations for stereoheterotopic ligands	173
4.7 Differentiation of stereoheterotopic ligands and faces	174
4.7.1 Some biochemical reactions	174
4.7.2 Nuclear magnetic resonance to distinguish stereoheterotopic ligands	179
4.7.3 Heterotopicity of faces of alkenes: NMR studies	185
4.7.4 Isochronous but anisogamous nuclei	186
Exercise 4	190

CHAPTER 5: Conformation of acyclic molecules **203-252**

5.1 Introduction	203
5.2 Conformational isomerism and tautomerism	205
5.2.1 Conformation and Configuration	205
5.3 Conformational analysis	209
5.3.1 Dihedral angle, torsion angle and naming of conformations	209

5.3.2 Conformational analyses of some typical but simple molecules	212
5.3.3 Conformations of some more typical compounds	219
5.3.4 Conformations involving rotation about C-heteroatom bond	225
5.3.5 Conformations arising out of rotation around $C_{(sp^3)}-C_{(sp^2)}$ bond	228
5.3.6 Conformations arising out of rotation around $C_{(sp^2)}-C_{(sp^2)}$ single bond	234
5.3.7 Conformations for rotation around $C_{(sp^3)}-C_{(sp)}$ bond	235
5.3.8 Conformational structure of proteins: The Ramachandran Plot	235
5.4 Stability of diastereomers: erythro (or meso) versus threo	236
5.5 Some Physical properties and conformational analyses	239
5.5.1 Dipole moment	240
5.5.2 Spectral properties	241
Exercise 5	247
 CHAPTER 6: Diastereomerism of the cis-trans type	 253-294
6.1 Introduction - stereogenic dyad	253
6.2 Cis-trans isomerism of alkenes	254
6.2.1 Isomerism of compounds: $C=N$ and $N=N$ bond(s)	256
6.2.2 Alkenes with low rotational barrier	256
6.2.3 Cumulenes with odd number of double bonds	257
6.2.4 Amide, peptides and thioamides	258
6.3 Terphenyls	259
6.4 Cis-trans isomerism in inorganic compounds	260
6.5 Designation of configuration of cis-trans isomers	260
6.5.1 Cis-trans designation	260
6.5.2 Syn-anti convention	261
6.5.3 <i>E-Z</i> notation	262
6.6 Cycloalkenes	263
6.7 The isomers in polyenes: non-cumulated double bonds	263
6.8 Isomers for compounds having both stereogenic double bonds and stereocentres	265
6.9 Stereoisomerism of ring compounds having substituents	267
6.9.1 Symmetry examination to test chirality	269
6.9.2 Constitutional structures having substituents at two or more ring atoms	269
6.9.3 General naming of configuration of cyclic diastereomers	271

6.10 Comparison of properties of cis-trans isomers	272
6.10.1 Physical properties	273
6.10.2 Spectral properties	277
6.11 ω -Fatty acids and drugs	286
Exercise 6	287
CHAPTER 7: Axial and planar chirality, and other forms of stereogenicity	295-344
7.1 Introduction	295
7.2 Stereochemistry of biphenyls	295
7.2.1 Conformational analysis	296
7.2.2 Chirality	298
7.2.3 Atropisomerism	298
7.2.4 Buttressing effect	301
7.2.5 Bridged biphenyls	304
7.2.6 Atropisomers other than biphenyls and binaphthyls	305
7.2.7 Designation of configuration of chiral biphenyls	309
7.2.8 Medicinally active atropisomers	311
7.3 Stereochemistry of allenes	312
7.3.1 Configurational notation to chiral allenes	313
7.3.2 Some synthetic chiral allenes	314
7.3.3 Naturally occurring chiral allenes	314
7.3.4 Chiral allenes with pharmaceutical properties	315
7.4 Stereochemistry of spiranes	315
7.4.1 Spiranes having ring stereocentre(s) other than spiroatom	319
7.5 Stereochemistry of cycloalkylidenes (Hemispiranes)	321
7.5.1 Configurational naming of chiral cycloalkylidenes	321
7.6 Axial chirality of adamantanoids	321
7.7 Planar chirality	322
7.7.1 Cyclophanes	323
7.7.2 Configurational naming	324
7.7.3 Trans-cycloalkenes	326
7.7.4 Annulenes	328
7.7.5 Metal complexes	329
7.8 Helical chirality	330
7.9 Cyclostereoisomerism	331
7.9.1 Cyclostereoisomerism of constitutional origin	331
7.9.2 Cyclostereoisomerism due to ‘gearing’ conformers	334
7.10 Miscellaneous chiral compounds	334
7.10.1 Propeller chirality: Triarylmethanes	334
Exercise 7	336

CHAPTER 8: Resolution and racemisation	345-382
8.1 Introduction	345
8.2 Racemic modification/racemic mixture	345
8.3 Resolution methods	348
8.3.1 Crystallisation methods	348
8.3.2 Biochemical method	351
8.3.3 Chromatographic techniques	351
8.3.4 Resolution via formation of diastereomers	352
8.3.5 via Inclusion compounds and Metal complexes	358
8.3.6 Kinetic methods	358
8.4 Racemisation	360
8.4.1 Physical processes	361
8.4.2 Chemical processes	362
8.4.3 Loss of optical activity not involving racemisation	369
8.4.4 Epimerisation	371
8.4.5 Asymmetric transformation of diastereomers	371
8.4.6 Mutarotation	372
Exercise 8	375
 CHAPTER 9: Monocyclic compounds: their configuration and conformation	 383-448
9.1 Introduction	383
9.1.1 Baeyer's strain theory	383
9.2 Small rings	385
9.2.1 Cyclopropane and its derivatives	385
9.2.2 Cyclobutane and its derivatives	389
9.3 Common rings	390
9.3.1 Cyclopentane and its derivatives	391
9.3.2 Cyclohexane	393
9.3.2a Conformational analysis	393
9.3.2b Ring reversal of cyclohexane	397
9.3.3 Cyclohexane bearing one or more substituents	401
9.3.3a Monosubstituted cyclohexane: conformational free energy (A-value)	401
9.3.3b Determining the conformational composition and A-values	406
9.3.3c Disubstituted cyclohexanes	410
9.3.3d Examples where twist-boat conformations are important	416
9.3.3e Some polysubstituted cyclohexanes	417
9.3.4 Cyclohexanone: alkyl ketone effects	419

9.3.4a Alkyl ketone effects	421
9.3.5 Alkylidenecyclohexanes: allylic 1,3-strain	424
9.3.5a Allylic 1,3-Strain	424
9.3.6 Cyclohexene: allylic 1,2-strain	425
9.3.6a Allylic 1,2 Strain ($A^{1,2}$ strain)	426
9.3.7 Oxane or oxacyclohexane: anomeric effect	427
9.3.7a Anomeric effect	428
9.3.7b Reverse Anomeric effect	432
9.3.8 Cyclohexane ring with two <i>O</i> as ring atoms (dioxanes)	432
9.3.9 Cycloheptane	434
9.4 Some medium rings	435
9.4.1 Cyclooctane	435
9.4.2 Cyclononane	435
9.4.3 Cyclodecane	435
9.4.4 Cycloalkenes of ring size 7 to 12	436
Exercise 9	438
 CHAPTER 10: Compounds containing two / three cyclohexane rings fused together	 449-486
10.1 Introduction	449
10.2 Fused ring compounds	450
10.2.1 Decalins	450
10.2.2 9-Methyldecalin: cis vs trans	454
10.2.3 9,10-Dimethyldecalin	456
10.2.4 Decalones	456
10.2.5 Decalols	458
10.2.6 Octalins	460
10.3 Compounds having three cyclohexane rings fused in succession	463
10.3.1 Perhydrophenanthrenes	463
10.3.2 Epimerisation of 9-perhydrophenanthrones	469
10.3.3 Configuration of perhydrodiphenic acids	472
10.3.4 Perhydroanthracenes	474
Exercise 10	479
 Appendix I: Homomers, enantiomers and diastereomers	 487
Exercise AI	495
 Appendix II: Some critical examples of <i>R,S</i> nomenclature	 503

Appendix III: The configuration of natural monosaccharides	505
Exercise AIII	513
Appendix IV: Stereoisomers with a constitutional structure	515
Exercise AIV	515
Solutions to the problems in exercises 1 - 10	519-612
Exercise 1	519
Exercise 2	523
Exercise 3	531
Exercise 4	549
Exercise 5	557
Exercise 6	566
Exercise 7	573
Exercise 8	581
Exercise 9	587
Exercise 10	604
Solutions to the problems in AI - AIV	613-624
Exercise AI	613
Exercise AIII	616
Exercise AIV	620
Index	- 625-634

Foreword

It is a pleasure to write to this foreword for the book “FUNDAMENTALS OF STEREOCHEMISTRY” by Professor Sudhir C Pal. The book is intended for college undergraduates majoring in chemistry and also to some extent to the post-graduate students as well. Although the stereochemistry has been an integral part of the undergraduate and postgraduate organic syllabus, and has been exclusively covered by many text books, newer books are always welcome to meet the requirements of the present generation of students and teachers. Professor Pal has exercised his 35 years of teaching experience to articulate the contents of the book. The coverage of the essentials of stereochemistry is thoughtful and beyond traditional approaches.

The author has rightfully focused on the symmetry elements and their applications in examining chirality of wide-ranging molecules. The topic of the conformational analysis is particularly informative and educational. It is likely to provide insightful understanding of the nature of the molecules. I personally like the exercises given at the end of each chapter of the book, which would provide enormous opportunities for refinement of thoughts and knowledge.

Congratulations to Professors Pal for an outstanding contribution to the chemistry fraternity. Hopefully, this book serves to give better opportunities to learn the stereochemical features of the complex organic molecules. For the teachers, the book would be a handy one.

Dipakranjan Mal, FRSC
Formerly Professor and Head
Indian Institute of Technology Kharagpur, INDIA
31st May, 2024

Acknowledgements

I am indebted to my parents who constantly worked hard and took pains for the continuation of my studies. I am proud of my two daughters, Sutanuka and Suchismita, the two sons-in-law (Avik and Saswata) and the two Grandsons (Shreyan and Aahan) who form a pleasing and cheerful environment around me. I am grateful to my loving wife who stood by me in times of crisis and all along my life.

I acknowledge the direct or indirect help of my close associates: Gourisankar Maiti, Nabin K Ghosh, Samik Nanda, Nirmal K Hazra, Sankar C Bhunia, Anirban Bhunia, Gopal Chandra Maity, Prof. Bimal Mahapatra, Late Prof. Anup K Dasmahapatra, Dr. Jayasree Laha (Principal) and Late Prof. Sudhansu S Pahari, and many others.

I am grateful to all the teachers of my student life. I am thankful to my research guide Prof. Avijit Banerji for arousing interest in the topic and organic chemistry in general.

Finally, I take this opportunity to thank M/s Cambridge Scholars Publishing to publish the work in print and in electronic media.

Sudhir C Pal

Preface

During my teaching days I found many bright students of chemistry who tried to avoid stereochemistry as far as practicable. This topic is not only a part and parcel of organic chemistry but undoubtedly a most interesting and important part of the subject.

These days there is a rapid growth of research in the field of stereoselective syntheses especially enantioselective syntheses. It is better that the students acquire the basic knowledge of stereochemistry in order to get the essence of such research and get motivated in this field. The present attempt is aimed to this direction. A large number of problems and their solution are given for the benefit of the learners. Moreover, some multiple-choice type questions (with answers at the end) are given to help the students in facing different competitive examinations.

This volume discusses mostly the basic aspects of stereochemistry. The application of these aspects / principles (dynamic stereochemistry) will be covered in a separate volume.

The work would be successful if at least a few students who are reluctant in the subject become inspired and find interest in this subject.

In spite of the best efforts some errors may creep in. I shall appreciate and be grateful if learned readers bring these errors to the notice of the author. Their suggestions in improving the quality of the book in any respect are most welcome.

Sudhir C Pal
Flat 3A, CD - 61
Street No. – 262, CD Block, Newtown Action Area 1C,
Kolkata – 700156
West Bengal, INDIA

CHAPTER 1

M. F., bonding, structure and naming of the molecules

1.1 Introduction

Before coming to the subject of stereoisomerism some relevant topics need to be discussed. The present chapter deals with these topics in brief.

1.2 Molecular formula

The saturated acyclic hydrocarbons (paraffins \equiv little affinity / poor chemical reactivity) have the general formula

$$C_nH_{2n+2} \text{ (n = the number of tetravalent atom)}$$

In a straight chain hydrocarbon (containing n Cs) each C is linked to two Hs (2n) except the two terminal carbons which are bonded to one extra H each (+2). For the branched chain hydrocarbons, the C at the branch point will have one H less but the same is increased due to one more terminal of the branched group. The general formula remains the same (see **Fig. 1.1**: C_6H_{14} for all hexane isomers).

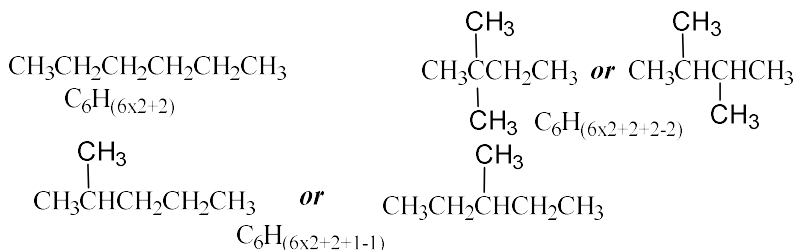


Fig. 1.1

In a compound having the monovalent atom(s) other than Hs e.g., halogens, the number of H will be lessened by an equal number of such atoms. The M.F. for such a compound would be

$C_nH_{2n+2-x}X_x$ (where x = number of the monovalent atoms X)
 or C_nX_{2n+2} (now X represents monovalent atoms including H)

1.2.1 Cyclic and multiple-bonded compounds

The two non-adjacent carbons (or heteroatoms) in an acyclic compound can be linked together to form a ring compound. The linked atoms lose one H each so that M.F. of a monocyclic saturated compound will have two hydrogen atoms less than the corresponding acyclic compound. The same thing happens when the compound contains one double bond (e.g., $C=C$, $C=O$, $N=N$, $C=S$, etc.); the H atoms being eliminated from a pair of the adjacent carbons or heteroatoms. One ring is thus equivalent to a double bond in this respect.¹ The general M.F. of the monocyclic saturated or ‘mono-unsaturated’² compounds takes the form

C_nH_{2n} (Hydrocarbon)
 or C_nX_{2n} (where X = monovalent atoms including H)

A triple bond (e.g. alkyne or nitrile) or two double bonds (e.g., an alkadiene or alkenone) or two rings (e.g., indane or decalin) or one double bond plus a ring (e.g., a cycloalkene or cycloalkanone) will have four H/monovalent atoms less in their M.F. in comparison to the saturated acyclic analogue. The general formula for them is then,

C_nH_{2n-2} (Hydrocarbon)
 or C_nX_{2n-2} (where X = monovalent atom including H)

A bivalent singly bonded heteroatom (e.g., -O- / -S-) can be inserted into a $C-C$ or $C-H/X$ bond without a change anywhere in the molecule. This will not affect the $C : X$ (X is any monovalent atom) ratio. Thus, the general molecular formula of the different types of compounds having the bivalent atom(s) (Y ; y in number) will take the form as shown in **Fig. 1.2**.

¹A mono-unsaturated alcohol / ether, a cycloalkanol, a cyclic ether, a ketone and an aldehyde can become isomers of each other (i.e. same M.F.); so are a carboxylic acid, a keto-alcohol, and a mono-unsaturated diol.

²here signifies compounds with a double bond.

	Saturated acyclic	Mono-'unsaturated' acyclic or monocyclic	Doubly unsatd., /Triple bonded acyclic or bicyclic or cyclic 'monounsaturated'
General			
M.F:	$C_nX_{2n+2}Y_y$	$C_nX_{2n}Y_y$	$C_nX_{2n-2}Y_y$

Fig. 1.2

When the compound contains a tervalent element (Z; usually *N*) it may be regarded as the insertion of ZH or ZX in the formula. The respective compounds will have the general formula as given in **Fig. 1.3**.

	Saturated acyclic	Mono-'unsaturated' acyclic or monocyclic	Doubly 'unsaturated' or triple bonded acyclic or bicyclic or cyclic mono-'unsaturated'
M.F:	$C_nX_{2n+2+z}Z_z$	$C_nX_{2n+z}Z_z$	$C_nX_{2n-2+z}Z_z$
M.F:	$C_nX_{2n+2+z}Y_yZ_z$	$C_nX_{2n+z}Y_yZ$	$C_nX_{2n-2+z}YZ_z$

y and z are the numbers of Y and Z in the molecule.

Fig. 1.3

It may be noted in this connection that the odd number of the monovalent atoms in the formula ensures the presence of one or any odd number of *N* (or any tervalent atom, Z), and even number of the monovalent atoms indicates an even number / zero *N* in the compound.

1.2.2 D.B.E. or I.H.D.

D.B.E. (double bond equivalent) or

I.H.D. (index of hydrogen deficiency) = the number of double bonds
+ twice the number of triple bonds + the number of rings.

This can easily be determined from the given M.F. The number of the monovalent atoms is compared with that of the corresponding saturated acyclic compound (**Fig. 1.4**). The factor $\frac{1}{2}$ is due to the fact that for every two H/X short D.B.E would be 1.

M. F. of the compound	M. F. of saturated acyclic compound	D.B.E. (calculated)
$C_nX_xY_y$ [<i>y</i> = 0 or any integer]	$C_nX_{2n+2}Y_y$	$(2n + 2 - x) / 2$
$C_nX_xY_yZ_z$	$C_nX_{2n+2+z}Y_y$	$(2n + 2 + z - x) / 2$

Fig. 1.4

The conclusion that can be drawn from a **D.B.E.** are given in **Fig. 1.5**. As seen, the number of the possibilities (ring / multiple bonds) increases largely as D.B.E. is increased. It is to be noted that a D.B.E. of 4 (or higher) is indicative (not certain) of the existence of a benzenoid ring in the molecule.

D.B.E.	Conclusion
0	No 'unsaturation' (acyclic saturated compound)
1	One double bond <i>or</i> a ring
2	Two double bonds <i>or</i> two rings <i>or</i> one triple bond <i>or</i> 1 double bond plus 1 ring
3	Three double bonds <i>or</i> three rings <i>or</i> two double bonds plus a ring <i>or</i> one double bond plus two rings <i>or</i> one triple bond plus a double bond <i>or</i> one triple bond plus a ring

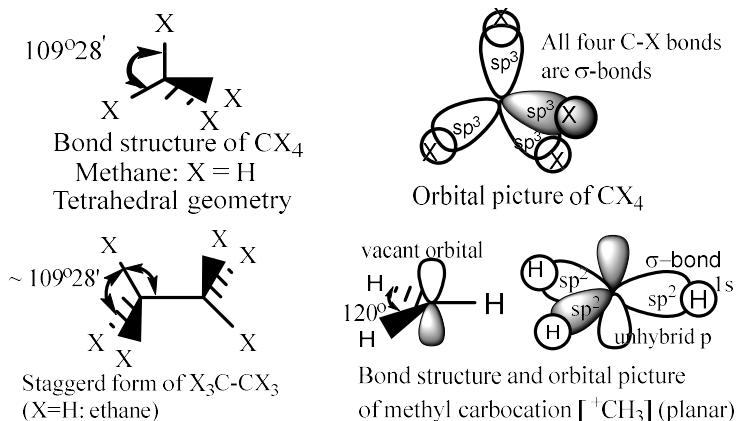
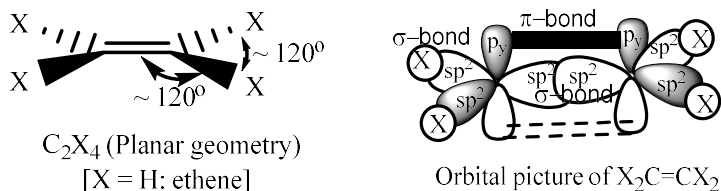
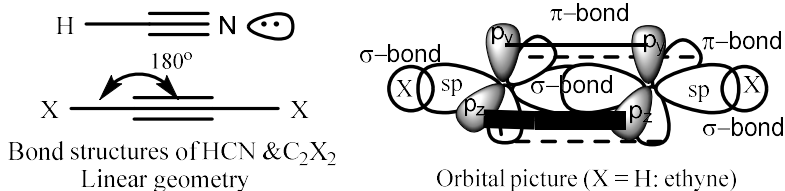
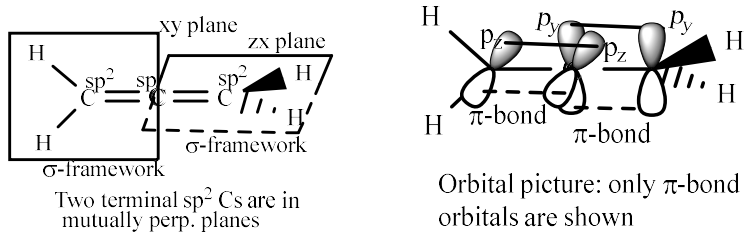
Fig. 1.5

1.3 Hybridisation of C orbitals and structure of molecules

The energetically close atomic orbitals are assumed to mix up and then generate a new set of the equal number of orbitals with 'averaged' energy (degenerate) and the same total electron capacity. This concept is known as **hybridisation**.³ The bonding capacity of the hybrid orbitals (or the degree of overlap) is higher (and hence stronger bonds are formed) than the unhybrid orbitals. This is the reason for forming bonds using the hybrid orbitals.

The hybrid orbitals are highly directional in characteristics (i.e., overlap of the orbitals are higher in a particular direction). This gives rise to a specific geometry to the molecules for the particular type of hybridisation. For C, three types of hybridisations namely the sp^3 , sp^2 and the sp hybridisation are recognised. The four (the 2s and three 2p), three (the 2s and two 2p) and two (the 2s and one 2p) orbitals are hybridised in the respective cases. The geometry, the bond angles and the orbital pictures of some simple molecules, as examples, are presented in **Figs. 1.6a - d**.

³The concept was introduced by **Linus Pauling** (1901 – 1994). He (a two-time Nobel laureate) was among the first scientists to work in the fields of the quantum chemistry and molecular biology.


Fig. 1.6a: Molecules having sp^3 C

Fig. 1.6b: Species/molecules with sp^2 hybrid C

Fig 1.6c: Molecules having sp hybrid C

Fig 1.6d: Allene having both sp^2 and sp hybrid Cs

The following features are noteworthy:

(i) The orbitals are all equi-spaced around the C for a maximum separation to minimise the inter-electronic repulsions. The respective bond angles are accordingly $109^{\circ}28'$, 120° and 180° respectively for the sp^3 , sp^2 and sp hybrid carbons.

(ii) The overlap capacity of the orbitals is in order $sp > sp^2 > sp > p$ (**Fig. 1.7**) and so the strength of the different C—H bonds: $C_{sp^3}\text{—H}$ ($\sim 500 \text{ kJ mol}^{-1}$), $> C_{sp^2}\text{—H}$ ($\sim 436 \text{ kJ mol}^{-1}$) $> C_{sp}\text{—H}$ ($\sim 425 \text{ kJ mol}^{-1}$). However, the total energy of the four σ -bonds of a sp^3 C $>$ energy of the three σ - and one π -bond of an sp^2 C $>$ energy of the two σ - and two π -bonds of an sp C. So, where permissible C forms bonds via the sp^3 hybridisation and never forms bonds from the unhybrid state.⁴

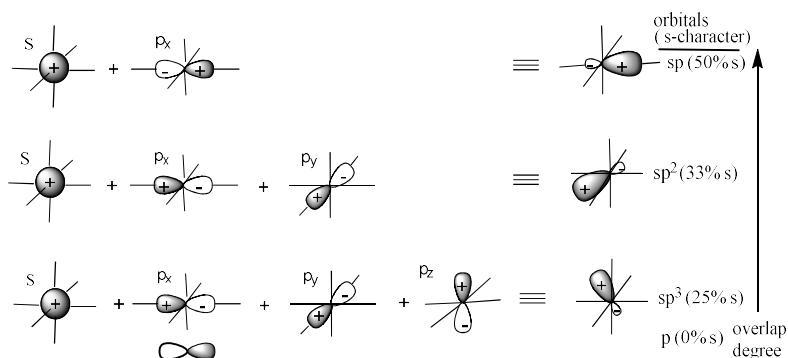


Fig 1.7

(iii) When the number of the ligands falls short C changes strategy⁵ to undergo the sp^2 or even the sp hybridisation. The carbons satisfy some of the valencies between themselves by lateral overlap of the unhybrid p-orbitals forming the pi-bonds.

(iv) The rotation about the C—C bond (a σ -bond: cylindrically symmetrical) is almost 'free' (the degree of overlap of the orbitals is not affected).⁶ This internal rotation (one C fixed, the other rotated) creates the different arrangements that are called **conformations**.

⁴Even in CO and in carbenes carbons form bonds in unhybrid states.

⁵A business policy, indeed!

⁶See **Chapter 7** for exceptions.

(v) As long as all the four ligands (X) in CX_4 are identical the structure remains a regular tetrahedron. This regularity is disturbed when the ligands are made different. When all the four are different the structure becomes asymmetric, and Cabcd type molecule can exist in the two non-superposable mirror image structures (called **enantiomer** of each other).⁷ See **Chapter 3** for details.

(vi) A π -bond does not allow the internal rotation (under normal circumstances). So, the ethylenic molecules like $abC=Cab$ / $abC=Cbd$ / $abC=Cde$ can exist in the non-superposable structures. These are **cis-trans** or **E-Z** isomers. See **Chapter 6** for details.

So long as the ligands (a,b,d,e) are achiral the alkenes cannot exhibit the chirality / enantiomerism.

(vii) In respect of the stereochemistry (in 3D) the triple-bonded (with sp-hybrid C) compounds (linear geometry) are not important. But, the sp C in the cumulated polyenes e.g., allenes are of stereochemical interest.

The central C in an allene uses its two different p-orbitals (perpendicular to each other) to form the two π -bonds. This gives rise to the molecule an elongated tetrahedron shape (**Fig. 1.6d**). The distortion of the geometry in $abC=C=Cab$ / $abC=C=Cbd$ / $abC=C=Cde$ type molecules results in a dissymmetric or an asymmetric shape. These compounds exhibit **enantiomerism**.⁸

1.3.1 Hybridisation of tri- and tetra-coordinated N, P, As

The group III elements like *N*, *P* and *As* also form bonds in the tri- and tetra-coordinated compounds using their hybrid orbitals. One of the four sp^3 hybrid orbitals is occupied by a lone pair of electrons in the tri-coordinated compounds so that the geometry (decided by the nuclei) becomes a trigonal pyramid. The distortion of the regular pyramidal structure in $:Xabc$ type ($X = N/P/As$) molecules can result in enantiomerism. For the simple un-bridged compounds, however, facile pyramidal inversion restricts their separation. This inversion barrier (**Fig. 1.8**) increases from *N* to *P* to *As*. The chiral arsenic compounds can be resolvable from the racemic form. The carbanions, formed at the stereocentre, changes the configuration due to the low barrier of their pyramidal inversion (see **Chapter 8**).

⁷This is one proof for the tetrahedral configuration of saturated C (see **Section 3.2**).

⁸This is factorised as **axial chirality**. See **Chapter 7** for details.

Compounds	Inversion barrier, in kJ mol ⁻¹
NH ₃	~24.0
(PhCH ₂) ₂ NC ₂ H ₅	~28.0
PH ₃	132.0
AsH ₃	~184


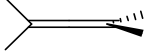
Fig. 1.8: Pyramidal inversion barrier

This inversion barrier for the *N* is much higher in the aziridines (15 – 20 kcal mol⁻¹), and is further increased when an electron-withdrawing substituent is present in the ring. In those cases, resolution of the enantiomers is possible.

The tetra-coordinated *N*, *P* and *As* in their sp³ state of hybridisation give tetrahedral compounds e.g., amine oxide, phosphine oxide etc. When asymmetrically substituted these would become chiral. These are separable from the racemic modifications (see **Chapter 3** for examples).

1.3.2 Polyenes

The polyenes with isolated double bonds have no special stereochemical characteristics. The conjugated polyenes also can exhibit the cis-trans isomerism like the simple alkenes (see **Chapter 6**). The cumulated polyenes are typical; those with an odd number of the double bonds exhibit the cis-trans isomerism (the ligands at the two termini are in common plane) and those with an even number of the double bonds show enantiomerism (the termini ligands are in perpendicular planes) (**Fig. 1.9**).

Constitution (a&b different)	Geometry	Isomerism	Structure pattern
ab(C=) _{2m+1} Cab	Planar	Diastereoisomerism (cis-trans)	
ab(C=) _{2m+2} Cab	Elongated tetrahedron	Enantiomerism	

[m is 0 or any integer; n = 2m+1 / 2m+2]

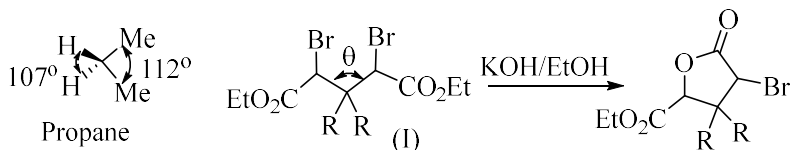
Fig. 1.9

With an increase in the number of the double bonds the configurational stability of the cumulenes is diminished. The bond order of the ‘double bonds’ is lowered resulting in the easier (barrier⁹ lessened) interconversion between the isomers. The barrier (192 – 197 kJ mol⁻¹) in allene is however sufficient to enable resolution of the isomers.

1.4 Bond angle

In the regular/perfect sp^3 , sp^2 and sp , states of hybridisation of carbon (or other tetra-covalent element) the bond angles are $109^\circ 28'$, 120° and 180° respectively around it (see **Figs. 1.6a-d**). If all the ligands to the C are not equal the bond angles are changed somewhat.

In propane $\angle C-C-C$ is increased (112°) and $\angle H-C-H$ is decreased (107°) due mainly to the steric reasons. The geminal di-substitution (I: R = alkyl) facilitates the intramolecular reaction due to the reduction of the angle θ (shown in the structure I). This is known as the **Thorpe-Ingold effect**.



The ‘imperfect’ or ‘non-ideal’ hybridisation resulting in the disproportionate orbital character can explain the observed bond angles in the examples given in **Fig. 1.10**. The carbon uses a hybrid orbital with more p-character to form a bond with the electronegative elements. This meets the higher electron demand of the latter. As such $\angle H-C-Cl$ is less than $109^\circ 28'$ in chloromethane. The same trend is observed in 1,1-dichloroethene; the $\angle Cl-C-Cl$ is reduced from 120° . Conversely a lone pair orbital gets more s-character (takes more space) to reduce bond angles in NH_3 , and more so in H_2O . There is also a generalisation that the lone pair – lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion (VSEPR theory). Both the electronegativity and size of the halogens are supposedly important to explain the observed bond angles in the trihalomethanes.

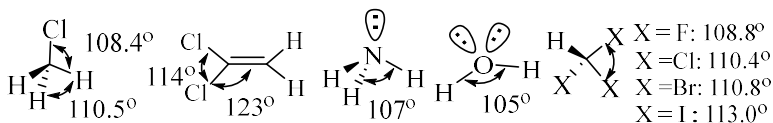


Fig. 1.10

⁹The approximate energy barrier (ΔG^\ddagger , kJ mol^{-1}): 260 ($n = 1$), 194 ($n = 2$), 132 ($n = 3$), 115 ($n = 4$), 80 ($n = 5$).

1.5 Bond Length

Bond length is the inter-nuclear distance of the two bonded atoms. It is effectively the sum of the covalent radii (r_1 & r_2) of two concerned elements (**Fig. 1.11**).

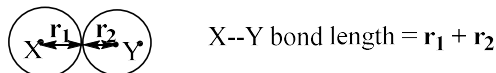
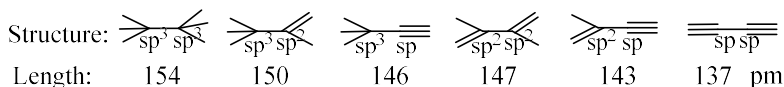


Fig. 1.11

The following criteria are to be noted for the bond length variation:

- (i) The bond order¹⁰ remaining same, the bond length increases as the bond involves larger atom(s) (i.e., atoms of higher row elements): $\text{H—H} < \text{C—H} < \text{C—C} < \text{C—S}$; $\text{C=C} < \text{C=S}$.
- (ii) With an increase of the bond order, the length decreases: $\text{C—X} > \text{C=X} > \text{C}\equiv\text{X}$ ($\text{X} = \text{C}, \text{N}$). A conjugation can change the bond order to some extent and this is reflected in the bond length variation: $(\text{C=})\text{C—C}(=\text{O}) > \text{C—C}$; $\text{C=C}-(\text{CN}) < \text{C=C}$, etc.
- (iii) An increase of the p-character in the hybrid orbitals increases the bond length slightly: $\equiv\text{C—C} < =\text{C—C} < \text{C—C}$.
- (iv) Both the conjugation and % s-/p-character in the orbitals are needed to account for the variation of the C—C bond lengths in the following cases:



The lengths of some common bonds in organic compounds are noted in **Table 1.1**.

It needs mention that for a particular type of bond, the length is more or less constant e.g., C—C bond distances in ethane, propane, butane, cyclohexane, etc. are essentially the same.

1.6 Bond energy and Bond dissociation energy

Bond dissociation energy (B.D.E.) is the energy necessary to cleave the particular bond to the product radicals – both the reactants and products are in the gaseous states. For a compound like methane successive bond

¹⁰Bond order in MO terms, is defined as: (Number of electrons in bonding M.O. – number of electrons in ABMO) / 2.