

Basic Stereochemistry of Organic Molecules

SECOND EDITION

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Preface to the Second Edition

The general plan of the second edition follows that of the first edition, but the opportunity has been availed to make the book more up to date for the students. Since the publication of the first edition of the book, no new fundamental concept or fact has emerged on the subject and hence the contents in the chapters remain unaltered. However, to make the book more useful for the students, additional 57 miscellaneous problems with complete answers have been included to Appendix-A, which now contains 240 miscellaneous problems. Another new feature of this edition is the addition of Appendix C comprising objective type questions, usually termed as MCQs. The new appendix includes 130 MCQs with answers, which will be handy to students preparing for various competitive examinations, including entrance tests for higher learning in chemistry as well as professional examinations.

As mentioned in the first edition, the book is addressed principally to undergraduates who opt for Chemistry as major subject (Hons). Moreover, a few topics included in this book will be helpful to postgraduate students as preliminary text. As an author, I am encouraged that the book has been accepted by both students and teachers as a useful book on the subject of stereochemistry.

Although, the book covers the most important aspects of the subject of stereochemistry required at this stage of learning, nevertheless, a text of this nature cannot be comprehensive. I have tried to present each chapter with many innovative examples, detailed drawings and figures which will enable students to easily understand the concepts through self-study. Solved problems, exercises and appropriate references have also been included in each chapter.

Acknowledgements

I express my sincere thanks to Oxford University Press (India) for taking the responsibility to publish the second edition of this book. I also express my sincere gratitude to the team at OUP who have actively helped in the publication of the book. I am also indebted to reviewers for their feedback.

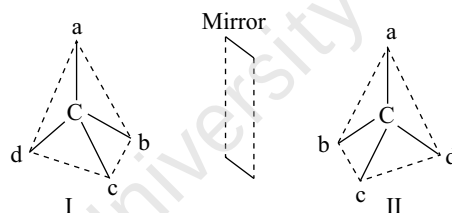
I remember my parents and teachers at school, college and university who gave me the right education that helped me attain the position from where I can now guide students. Finally, I want to thank my wife Mrs. Arundhati Sen Gupta and son Dr. Anirban Sen Gupta for their encouragements to write this book.

I welcome constructive suggestions and feedback to further improve this book. These can be sent to me at: pushpal_@hotmail.com and subratasgt@gmail.com

Subrata Sen Gupta

Preface to the First Edition

Organic chemistry—commonly designated as chemistry of carbon compounds—is a vast subject, supported by more than four million known compounds. It is a very important and integral part of all fields of chemistry such as biochemistry, molecular biology, microbiology, medicinal chemistry, phytochemistry, and almost all biological sciences including zoology, botany, and physiology. For instance, most simplest organic compound is ‘methane’ having the molecular formula ‘CH₄’, but in early 19th century its structure was a puzzle for chemists. The puzzle was solved in 1874 when two young chemists, J.H. Van 't Hoff and J.A. Le Bel, independently proposed that molecules like C_{abcd} including C₄ have a regular tetrahedral rigid structure. They also showed that in case of molecules like C_{abcd} (a, b, c, d being different substituents), substituents can be arranged in two different ways at the apexes of a regular tetrahedron with the carbon atom at the centre of that tetrahedron. They had successfully demonstrated that these two structures differing in the arrangements of the substituents in space around the central carbon atom had same bond connectivity and elemental compositions. This can be shown by the following diagram.



In the above diagram, I and II represent two different arrangements of the groups a, b, c, d in the molecule C_{abcd} around the carbon. They are mirror images to each other but not superimposable. They represent two different compounds, called ‘enantiomers’.

When this proposition was applied to some mystifying problems of structural organic chemistry at that time, the problems got solved easily and consistently. This was the humble beginning of a new fascinating branch of organic chemistry, which is now known as ‘stereochemistry’. Initially, the study of stereochemistry was very theoretical and remained confined to a set of brilliant chemists, within the walls of their laboratories. But the importance of stereochemistry became apparent when scientists began to investigate its role in biomolecules in the human body. When the structures of biomolecules such as proteins, lipids, vitamins, and nucleic acids were determined, it was found that their chemical roles within our body are fully dependent on their very specific stereochemical structures. Any minor change of the stereochemical aspects of these molecules will stop all biochemical processes within our body and that would be life-threatening. Thus, the life processes of all living creatures are dependent not just on their chemical compositions, but also on the stereochemistry of biomolecules. It is a very interesting fact that in the synthesis of millions of protein molecules within our body, only L-isomer of α -amino acids participates. Except the primary structure of protein molecules, the secondary, tertiary, and quaternary structures are all dependent on scrupulous stereochemical manipulations, without which they cannot play their specific roles in life-sustaining activities. Also, in the case of medicines, exact molecules are being synthesized with stereospecific structures so that they function in a manner we want them to. Without these structures having specific stereochemistry, they are no longer useful as medicines.

During my study of organic chemistry, I was always fascinated by the amazing role of stereochemistry in organic molecules. This provided the impetus to write this book in a simple manner, so that the students can understand the fundamentals of the subject and apply them in their future research and professional activities.

About the Book

Basic Stereochemistry of Organic Molecules embodies the basic conceptual facts of stereochemistry, called *static stereochemistry*, and also describes the stereochemical outcomes of a large number of organic reactions, known as *dynamic stereochemistry*. Static stereochemistry part has been written elaborately with a large number of illustrative structures and examples which make this an ideal book on the subject of stereochemistry for undergraduate Chemistry (Hons) students. It will also serve as a preliminary text for postgraduate students. The solved problems in each chapter during exam preparations. Over 200 solved problems of stereochemistry provided and in the appendix would be helpful to students for higher studies.

Key Features

- Large number of exercise problems at the end of each chapter for practice
- Adequate number of figures, reactions, and tables to simplify the understanding of concepts
- Glossary of important terms used in stereochemistry, as recommended by IUPAC at the end of the book
- List of topic-based references for those interested in further study
- Appendix with 182 additional solved problems on stereochemistry for further practice.
- Advanced chiroptical methods like optical rotatory dispersion (ORD) and circular dichroism (CD)

Contents and Coverage

The book is divided into ten chapters.

Chapter 1, *Symmetry in Molecules*, deals with the fundamental concepts of the symmetry properties of molecules. The capability of molecules to exhibit stereoisomerism depends on their symmetry properties. Numerous examples and diagrams have been incorporated in this chapter so that the subject can be understood easily.

Chapter 2, *Dissymmetric Molecules*, includes the fundamental aspects of dissymmetric molecules with definitions and explanations.

Chapter 3, *Stereoisomerism of Chiral Molecules*, comprises discussions on chiral molecules and methods of assigning stereochemical symbols to identify different classes of stereoisomers. It also deals with a fundamental property of chiral molecules called the *optical activity*.

Chapter 4, *π and Ring Diastereoisomerism*, comprises discussions on the type of stereoisomerism that we encounter in compounds containing π -bonds and ring systems.

Chapter 5, *Conformation of Acyclic Organic Molecules*, is a unique chapter which discusses conformational aspects of different classes of open-chain organic compounds. Certain definitions used in case of conformational isomers have also been discussed in this chapter in detail.

Chapter 6, *Conformations of a Few Cyclic Organic Molecules*, consists of the conformational aspects of a good number of cyclic compounds which have also been discussed in detail. Certain important rules like Baldwin's rules for cyclization reaction have been discussed here.

Chapter 7, *Dynamic Stereochemistry*, focuses on the role of stereochemistry on the nature of product/products that are formed during various types of organic reactions. Certain important rules like Cram and Prelog's rules for stereoselective synthesis of organic molecules have also been discussed here.

Chapter 8, *Conformational Analysis of Cyclohexanes*, deals with the conformations of cyclohexane and its substituted compounds. Discussions have also been done on the reactions of cyclohexane derivatives.

Chapter 9, *Pericyclic Reactions*, illustrates the fundamental stereochemical roles in a class of reactions classified as 'pericyclic reactions'.

Chapter 10, *Stereochemical Aspects of a Few Important Organic Reactions*, discusses the stereochemistry of a few very important organic reactions that are used in the laboratories for the synthesis of organic compounds.

Appendices A and B discuss miscellaneous solved problems and additional unsolved problems, respectively.

Online Resources

The online resource centre provides resources for faculty and students. The following resources are available at <http://oupinheonline.com/book/sengupta-basic-stereochemistry-organic-molecules/9780199451630> for faculty and students using this text:

For Faculty

- PowerPoint Slides

For Students

- Link to interactive 3D animations

Acknowledgements

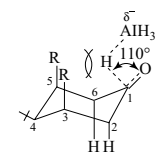
I express my heartfelt gratitude to Oxford University Press for giving me the opportunity to publish this book through their esteemed publishing house. I am particularly thankful to the editorial team for their guidance and cooperation in the successful publication of this book within the scheduled time.

I am grateful to the people who encouraged me to write this book when it was first published in 1993 by a Kolkata-based publisher; many of whom are no longer with us in this world but their memories still motivate me. I sincerely thank past and present students of chemistry, for their interest in this book, which has encouraged me to keep this book going strong with proper updates. I also appreciate the support that was provided by my spouse, Mrs Arundhati Sen Gupta and son, Dr Anirban Sen Gupta, to pursue my academic activities and interests successfully.

Suggestions and feedback are welcome and can be sent to me at pushpal_@hotmail.com/pushpal314@dataone.in.

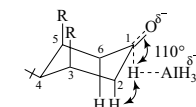
SUBRATA SEN GUPTA

Features of



Transition state involving steric hindrance)

Fig. 8.23

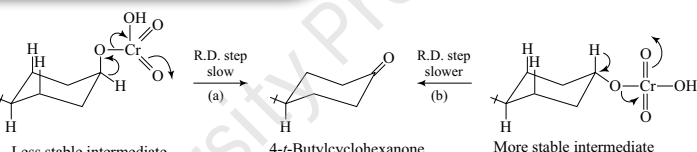


Transition state involving torsional strain

Fig. 8.24

Figures, Reactions, and Tables

Numerous figures, reactions, and tables simplify the understanding of concepts.



Path (b) is about four times slower than path (a)

Fig. 8.13

Table 6.1

Size of ring	Heat of combustion (kJ mol ⁻¹)	Total strain (kJ mol ⁻¹)	Strain per CH ₂ (kJ mol ⁻¹)	Angle strain (deviation from 109°28')
3	2091.3	115.1	38.4	24°44'
4	2745.0	110.1	27.5	9°44'
5	3319.6	26.0	5.19	0.44'
6	3952.9	0.5	0.09	-5°16'
7	4637.3	26.2	3.74	-----
8	5310.3	40.5	5.06	-----
9	5981.3	52.7	5.86	-----
10	6639.1	51.8	5.18	-----
11	7293.3	47.3	4.30	-----
12	7921.9	17.2	1.43	-----
13	8585.0	21.5	1.66	-----
14	9230.9	8.0	0.57	-----
15	9888.7	7.8	0.51	-----

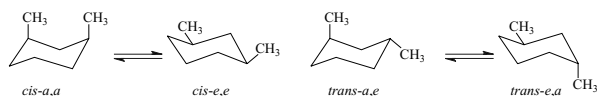
Solved Problems

Solved examples at the end of each chapter will facilitate the understanding of the concepts discussed.

SOLVED PROBLEMS

Q.1. Draw all the possible conformations of *cis*- and *trans*-1,3-dimethylcyclohexane. Comment on their relative stability based on steric interactions. Are the compounds resolvable? Discuss the result of ring inversion in each case.

Ans. The *cis*- and *trans*-1,3-Dimethylcyclohexane have chair conformations as shown below.



the Book

Exercises

Exercises at the end of each chapter will help students to test their skills and also prepare for examinations

EXERCISES

1. Why cyclobutane is more stable in its puckered structure? Draw the puckered structure of cyclobutane. Is it a rigid structure? What are point groups in planar and puckered structures of cyclobutane? Is puckered structure optically active?
 2. Unlike cyclobutane, thiatane and oxetane are planar. Give an explanation for this observation.
 3. Write down the C_2 and C_s structures of cyclopentane. Why are they so designated? Are they chiral structures? What do you mean by the phenomenon 'pseudorotation' in cyclopentane ring system? What are the elements of symmetry in planar cyclopentane?
 4. Write down the chair and boat conformations of cyclohexane and discuss their relative stability.
- of inversion of cyclohexane chair form? Draw energy diagram of these inversion path.
7. Compare among the planar, chair, boat, and twist boat conformations of cyclohexane with reference to (i) elements of symmetry, (ii) stability based on angle, and torsional strains (iii) chirality.
 8. Chair form of cyclohexane-1,4-dicarboxylic acid can have three stereoisomers. What are they? Relate them as conformational isomers or configurational isomers?
 9. Write down the chair conformation of each of the following compounds and discuss its stability relative to cyclohexane itself.
 - (i) (a,a) *Trans*-1,2-dimethylcyclohexane
 - (ii) *cis*-1,3-Dimethylcyclohexane
 - (iii) (a,e)-*Trans*-1,2-dimethylcyclohexane

REFERENCES

- Anet, F.A.L., *Conformational Analysis of Cyclohexanes*, P.W., p. 1, (1989).
- Baldwin, J.E., *J. Chem. Soc. Commun.*, 734, 738 (1976).
- Baldwin, J.E., *Rules for Ring Closure*, Ciba Foundation Symposium 53, Further Perspectives in Organic Chemistry, Elsevier, New York (1978).
- Barton, D.H.R., *Experientia*, 6, 316 (1950).
- Barton, D.H.R., O. Hassel, K.S. Pitzer, V. Prelog, *Nature* (London), 172, 1096 (1953).
- Barton, D.H.R., O. Hassel, K.S. Pitzer, and V. Prelog, *Science*, 119, 49 (1954).
- Bredt, J., Justus Liebigs. *Ann. Chem.*, 437, 1 (1924).
- Cross, L.C. and W. Klyne, *Rules for Nomenclature of Organic Chemistry*, Section E, Stereochemistry, *Pure Appl. Chem.*, 45, 11 (1976).
- Hassel, O., Tidsskr. Kjem. Bergvesen Met., 3 [5] 32; (1943), *Engl. Transl. K. Hedberg, Top. Stereochem.*, 6, 11 (1971).
- Mohr, E., *J. Prakt. Chem.*, [2] 98, 315 (1918).
- Prelog, V. and G. Helmchen, 'Basic Principles of the CIP System and Proposals for a Revision', *Angew. Chem. Int. Ed. Engl.*, 21, 567 (1982).
- Rabideau, P.W., *Conformational Analysis of Cyclohexenes, Cyclohexadienes, and Related Hydroaromatic Compounds*, VCH, New York, (1989).
- Reisse, J., 'Quantitative Conformational Analysis of Cyclohexane Systems', in G. Chiurdoglu, Ed., *Conformational Analysis, Scope and Present Limitations*, Academic, New York, (1971).
- Riddell, F.G., *The Conformational Analysis of Heterocy-*

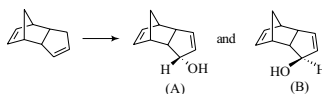
References

A list of references has been added at the end of each chapter for those interested in further study

Additional Solved and Unsolved Problems and MCQs

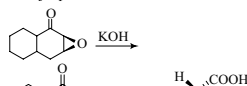
A wide collection of additional solved and unsolved problems as well as multiple choice questions are provided for practice at the end of the book in appendices A – C.

34. For the following allylic oxidation reaction, the appropriate statement is:



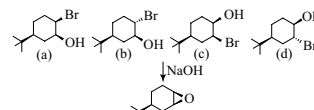
- (a) suitable reagent – KMnO_4 ; major product – (A)
- (b) suitable reagent – KMnO_4 ; major product – (B)
- (c) suitable reagent – SeO_2 ; major product – (A)
- (d) suitable reagent – SeO_2 ; major product – (B)

35. The major product of the below reaction is:

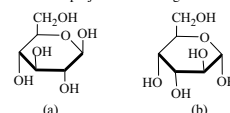


- (a) CHBr_3 and a racemic acid
- (b) CHBr_3 and a chiral acid
- (c) CHBr_3 and a racemic ester
- (d) CH_2Br_2 and a chiral ester

38. Identify the starting compound which will give the compound shown below on treatment with NaOH.



39. The Haworth projection of α -D-glucose is:



GLOSSARY

A-value Synonymous with conformational free energy. E. L. Eliel and M. Gianni, *Tet. Lett.*, 97 (1962).

Absolute Configuration The spatial arrangement of the atoms or groups in a chiral molecule that distinguishes it from its mirror image.

Achiral A geometric body with rigid structure is considered as achiral when it is superposable on its mirror image. A molecule with rigid structures is equivalent to a geometric body.

Achirotopicity When the local symmetry of an atom or group within a molecule is not chiral then that atom or group is called achirotopical and the term achirotopicity is used phenomenologically.

Ref. K. Mislow and J. Siegel, *J. Am. Chem. Soc.*, 106 (1984), 3319.

'amb' Descriptor Formation of diastereoisomers by reaction at a non-stereogenic centre of a chiral molecule or the reaction of a chiral compound with a racemic compound will not always give a 50–50 mixture. To indicate this the prefix 'amb' is used.

Glossary

Glossary at the end of book provides the definition of important terms in stereochemistry.

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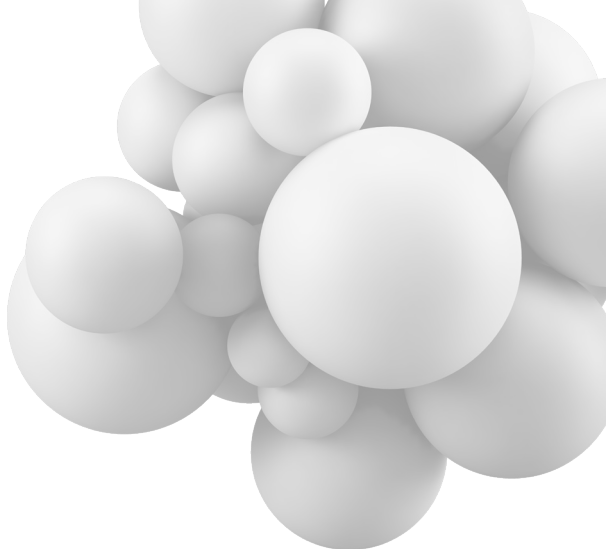
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Introduction



The term ‘Stereochemistry’ was coined from the Greek word *stereos*, meaning solid. In contemporary chemistry, the term refers to chemistry that involves three dimensions. The development of stereochemistry in its present form is not very remote. In the past fifty years chemists from all branches have contributed to make the subject fascinating and at present no chemist can afford to be without a reasonably detailed knowledge of the topic. The development of computer-assisted investigations of structures of complicated organic and inorganic molecules has raised the subject to new heights and newer conceptions are enriching it every year.

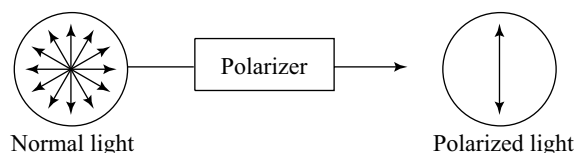
Stereochemistry is now the subject of study in every branch of chemistry. Because of the structural variations of organic molecules, the subject is dealt more deeply in organic chemistry and hence stereochemical investigations are mostly done on organic molecules.

We cannot see an atom of carbon but when a large number of carbon atoms join in a specific geometric order we get the most precious jewel called ‘diamond’. Thus, when people are ‘charmed’ by diamonds, they are in fact attracted not by its constituent atoms but by their unique arrangements in space, that is, stereo-arrangements. A particular type of protein molecules within our body plays a specific biological role because of their unique three-dimensional framework. If these shapes are distorted, their biological activity is lost and they are no longer useful within our body. In fact the very existence of life on earth depends on the geometric shapes of organic molecules, which are made of a few elements like carbon, oxygen, hydrogen, nitrogen, sulphur, and phosphorus. Therefore, we can conclude that atoms can produce some unique properties only when they are arranged in specific geometric shapes.

Organic molecules are covalent molecules, that is, atoms bonded together share a pair of electrons, one given by each atom. Formation of a covalent bond has been explained from two different angles: (a) the valence bond (VB) theory and (b) the molecular orbital (MO) theory. Before any discussions on VB and MO theory of bonding, one should be aware of the nature of an electron within an atom. Bohr’s theory of atomic model led to the equation $mvr = nh/2\pi$, where mvr = angular momentum of an electron within an atom, m = mass of the electron, v = velocity of the electron and r = radius of the orbit following which the electron is moving around the central nucleus.

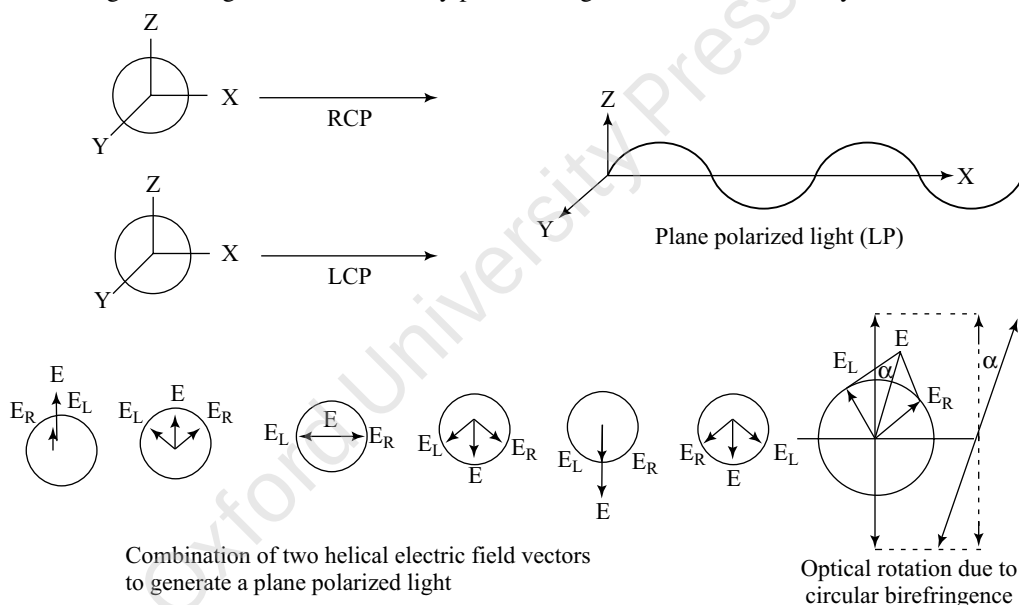
Linearly and Circularly Polarized Light

Enantiomers (see Chapter 2) can be discriminated only in chiral environment like plane polarized light. Light is the result of the wave-like movement of two changing fields, electric and magnetic, which are perpendicular to each other. Normal light (electromagnetic radiation) when passed through a polarizer like a Polaroid film or Nicol prism made of calcite crystals, the electrical vector, associated with the propagation of light, oscillates in a single plane perpendicular to the direction of propagation. This is called plane-polarized light.



The plane polarized light, in fact, is composed of two enantiomorphic (mirror image to each other) helical light waves circulating around the axis of propagation in opposite directions. Helical motion is a combination of translation and rotation occurring at the same time.

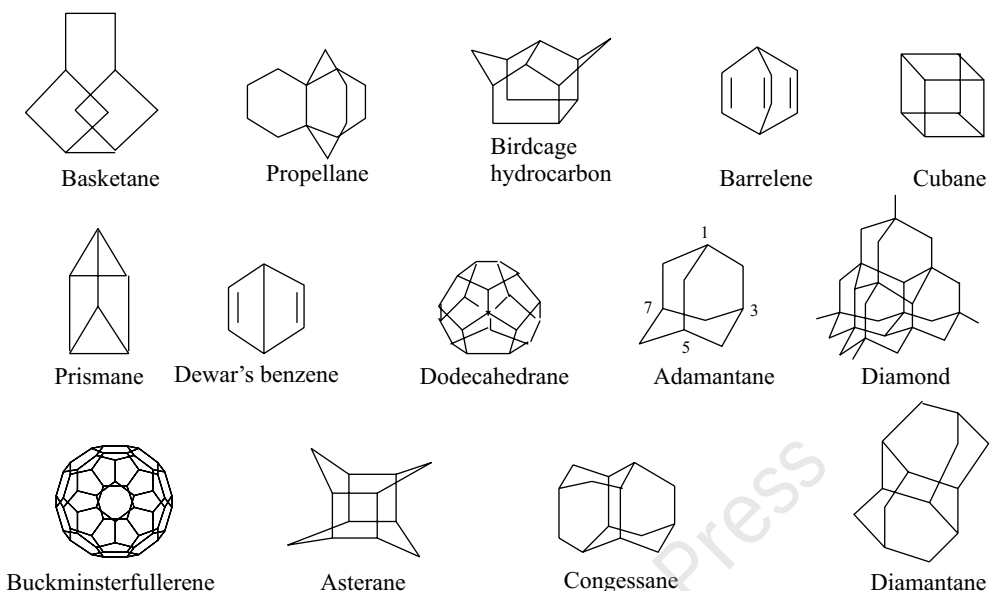
Two-dimensional projection of helical wave is a circle; each helix has an associated electric field vector. One of these helical paths having clockwise motion is called 'Right Circularly Polarized light' (RCP) and the other having anticlockwise motion is called 'Left Circularly Polarized light' (LCP). The RCP and LCP always have the same amplitude and at any time the contributions of the two electric field vectors to the propagation cancel each other and resulting in the formation of a plane-polarized light (LP). The formation of plane polarized light from right and left circularly polarized lights can be schematically shown as below.



When plane polarized light is passed through a solution containing a chiral compound, diastereoisomeric interaction occurs between the chiral compound and the plane polarized light. The chiral molecules refract one helical electrical vector more than the other. Two circularly polarized components of plane polarized light have different refractive indices and different absorption coefficients. If the medium contains only one type of chiral molecules, or one enantiomer is in excess, the plane of polarization gets rotated with respect to the original plane. This phenomenon is called *circular birefringence*. This is shown above. The direction and extent of rotation (α) may be measured by using a second polarizing filter known as detector or analyser. This phenomenon is the basis for the detection and analysis of enantiomers by their optical rotations.

A Few Unique Three-Dimensional Organic Molecules

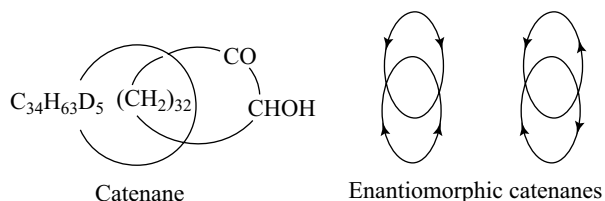
There was an upsurge in research work since the early 1960s to synthesize some complex three-dimensional cyclic organic molecules posing academic challenge to the leading scientists. It would be mentioned that some of these were more than mere synthetic exercises. Some typical examples, together with their whimsical trivial names are given below.



Dewar's benzene was the structure proposed by Dewar for the benzene molecule. It was synthesized by Van Tamalen in 1963. Barrelene was synthesized so as to ascertain whether any spatial influence was possible by one double bond on the other. Congessane has its carbon atoms arranged in the same pattern as diamond and it was synthesized to study the special stability of diamond-like structures. A particularly interesting and fascinating hydrocarbon is adamantane, which also has a diamond-like arrangement of carbon atoms (the name diamond is derived from the Greek, *adamantos*, meaning, 'untamed'). It is interesting to note that adamantane, congessane and diamond are constructed of units of the stable chair conformer of cyclohexane. Thus chair form of cyclohexane plays a very significant role in saturated cyclic systems in injecting unique stability in many organic molecules.

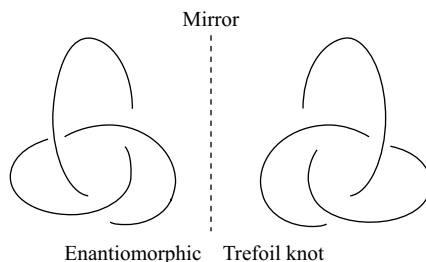
Adamantane is a strain-free molecule and is extremely stable thermally and chemically. Its melting point is 2690°C, the highest ever recorded for a saturated hydrocarbon. Adamantane has a centre of symmetry (see Chapter 2) and hydrogens at 1, 3, 5, and 7 are all equivalent, thus, adamantane can be regarded as an enlarged methane molecule. When 1, 3, 5 and 7 positions are substituted by non-equivalent ligands then it is capable of existing as a pair of optically active enantiomers. This has been confirmed in 1969 through the resolution of 1,3,5,7-substituted adamantane.

Perhaps the most fascinating carbon compounds that have caught the attention of synthetic chemists in recent years are 'Catenanes' (Latin, *Catena*, Chain). Catenanes are molecules whose parts are held together as links of chain and not by traditional covalent bonds. The first catenane was produced by Wassermann in 1960 and is schematically shown below.



Catenanes having two rings can exist as a pair of enantiomers because one sequence of atoms encountered on traversing a ring may be clockwise and the other anticlockwise. Isomeric catenanes are called topological isomers. However, no synthetic catenanes are known to be resolved into their optically active enantiomers.

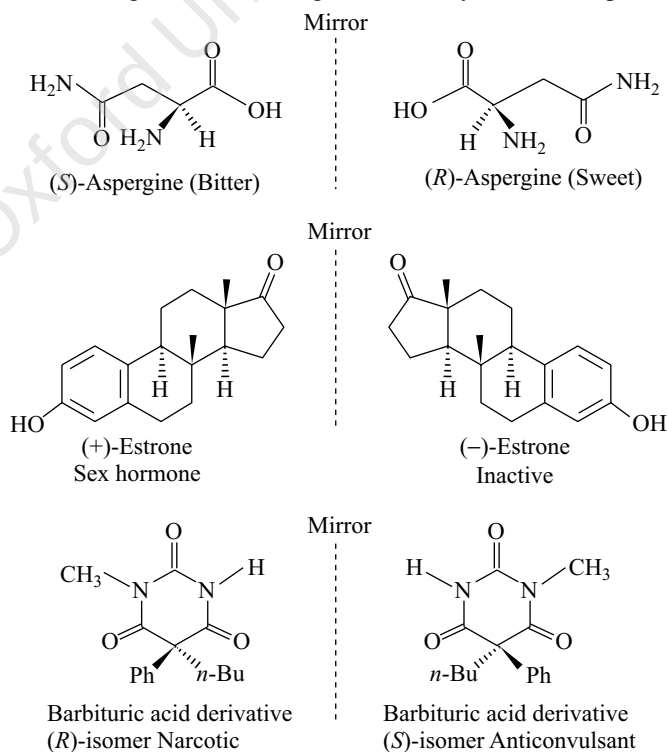
Another interesting topological isomers are trefoils in which a single chain is knotted. The simplest example of such a knotted three-dimensional chain is shown below. These trefoils are also capable of existing as a pair of enantiomers.



It is to be noted that many nucleic acids have been shown to contain catenary chains and knots in their structures which are responsible for their specific biological activities within our body. Model experiments with relatively simple compounds of these classes can provide valuable information to carry out comprehensive investigation of these complex macromolecules.

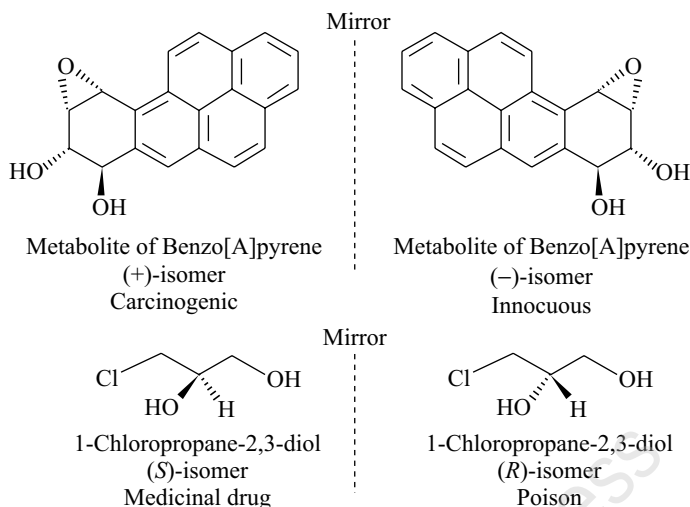
Another unique structural masterpiece made of only carbon atoms is 'buckminsterfullerene'. The molecule is a C_{60} unit and was obtained by Kroto et al. in 1985 by vaporizing graphite into a high-density helium flow. It is a mustard-coloured crystalline solid having a closed-shell polygon with 60 vertices and 32 faces of which 20 are hexagonal (benzenoid) and 12 are pentagonal. It has got its name from the fact that its structure has similarity with a geodesic dome designed by the architect Buckminster Fuller. It is also known as 'footballene' (Chemical Abstract) or 'soccerballene'. The isolation of another form of allotrope of carbon has generated immense interest among the scientists and a comprehensive review is published by Kroto et al. in 1991 [Kroto et al., C_{60} : buckminsterfullerene, *Chem. Rev.*, 91, 1213 (1991)].

It is very strange that in many cases, enantiomers behave differently towards its interactions with human body. This stereospecificity in interactions is of great interest in organic chemistry. A few examples are given below.



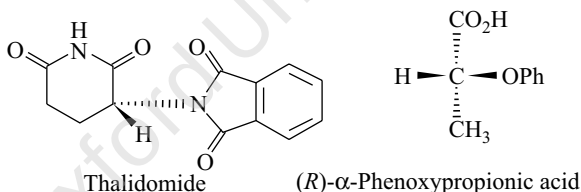
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It is obvious from the above examples that use of specific stereoisomer is of utmost importance in the treatment of diseases. At present most of the commercial drugs with a stereogenic centre are still sold as a 50 : 50 mixture of enantiomers, though most of the activity resides in one enantiomer. In this regard, cases are known of toxic effects in the wrong enantiomer. For example, thalidomide comes in two forms: the left handed compound is a powerful tranquilizer and the right-handed version can disrupt foetal development. In the early 1960s the two forms were present in equal proportions in the marketed drug, and lead to catastrophic consequences.

The phenomenon of stereospecificity in biological action is not restricted to pharmaceuticals, but is characteristic of all biologically active agents. For example, it is well known that the herbicidal activity of the α -phenoxypropionic acid group of agrochemicals resides predominantly in the (*R*)-isomer.



A Short History of the Development of Stereochemistry

The origin of stereochemistry may be considered from that time when the French physicist Malus discovered plane polarized light in 1809. Discovery in 1812 by another French scientist Biot that quartz crystals, when cut at right angles to its crystal axis, show a unique property of rotating the plane of plane polarized light, led to the discovery of the phenomenon of optical rotation. In 1815, Biot observed that certain natural organic compounds like sucrose, camphor, tartaric acid, and turpentine could also rotate the plane of a plane polarized light, even when they are in liquid or in the form of solutions and the rotational direction might be clockwise or anticlockwise. He further recognized that the cause of optical rotation exhibited by these compounds was not the same as in the case of quartz crystals. In 1822, a British scientist Sir John Herschel observed that the direction of rotation of plane polarized light by quartz crystals was related to the geometric shape of the crystals. Hemihedral quartz crystals are found to have two different forms having mirror image relationship. Such mirror-image crystals are called *enantiomorphs* from the Greek *enantios* meaning opposite and *morphe* meaning form. Quartz crystals of one type rotate the plane of polarized light in clockwise direction and its enantiomorphous crystals in anticlockwise.

In 1848, Louis Pasteur separated two types of crystal of sodium-ammonium tartrates mechanically and confirmed that optical activity of tartaric acids was a molecular property and not dependent on its crystalline shape. He believed that two types of tartaric acids were dissymmetric in the same way as the two types of quartz crystals. The acids are, therefore, enantiomorphous at the molecular level. Pasteur did not continue his investigations on this subject any more and the problem remained dormant for a long time.

In 1858, the German chemist Kekule laid the foundation of modern structural chemistry and concluded that carbon exhibits tetravalency in all organic molecules irrespective of their structures.

In 1874, J.H. van't Hoff (J.H. van't Hoff, *Bull. Soc. Chim. France*, [2]23, 295, 1875) and J.A. Le Bel (J.A. Le Bel, *Bull. Soc. Chim. France*, [2]22, 337, 1874) solved the problem of dissymmetry at the molecular level by their separate but similar proposition on the geometric shape of an organic molecule with the general formula Cabcd, where a,b,c, and d are different substituents. They proposed a tetrahedral rigid geometric shape for this class of compounds and showed that under this condition the four groups can be arranged in two different ways pointing to the corners of a regular tetrahedron. The central carbon is at the centre of gravity of the tetrahedron. The two forms are enantiomorphous to each other and not superimposable. The non-superimposability of two models of Cabcd type molecules in their tetrahedral shape had a tremendous impact on the unsolved organic problems at that time and in recognition of their study both van't Hoff and Le Bel were awarded the Nobel Prize in Chemistry in 1901. A further proof for the tetrahedral theory was given by E. Fischer who showed that optical activity disappears when two identical substituents are placed on a central carbon atom (E. Fischer, *Ann. Chem.*, 402, 364, 1914). The hypothesis of van't Hoff and Le Bel regarding the tetrahedral nature of a saturated molecule was proved by the development of the visualization of a molecule by methods involving X-ray, electron diffraction, IR, and Raman spectra.

At the beginning of the twentieth century, Werner made a significant contribution in the field of structures of metal complexes. Werner was awarded the Nobel Prize 1913 for his work. The importance of conformational changes in cyclic compounds was initiated by the observation made by Sasche (1892) that the cyclohexane ring could be puckered and made to maintain the tetrahedral bond angles for carbon thereby avoiding any bond angle strain proposed by Baeyer in 1885. Mohr in 1918 indicated that the so-called chair conformations of cyclohexane may be interconverted by rotation around carbon-carbon single bonds. The concept of conformational aspect of stereochemistry was further supported by the observation of stereoisomerism in biphenyls (1926) and Boeseken's study (1928) of the effect of diastereoisomeric butan-2, 3-diols on the conductivity of boric acid. In 1930, Weissberger and Wolf independently studied the dipole moments of stilbene dichlorides and came to the conclusion that the rotation around carbon-carbon single bond was not entirely free. Kohlrausch, in 1936, confirmed the existence of two distinct types of bonds in the chair conformations of cyclohexane, which are subsequently called axial and equatorial.

The subject stereochemistry assumed a new dimension when it was established that the phenomenon of symmetry plays a pivotal role in determining the existence of stereoisomers. The molecules are classified into *symmetric* and *dissymmetric* based on conventional elements of symmetry, normally used for rigid solids with geometric shapes. Since 1960 a good number of eminent scientists enriched the subject with new ideas and new terms backed by marvellous pieces of experimental work. Hassel and Barton studied conformational aspects of cyclohexane and were jointly awarded the Nobel prize in 1969. Mislow introduced the classification of enantiomorphous molecules with the terminology 'chiral' into stereochemical literature in 1965. The term chiral was originally coined by Thomson (1884) from *cheir*, the Greek word for hand, a familiar chiral object. R.S. Cahn, C. Ingold, and V. Prelog have introduced an unambiguous method of naming stereoisomers (known as CIP rules) in 1966. C. Djerassi studied extensively the quantitative relation between the wavelength of electromagnetic radiation and molar rotation (ORD and CD) following the equation developed by Drude in 1900. Significant contributors in the field of stereochemistry are E. Fischer, M.S. Newman, J.E. Baldwin, P. Deslongchamps, R.B. Woodward, R. Hoffmann, and E.L. Eliel.

Stereochemistry is being studied today under the headings static and dynamic. Static stereochemistry deals with the numbers, naming, classifications, energy, and physical properties of stereoisomers. Dynamic stereochemistry determines the stereochemical requirements and the stereochemical outcome of chemical reactions, including the interconversion of conformational isomers.

Symmetry in Molecules

CHAPTER

1

INTRODUCTION

Mechanical models that have definite geometric shapes can be classified as *symmetric* and *non-symmetric* on the basis of the presence or absence of certain basic elements of symmetry. Organic molecules are covalent compounds that have definite bond lengths and bond angles among the constituents atoms. They have definite *bond-connectivity* that describes the manner the atoms are bonded among themselves. They can be confidently taken as idealised static entities that can be represented by rigid mechanical models. The same arguments may be applied on the rigid organic molecules.

1.1 ELEMENTS OF SYMMETRY AND SYMMETRY OPERATIONS

Four fundamental elements of symmetry are encountered in organic molecules (in fact in all geometric bodies). They are (i) *rotational axis of symmetry*, (ii) *plane of symmetry*, (iii) *centre of symmetry*, and (iv) *alternating axis of symmetry*. Symmetry elements are in fact can be considered as operators that generate the repetition of the geometric shape of the molecule as observed before carrying out symmetry operations.

1.2 ROTATIONAL AXIS OF SYMMETRY (C_n): PROPER AXIS OF SYMMETRY

Rotational axis of a molecule is an imaginary axis passing through the molecule such that if the molecule rotates about the axis through an angle of $360^\circ/n$, then results in an equivalent structure or orientation that is superimposable with the original one. It is denoted by the symbol C_n (Latin word *Circulate*) and is also called *proper axis*. The subscript 'n' denotes the *fold* or *order* of rotation and it is determined by dividing 360° by the smallest angle through which the molecule has rotated about the axis to give a superimposable structure on the original one. The value of n can never be a fraction, because in that case every C_n operation will not give superimposable structure, that is, equivalent structure. If a molecule possesses C_n axes with different values of n then the C_n axis having maximum value of n (fold) is called the *principal axis*. When there are several C_n axes with same value of n , then the principal axis is one that involves maximum number of atoms of the molecule. A few molecules having C_n axes are shown in Figs 1.1 and 1.2.

H_2O molecule (Fig. 1.1) is angular in shape (based on VSEPR theory) and it has C_2 rotational axis, where C stands for *circulate* and 2 is the fold. Rotation by 180° about the axis will give an indistinguishable orientation of H_2O but the positions of H^a and H^b are changed mutually. Benzene (planar) molecule (Fig. 1.2) has a C_6 axis, passing vertically through the centre

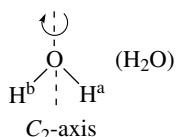


Fig. 1.1

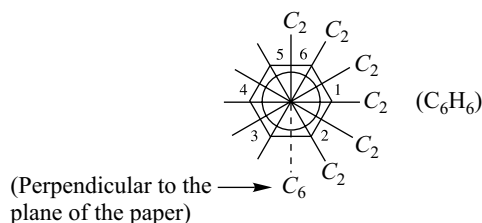


Fig. 1.2

of the molecule. Along with this, it has six C_2 axes passing through each pair of opposite sides and corners of the planar molecule. Here C_6 is the principal proper axis because of higher value of n . If the molecule is rotated about the axis through an angle of 60° , then we get a structure of benzene, which is indistinguishable from the original one. Again, if we rotate the molecule by 180° about any of the C_2 axes we get indistinguishable structure. Benzene also has a C_2 axis collinear with C_6 axis but that is not taken into consideration. For total symmetry elements in the benzene type molecules, see Section 1.9.

It should be remembered that the new structure of benzene, obtained by the rotation about the C_2 or C_6 axes, is called *indistinguishable* instead of *identical* because the carbon atoms, denoted by numerals in Fig. 1.2 will change their positions after rotation about C_6 axis by 60° . Therefore, we are not getting an identical structure in the sense that the C-1 atom of the rotated molecule is not coinciding with the C-1 of benzene as depicted originally.

One should note that C_n axis where $n = 1$, does not represent a rotational axis in true sense of the definition because all molecules in the universe must possess C_1 axis. Rotation through an angle of 360° about any axis through any molecule gives back the identical structure. C_1 axis is, therefore, known as *trivial axis* and is not included in the category of C_n axis. C_1 axis is in fact an *identity operation* (E or I , see Section 1.6) according to the group theory. Rotational axis of symmetry is also symbolized as C_p (p = fold).

1.3 PLANE OF SYMMETRY (σ)

Plane of symmetry of a molecule represents a plane bisecting a molecule such that each atom on one side of the plane, when reflected through the plane (considering it as a mirror plane) encounters an equivalent (identical) atom on the other side. This is why plane of symmetry is also called a mirror plane. The designation sigma (σ) comes from the German word *spiegel*, meaning mirror. The structures of molecules of H_2O , *cis*-1,2-dichlorocyclopropane, and *cis*-1,2-dimethylcyclopentane with their possessing mirror planes are shown in Figs 1.3–1.5.

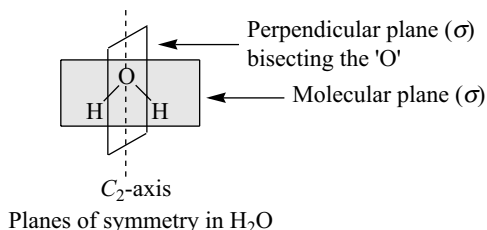


Fig. 1.3

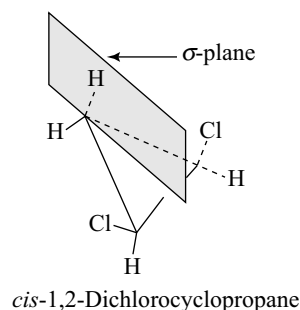


Fig. 1.4

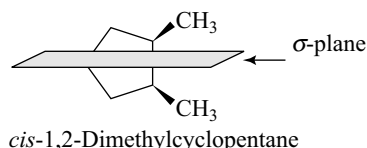


Fig. 1.5

It should be remembered that every planar molecule necessarily has a plane of symmetry, namely the *molecular plane*. For example, H—Cl molecule (Fig. 1.6) has a plane of symmetry that passes through the molecular axis joining the H and Cl nuclei and lie with the molecular plane. Remember that in the process of getting such a plane of symmetry, one can divide atoms or achiral groups into halves considering them as regular geometric bodies, say sphere.

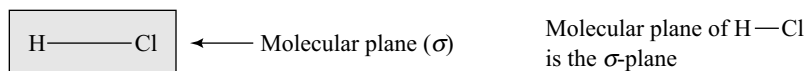


Fig.1.6

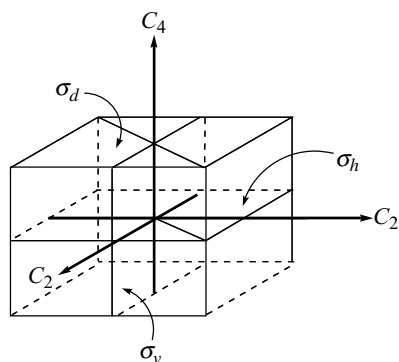


Fig. 1.7

$\sigma_h, \sigma_v, \sigma_d$

The symbol σ is usually found to carry three subscripts indicating the position of the symmetry plane/planes relative to the principal axis (C_n). These are shown in Fig. 1.7.

σ_h Represents reflection in the plane perpendicular to the principal axis of rotation, that is, axis with highest value of 'n' (h stands for horizontal).

σ_v Represents the reflection in the plane containing the principal axis (v for vertical).

σ_d Represents reflection in the plane, which contains the principal axis and bisects the angle between the two C_2 axes (d for diagonal).

When both σ_v and σ_d planes are present, then the σ_v plane contains the greater number of atoms.

The presence of σ_h , σ_v and σ_d in a molecule is shown in Figs 1.8 and 1.9 diagrammatically.

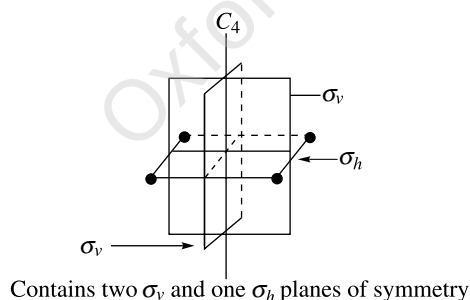


Fig. 1.8

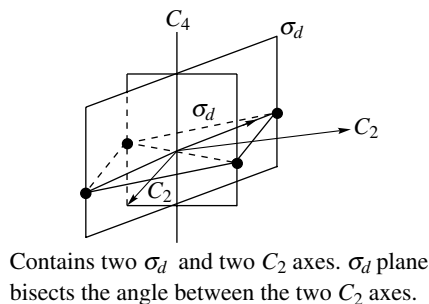


Fig. 1.9

Plane of symmetry is a symmetry operation of second kind or improper operation because, this operation brings into coincidence one real material point with the reflection of another. It is a case of virtual coincidence rather than real.

1.4 CENTRE OF SYMMETRY (i)

The centre of symmetry is a point within a molecule such that if a straight line is drawn from any part of the molecule through that point and extended an equal distance by a straight line on the

other side, a like atom or part of the molecule is encountered. Centre of symmetry is also called *centre of inversion* and is symbolized as i . This may be exemplified by α -truxillic acid (Fig. 1.10) and *meso*-tartaric acid (Fig. 1.12).

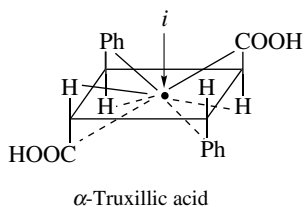


Fig. 1.10

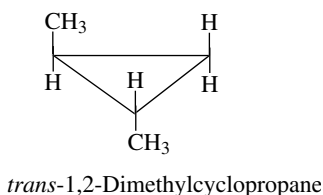


Fig. 1.11

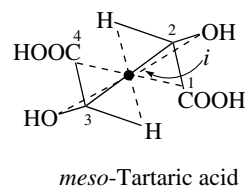


Fig. 1.12

It should be noted that each of all straight lines passing through the centre of inversion must encounter identical atoms on either side of the centre. If any one of the straight lines drawn through the centre of the molecule fails to do so then the molecule is devoid of any centre of symmetry. For example, 1,2-dimethylcyclopropane (Fig. 1.11) does not have a centre of symmetry i . All C_n and σ elements, if present in addition to i , must pass through i .

The conformation (see Chapter 5) of *meso*-tartaric acid shown in Fig. 1.12 has a centre of symmetry, shown by *dot* ($\bullet$) on the line joining the two carbons, C-2 and C-3. If the centre of inversion (centre of symmetry) is considered as origin of a Cartesian co-ordinate system, then the operation of inversion is to change the point of co-ordinates x, y, z into a point of co-ordinates $-x, -y, -z$.

In this regard, it should be remembered that reflection (σ plane) changes one co-ordinate but not the other two (e.g., x, y, z to $-x, y, z$) and C_2 operation (two-fold simple axis) changes two of the three co-ordinates (e.g., x, y, z to $-x, -y, z$).

1.5 ALTERNATING AXIS OF SYMMETRY (S_n): ROTATION-REFLECTION SYMMETRY

A molecule possesses an *alternating axis of symmetry* (S_n) of n -fold (or order) if rotation of the molecule about the axis by $360^\circ/n$ followed by reflection through a plane perpendicular to this axis produces an indistinguishable structure with the original one. Neither of these two operations (rotation or reflection) alone is a valid symmetry operation, but only the outcome of the combination of both transformation.

Alternating axis of symmetry is designated as S_n . It is also known as *improper rotation axis*, where n is known as the fold or order of alternating axis and is determined by dividing 360° by the smallest angle of rotation, which satisfy the condition stated above. *Alternating axis* of symmetry is also called *rotation-reflection symmetry* or *rotary-reflection axis*. The name alternating axis is derived from the fact that under the S_n operation the equivalent atoms are carried from one side of the reflection plane to the other in an alternating sequence. The alternating axis is also symbolized by S_p (p = fold).

It should be noted that when S_n is the only symmetry element in a molecule then the value of fold (n) must be even. When n is odd, then S_n is equivalent to other symmetry elements. In case of S_n axis (n = odd), the structure must have C_n axis and a perpendicular plane. S_n (n = odd) cannot be the sole symmetry element in a group. If S_n with even ' n ' exist then $C_{n/2}$ exists. If S_n with odd ' n ' exist then both C_n and σ perpendicular to C_n exist, that is, C_{nh} .

Examples of molecules with S_n -axis are given in Fig. 1.13. Structures I and II are indistinguishable. Therefore, I has a S_2 alternating axis of symmetry.

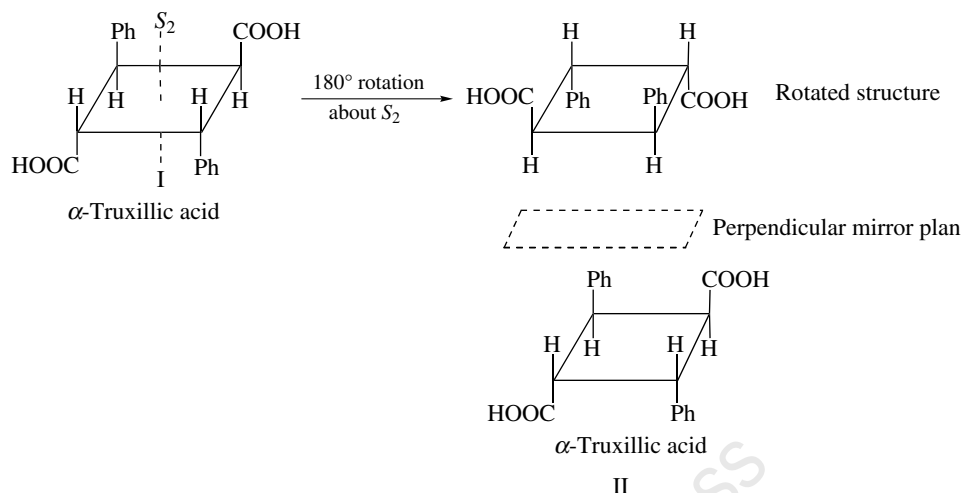
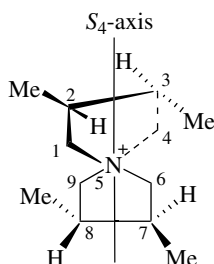


Fig. 1.13

It should be noted that S_2 axis is equivalent to i and S_1 axis is equivalent to σ -plane. An example of a molecule with S_4 axis is given in Fig. 1.14.

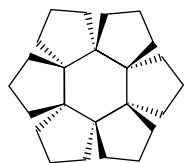
This *spiro*-compound has S_4 alternating axis. If it is rotated through an angle of 90° about that axis and then the resultant structure is reflected in a plane perpendicular to that axis, then a structure, indistinguishable from the original one, is obtained. The same result is obtained when reflection is done first followed by rotation. It also has a C_2 axis.



5 λ^5 -Azaspiro[4.4]-2,3,7,8-tetramethylnona-5-ylum

Fig. 1.14

It should be noted that in case of S_n ($n = \text{odd}$), C_n and σ operations are related to each other by the following expression, $S_n = C_n \sigma_h = \sigma_h C_n$. When one operation is represented as the multiplication of other symmetry elements, one has to perform the operation indicated in the right part of the product first and the order is followed from right to left. Again $S_n^{n/2} = i$, if n is even and $n/2$ is odd and $S_{2n}^n = i$, if n is odd and $2n$ is even. The converse is not necessarily true. A unique molecule with S_6 axis is given on the left side (Fig. 1.15). It is named as [6.5] coronane.



[6.5]Coronane (S_6)

Fig. 1.15

1.6 NOTATION FOR SYMMETRY OPERATIONS

The notations for symmetry operations are given in Table 1.1.

Table 1.1

E	The identity transformation. E is taken from the German word 'Einheit', meaning unity.
C_n	Clockwise rotation through an angle of $2\pi/n$, where 'n' is an integer. The axis for which 'n' is greatest is termed the <i>principal</i> axis.
C_n^k	Rotation clockwise through an angle of $2k\pi/n$. Both n and k are integer.
S_n	An improper clockwise rotation through an angle of $2\pi/n$. Improper rotations are regular rotations followed by a reflection in the plane perpendicular to the axis of rotation. It is also known as <i>alternating axis of symmetry</i> and <i>rotation-reflection axis</i> .

(Contd.)

Table 1.1 Contd.

i	The inversion operator (the same as S_2). In Cartesian coordinates, $(x, y, z) \rightarrow (-x, -y, -z)$.
σ	A mirror plane from the German word for mirror- <i>Spiegel</i> .
σ_h	Horizontal reflection plane-passing through the origin and perpendicular axis with the 'highest' symmetry.
σ_v	Vertical reflection plane passing through the origin and the axis with the 'highest' symmetry.
σ_d	Diagonal reflection in a plane through the origin and the axis with the 'highest' symmetry, but also bisecting the angle between the twofold axes (C_2) perpendicular to the symmetry axis. This is actually a special case of σ_v .

Significance of E ' E ' is called the *identity* operation and leaves any molecule untouched, the corresponding symmetry element is the entire object (molecule) itself. The reason for including this symmetry operation is that some molecules have only this symmetry element and no other symmetry properties. Another reason is the completeness of the mathematical description of group theory. All molecules which do not have any other symmetry element than the *identity* operation must belong to the C_1 point group and thus must be chiral but the reverse conclusion is not true. Chiral molecules may not necessarily be a member of the C_1 point group (discussed later).

1.7 EQUIVALENT SYMMETRY OPERATIONS

Different manipulations of elements of symmetry that transform molecules into indistinguishable and identical structures are called *symmetry operations* and *operation of identity*, respectively. The element of identity is designated as E or I .

For example, $C_n^n = E$, that is when molecule is rotated n times about a C_n axis we get identical molecule.

$\sigma^2 = E$, because reflection of a molecule in a plane, followed by reflection back again, returns all points of the molecule to the position from which they started, that is, to the identical position.

$i^2 = E$, because inversion of a molecule followed by second inversion amounts to retention of the original orientation.

$S_n^n = E$ (n = even), because one S_n operation is equal to $1/n$ of a turn of a whole circle followed by reflection in a plane perpendicular to the S_n axis. Therefore, when n times of S_n rotation are carried out followed by reflection in a plane perpendicular to the axis, we get identical structure.

Again, $S_n^{2n} = E$ (n = odd), because S_n^n operation amounts to reflection in a plane (σ) and so $S_n^{2n} = \sigma^2 = E$.

1.8 POINT GROUPS

Symmetry operation is a manipulation that converts a geometric body into a new orientation, which is indistinguishable from and superimposable on the original geometric body. Since covalent molecules are considered as having definite geometric shapes, symmetry operations are equally applicable to organic molecules. Symmetry operations may not be combined arbitrarily with each other.

Molecules having specific rigid structures can be subjected to symmetry operations that can be performed on elements of symmetry, that is, E , σ , C_n , i , S_n . All these five operations are called point symmetry operations because under such symmetry operations one point, the centre of mass always remains unchanged. By the term *point group*, we mean a short hand notation for specifying the symmetry class of a molecule. The sum total of all possible symmetry operations defines a group. Therefore, to convert a set of symmetry elements into a group, the rule of correspondence should be specified. The criteria for a set of operations to constitute a point group are as follows.

- (i) The product of two members of the group and the square of any member is also a member of the group. For example,

$$C_4^1 \times C_4^2 = C_4^3, C_2 \times \sigma_h = S_2$$

- (ii) One of the symmetry operations must be the operation of identifies E , which commutes with all other operations and leave them unaltered,

$$E \times C_4^3 = C_4^3$$

- (iii) The combination of operation must obey association law,

$$(A \times B) \times C = A \times (B \times C)$$

$$(C_4^1 \times C_4^2) \times C_4^1 = C_4^3 \times C_4^1 = E$$

$$C_4^3 \times C_4^1 = (C_4^2 \times C_4^1) \times C_4^1 = E$$

- (iv) Every member of the group must have an inverse, that is, if A is a member, then A^{-1} must also be a member, where $AA^{-1} = E$. If,

$$C_4^1 \times C_4^3 = E \text{ then } C_4^3 \text{ is inverse of } C_4^1 \text{ and vice versa}$$

Symmetry operations do not necessarily commute, that is, AB does not always equal to BA .

Order of a point group represents the number of different operations that can be performed in a group. For example, a molecule having C_4 , there are four possible operations that can be performed on this symmetry element leading to indistinguishable-superimposable orientation. They are $C_4^1, C_4^3, C_4^2, C_4^1$. Therefore, the order of the point group is 4.

Specifying the symmetry class of a molecule according to point groups are discussed below in short.

1.8.1 C_1 Point Group

The molecules in which the only element of symmetry is E (identity operation) are said to belong to C_1 point group. That is, this point group has the lowest degree of symmetry. This point group has neither mirror planes, nor rotation-reflection axes, nor centre of inversion. The order of this point group is 1. The molecule of the type C_{abcd} belongs to this point group. A few structures with C_1 point group are given in Fig. 1.16. This is the point group of all asymmetrical molecules or molecular conformations. The molecules belong to this point group must be chiral.

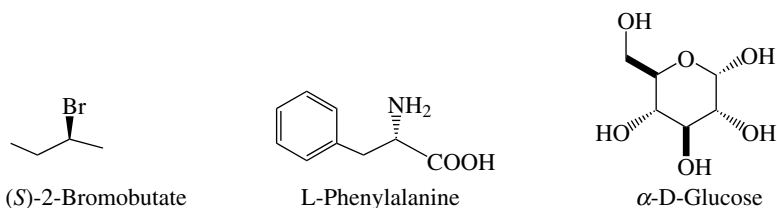


Fig. 1.16

1.8.2 C_n Point Group

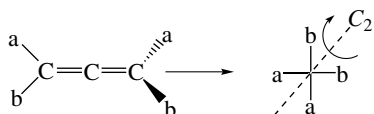


Fig. 1.17

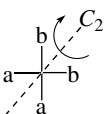


Fig. 1.18

In this case, the only element of symmetry in the concerned molecules is C_n axis ($n > 1$). Point group C_2 is of very common occurrence among the organic molecules. For example, allenes shown in Figs 1.17 and 1.18 has a C_2 point group.

Active tartaric acids, shown in Fig. 1.19, by Fischer projections (see Chapter 3), also have C_2 point groups.

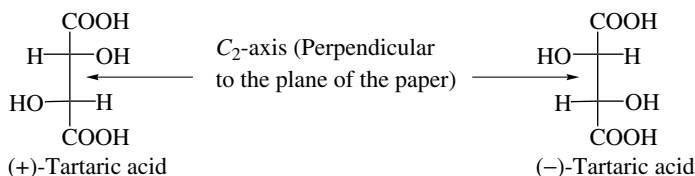


Fig. 1.19

Following two compounds also have C_2 axis (Fig. 1.20).

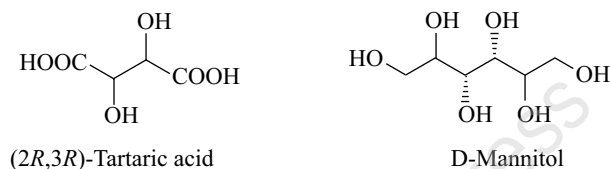


Fig. 1.20

Molecules having point group C_3 only are very rare. Three examples of molecules having C_3 point group are *trans-trans-trans*-3,7,11-trimethylcyclododeca-1,5,9-triene, 2,6,7-trimethyl-1-*a*Za-bicyclo[2.2.2]octane and 9*bH*-Phenylene (Fig. 1.21).

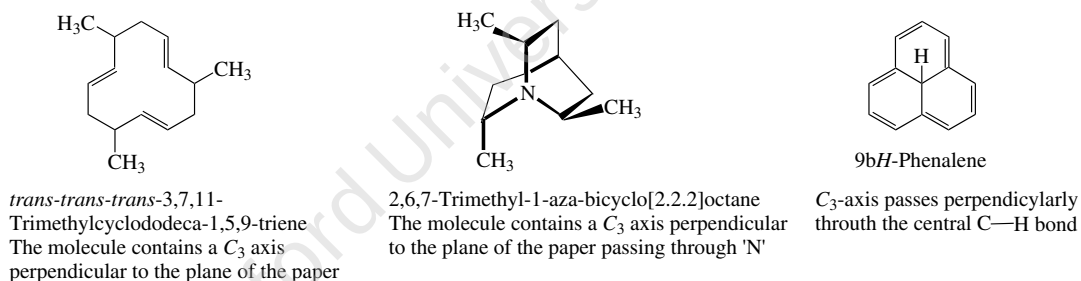


Fig. 1.21

Molecules with C_4 and C_6 point groups are given in Fig. 1.22.

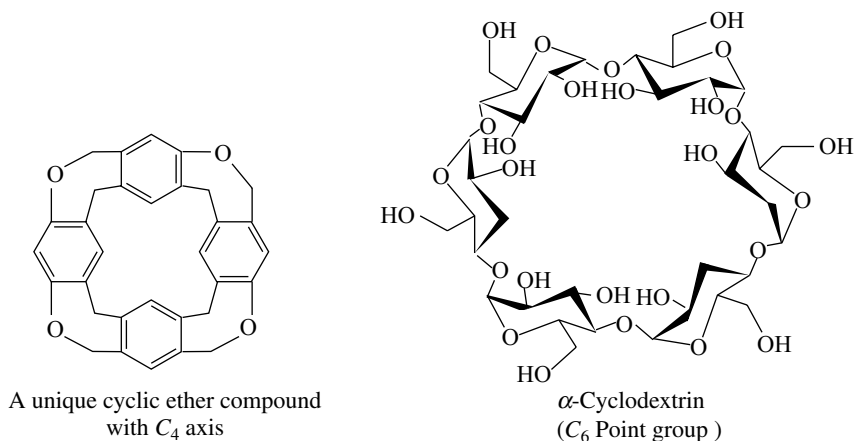


Fig. 1.22

1.8.3 $C_{\infty v}$ Point Group

Linear molecules having symmetry axis (C_n) joining the nuclei of atoms but without any σ_h are said to have $C_{\infty h}$ symmetry group. These types of molecules have infinite number of σ_v which are coplanar with the symmetry axis (C_{∞}) because there are innumerable angles of rotation carrying the molecules into themselves. Examples of such molecules are H–CN, H–Cl, N=O, etc. Such symmetry characteristic is also called *conical symmetry* (Fig. 1.23).

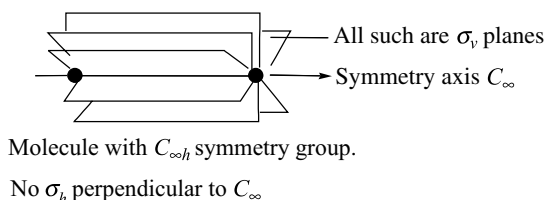


Fig. 1.23

1.8.4 C_{nh} Point Group

Molecules having C_n ($n > 1$) and a single σ_h as elements of symmetry are said to have C_{nh} point group. For example, *trans*-1,2-dichloroethylene has a C_2 axis and σ_h in molecular plane. Therefore, it has C_{2h} point group.

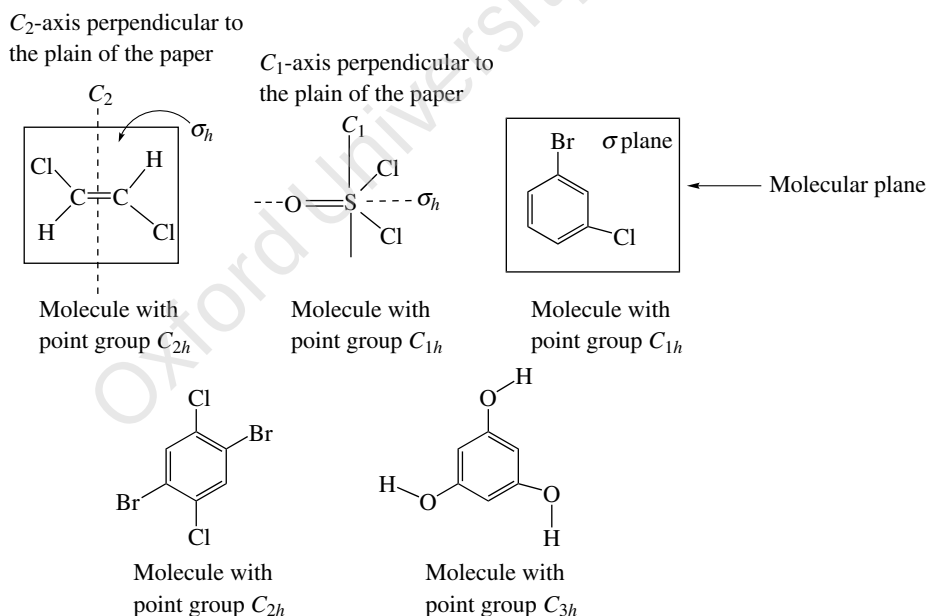


Fig. 1.24

The molecules SOCl_2 and *m*- $\text{C}_6\text{H}_4\text{ClBr}$, shown in Fig. 1.24, belong to C_{1h} group, but C_{1h} is equivalent to S_1 point group.

1.8.5 C_{nv} Point Group

C_{nv} point group is a combination of n -fold symmetry axis C_n and n symmetry planes (σ_v). *cis*- $\text{C}_2\text{H}_2\text{Cl}_2$ belongs to the C_{2v} point group while PCl_3 , NH_3 , etc., belong to the C_{3v} point group (Figs 1.25–1.28).

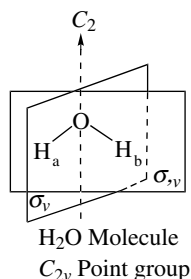


Fig. 1.25

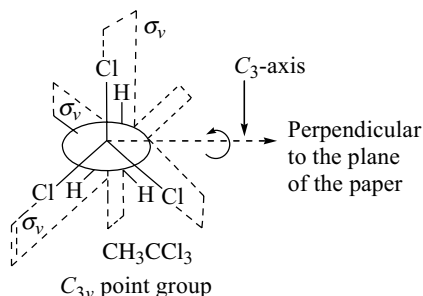


Fig. 1.26

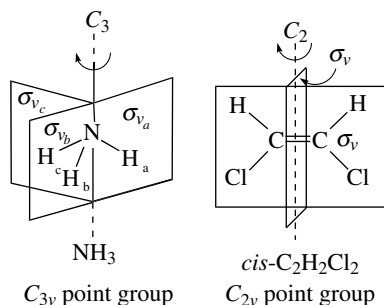


Fig. 1.27

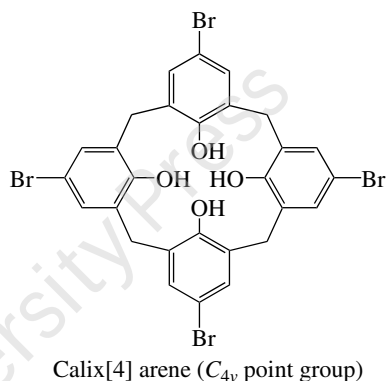


Fig. 1.28

1.8.6 C_s Point Group

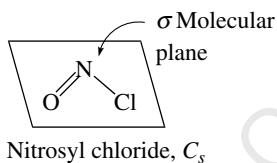


Fig. 1.29

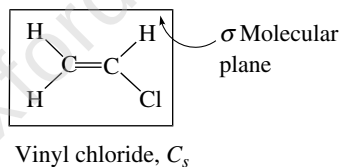


Fig. 1.30

Molecules having a single plane of symmetry (σ) belong to C_s point group. For example, NOCl (nitrosyl chloride), CH₂=CH-Cl (vinyl chloride), etc., have only one plane of symmetry which is coplanar with their respective molecular plane. Molecules belong to C_s point group cannot have any C_n ($n > 1$) axis (Figs 1.29 and 1.30).

1.8.7 S_n Point Group

Molecules in which there is only S_n ($n = \text{even}$) axis but without any symmetry planes belong to point group S_n. The molecules having point group S_n ($n = \text{even}$) will necessarily possess a proper rotation axis of the fold C_{n/2} coexistent with S_n axis. When $n = 4x + 2$ ($x = 0, 1, 2$, etc.), there is also a centre of symmetry, but when $n = 4x$, there is no centre of symmetry. When the value of n in case of an S_n axis is odd, the molecule must coexist with C_n and σ_h . Point groups in this case are customarily called C_{nh} rather than S_n ($n = \text{odd}$). S₂ point group is equivalent to C_i and S₁ is equal to σ -plane (point group C_s).

Any molecule featuring a S_n axis must be achiral. In fact, the most general description of chirality is the absence of any S_n rotary-reflection in a molecular geometry.

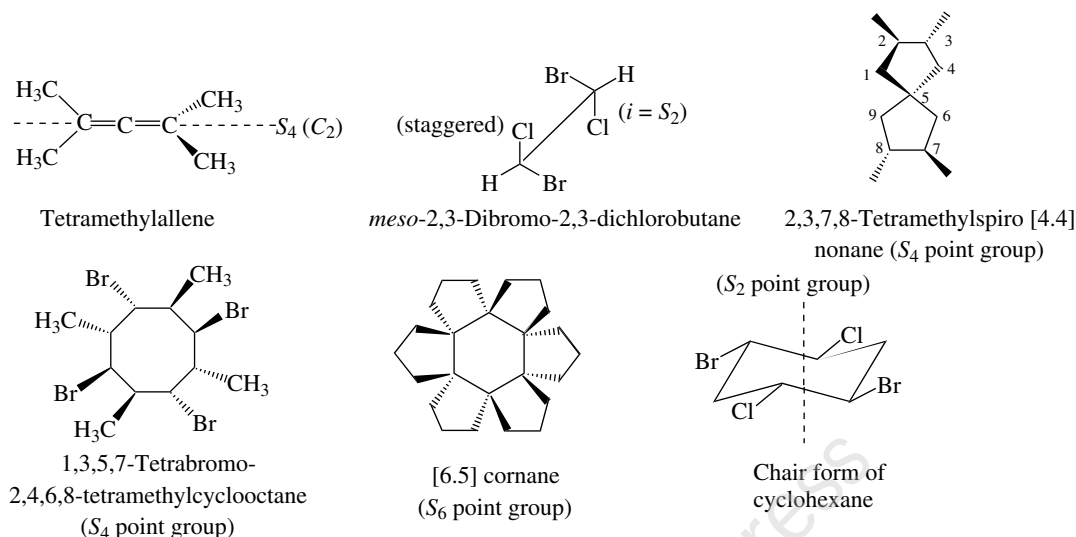


Fig. 1.31

1.9 DIHEDRAL SYMMETRY

Molecules with a principal C_n axis in addition to nC_2 axes in a plane perpendicular to the principal axis are said to possess *dihedral point groups*.

Dihedral symmetry includes three different point groups. They are D_n , D_{nh} , and D_{nd} . Characteristics of these groups are stated below:

1.9.1 D_n Point Group

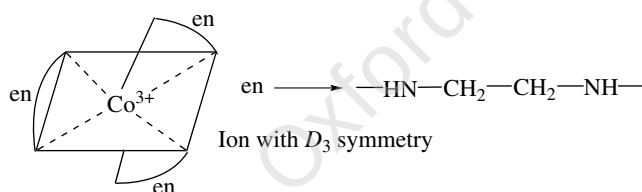


Fig. 1.32

A model of the above ion is necessary to see the three C_2 axes and the principal C_3 axis. The following organic molecules belong to the point groups D_2 and D_3 (Figs 1.33–1.35).

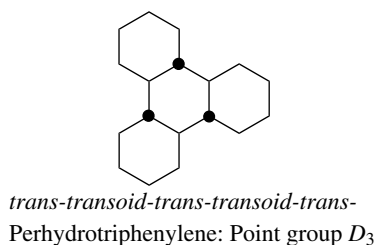


Fig. 1.33

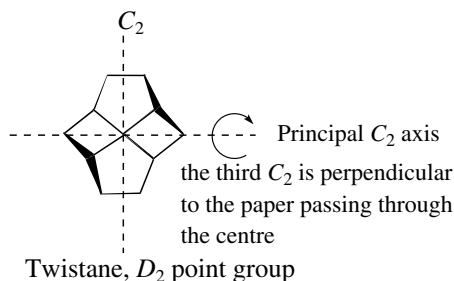


Fig. 1.34

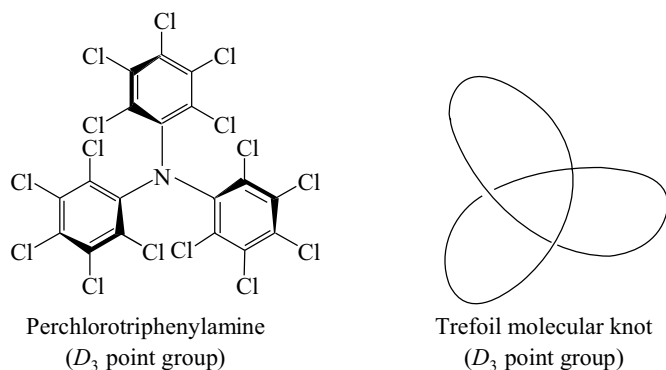


Fig. 1.35

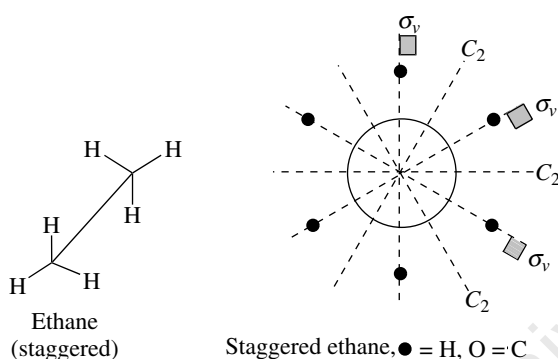


Fig. 1.36

Ethane in the staggered conformation belongs to D_{3d} point group.

In Fig. 1.36, there are three vertical planes (σ_v) but no σ_h . It has three C_2 axes. Each vertical plane bisects the angle between the two C_2 axes. There is a C_3 principal axis passing vertically through the C–C bond. A model will be helpful to understand these symmetries.

Allene and in certain spiranes and biphenyl where the rings are perpendicular to each other, have D_{2d} point group. These molecules also have S_4 axis (Fig. 1.37).

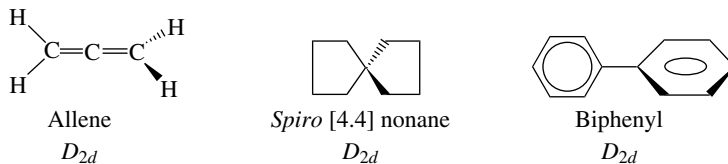


Fig. 1.37

Chair form of cyclohexane belongs to point group D_{3d} (see Chapter 6). The order of point group D_{nd} is $4n$. For example, the allene with D_{2d} point group, the order is 8 and the operators are C_2 , $2C_2'$, $2\sigma_d$, S_4^1 , S_4^3 , and E . D_{2d} is also symbolized as V_d (German: *Vierergruppe*).

1.9.3 D_{nh} Point Group

When molecules with D_n point group also possess $n\sigma_v$ planes and a σ_h perpendicular to the principal axis, then these are said to have D_{nh} point group. That is D_{nh} point group includes

The order of a D_n point group is equal to $2n$. Thus, for twistane (D_2), the possible symmetry operations are C_2 , C_2' , C_2'' , and E . That is, molecule contains a principal C_2 axis along with two other proper axes (C_2' , C_2'') perpendicular to the principal axis. It has also an operation of identity (E).

1.9.2 D_{nd} Point Group

Molecules with C_n symmetry axis in addition to perpendicular nC_2 axes and $n\sigma_v$ planes but without σ_h plane are known to have D_{nd} point group (d = diagonal). Here σ_v planes bisect the angles between the two C_2 axes and may be identified as σ_d .

C_n axis, nC_2 axes perpendicular to C_n axis, $n\sigma_v$ planes and a σ_h perpendicular to C_n axis. For example, ethylene has D_{2h} and benzene has D_{6h} symmetry, n always indicates the fold of the principal axis (highest order). The order of the D_{nh} point group is $4n$. For example, molecules with D_{2h} point group have the order 8, that is, the operators are C_2 , $2C_2'$, $2\sigma_v$, σ_h , i and E .

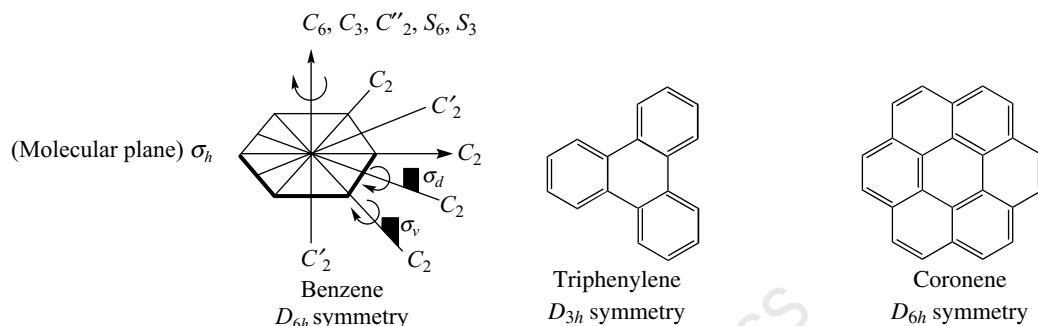


Fig. 1.38

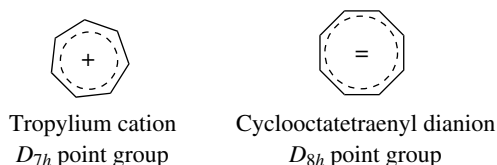


Fig. 1.39

and cyclooctatetraenyl dianion, respectively, as shown in Fig. 1.39.

1.9.4 $D_{\infty h}$ Point Group

In linear molecules the line along which nuclei are located is the symmetry axis of an infinite order (C_∞) since there are innumerable angles of rotation carrying the molecules into themselves. When the linear molecule also has a symmetry plane perpendicular to its axis (C_∞), the molecule is said to belong to $D_{\infty h}$ symmetry point group. For example, $H-H$, $HC\equiv CH$, $O=C=O$, etc., have $D_{\infty h}$ symmetry. Such molecules also have infinite number of σ_v , coplanar with C_∞ axis and infinite number of C_2 axes perpendicular to the C_∞ axis.

All diatomic homonuclear molecules have $D_{\infty h}$ point group. This symmetrical characteristic is also called *cylindrical symmetry*, since a cylinder displays it.

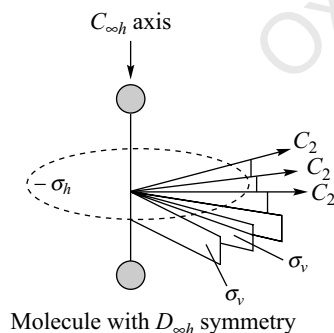


Fig. 1.40

These have the following meaning.

- The subscript number indicates the order of the principal (highest order) axis.
- The axis conventionally defines the vertical direction.
- The capital letter ' D ' is used if n -fold principal axis is accompanied by n number of two-fold axes at right angles to it; otherwise the capital letter ' C ' is used.

- (iv) The small letter 'h' is used as a subscript if a horizontal plane is present bisecting the principal axis together with vertical planes running with the principal axis. If only vertical planes are present then the small letter 'v' is used as subscript. The small letter 'd' along with the capital letter 'D' are used when vertical planes are indicated. The letter 'h' takes precedence over 'v' or 'd'. If no vertical or horizontal planes are present, these small letters are omitted.

1.10 DISSYMMETRIC AND NON-DISSYMMETRIC MOLECULES ON THE BASIS OF POINT GROUPS

Based on the symmetry group present in a molecule, it can be placed in dissymmetric or non-dissymmetric category. This is summarized in Table 1.2.

Table 1.2

Dissymmetric molecules		Non-dissymmetric molecules	
Point group	Elements of symmetry	Point group	Elements of symmetry
C_n	C_n only ($n > 1$)	C_s	One σ_v plane
D_n	$C_n + nC_2$ only	S_n	S_n ($n = \text{even}$) no σ plane
		C_{nv}	$C_n + n\sigma_v$ only
		C_{nh}	$C_n + \sigma_h$ only
		D_{nd}	$C_n + nC_2 + n\sigma_v$, but no σ_h
		D_{nh}	$C_n + nC_2 + n\sigma_v + \sigma_h$

Molecules containing C_1 axis only are always asymmetric molecules. Molecules having C_1 , C_n , and D_n point groups are called *chiral* molecules. They exhibit optical activity (see Chapter 3).

1.11 TETRAHEDRAL, OCTAHEDRAL, AND ICOSAHEDRAL SYMMETRIES

Regular tetrahedron, octahedron and icosahedron are highly symmetric systems and need special attention.

1.11.1 Tetrahedral Symmetry

The characteristic elements of symmetry of a regular tetrahedron are

- three C_2 axes passing through pairs of opposed edges, that is, edges ending in noncommon vertices,
- four C_3 axes passing through each apex and the centre of the opposite face,
- three S_4 axes,
- six σ_d planes, each containing one edge and bisecting the opposite one.

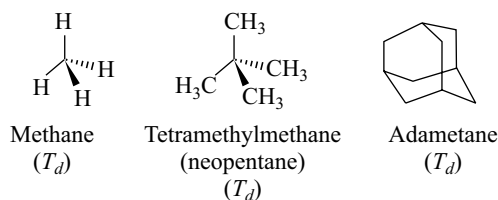


Fig. 1.41

Tetrahedral symmetry (point group) is designated as T_d . For example CH_4 , CCl_4 , $\text{C}(\text{CH}_3)_4$, adamantane are molecules with T_d symmetry (Fig. 1.41).

1.11.2 Octahedral Symmetry

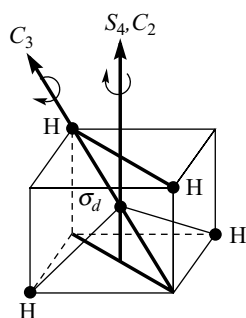
A regular octahedron has the following elements of symmetry:

- four C_3 axes passing through the centres of opposite faces in the octahedron,

- (ii) three C_4 axes passing through the centres of opposite faces of the cube or opposite apices of the octahedron,
- (iii) six C_2 axes passing through the centres of opposite edges,
- (iv) three σ_h passing through the middle of the opposite faces bisecting the edges,
- (v) six σ_d planes passing diagonally through opposite faces,
- (vi) as distinct from the T_d symmetry, octahedral symmetry also possesses the inversion centre i .

Octahedral symmetry is designated as O_h . It is also known as *Cubic point group*. The cube and the octahedron belong to this point group. Examples of molecules with octahedral symmetry are UF_6 , SF_6 , etc. The order of O_h is 48.

Basic symmetry elements of T_d and O_h groups are shown in the following diagrams. Not all symmetry elements are shown in the diagrams. For the sake of simplicity only one characteristic symmetry element of each kind is shown in Fig. 1.42 and Fig. 1.43.



CH_4 molecule with T_d symmetry

Fig. 1.42

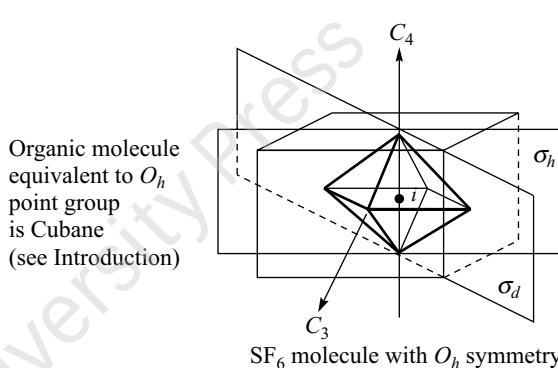


Fig. 1.43

Models of these molecules would be helpful for proper understanding of the symmetry elements.

1.11.3 Icosahedral Symmetry

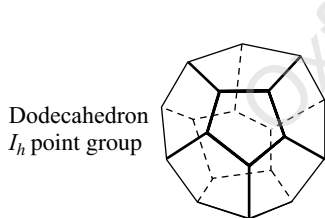


Fig. 1.44



Fig. 1.45

There is another special class of symmetry group, known as dodecahedral or icosahedral symmetry or *Icosahedral point group*. It is symbolized as I_h . The molecules having I_h point group have:

- (i) 6 C_5 axes, (ii) 10 C_3 axes, (iii) 15 C_2 axes,
- (iv) 15 σ planes.

The order of the icosahedral point group is 120. Dodecahedron (see Introduction) belongs to the point group I_h . The compound has been synthesized by Paquette in 1982 (Fig. 1.44).

The substance 'Buckminsterfullerene' corresponds to a truncated form of icosahedron and has I_h symmetry (Fig. 1.45).

1.11.4 T , O , and I Symmetry

These three symmetries are in fact distorted forms of T_d , O_h , and I_h point groups of symmetry, respectively. They can be achieved by desymmetrization technique causing distortion. In desymmetrization process, planes of symmetries are eliminated but axes are retained. Therefore, molecules with T , O , and I point groups are chiral. A molecule with T point group has four C_3 axes passing through each apex and the centre of the opposite face and three C_2 axes

passing through pairs of opposite edges, that is, edges ending in noncommon vertices. Hounshell and Mislow concluded that tetra-*tert*-butyltetrahedrane (synthesized by Maier et al.) has point group T because of unique disposition of *tert*-butyl groups in their most stable conformations. However, since rotation about the $(\text{CH}_3)_3\text{C}$ -bond is so rapid, the *average* symmetry of tetra-*tert*-butyltetrahedrane is T_d . The order of T point group is 12. They are operation of identity, two operations for each of the $4C_3$ axes and one for each of the C_2 axes (Fig. 1.46).

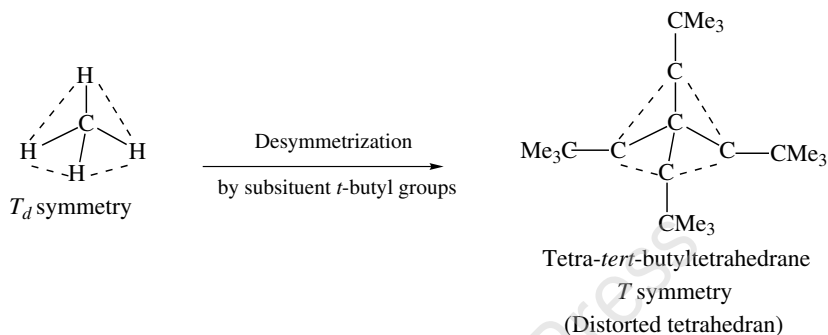
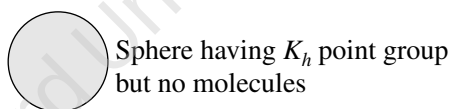


Fig. 1.46

1.11.5 Spherical Symmetry

The symmetry element having the symbol K_h is applicable to objects having all possible symmetry elements. A sphere has K_h symmetry point group. K is taken from German *Kugel*, meaning sphere. No molecule belongs to this point group. Spherical atoms have this symmetry.



1.12 SYMMETRY NUMBER (σ) AND ORDER OF POINT GROUP

It is defined as the number of indistinguishable but nonidentical orientations into which the molecule can be turned by simple rigid rotation, that is, the rotation of the molecule as a whole. This is symbolized by σ (should not be confused with the plane of symmetry). The very concept of indistinguishable but nonidentical orientation is perceptible by hypothetical labelling of the molecule. It should be noted that for chiral molecules the order of the point group is equivalent to symmetry number. For molecules belonging to achiral point groups, the symmetry number is one-half the order. Exceptions are molecules having the point group $C_{\infty v}$ and $D_{\infty h}$, whose orders are infinite but symmetry numbers are 1 and 2, respectively. The term 'order' of a point group denotes the number of different identity operations that can be performed in a point group. For example, in case of C_4 , the operations are E , C_4^1 , C_4^2 , C_4^3 .

Molecules with C_s and C_i ($= S_2$) point groups have symmetry number 1. For molecules with C_n , C_{nh} , C_{nv} ($n \neq 1$), symmetry number is equal to n . Molecules having dihedral symmetry D_n , D_{nd} , D_{nh} , the symmetry number is $2n$. For tetrahedral symmetry (T_d) and octahedral symmetry (O_h), the symmetry numbers are 12 and 24, respectively. For I_h symmetry, the symmetry number is 60. Table 1.3 shows the point groups, their order, and their symmetry number.

Table 1.3

Symmetry point group	C_1	C_n	D_n	C_s	S_n^a	C_{nv} C_{nh}	$C_{\infty v}$	D_{nd} D_{nh}	$D_{\infty h}$	T_d	O_h	I_h
Order of point group	1	n	$2n$	2	n	$2n$	∞	$4n$	∞	24	48	120
Symmetry number (σ)	1	n	$2n$	1	$n/2$	n	1	$2n$	2	12	24	60

1.13 SYSTEMATIC CLASSIFICATION OF MOLECULES INTO POINT GROUPS

C = Rotation axis i = Inversion centre
 S = Improper axis (alternating axis) σ = Plane of symmetry

Examine for special point groups

- (a) Linear, no σ plane perpendicular to molecular axis ($C_{\infty v}$)
- (b) Linear, σ plane perpendicular to molecular axis ($D_{\infty h}$)
- (c) Tetrahedral (T_d)
- (d) Octahedral or cubic (O_h)
- (e) Icosahedral (I_h)

T_d , O_h , and I_h point groups are known as *isotropic groups*. The compounds having these symmetry point groups are called *platonic solids* (mentioned in Plato dialogue *Timaeus*).

Examination of point group of molecules having C_n axis as one of the elements of symmetry

Two types are possible:

Molecules with nC_2 axes along with C_n axis

Three possibilities of (a) type of molecules are as follows:

- (i) the molecule has nC_2 axes perpendicular to C_n axis but no symmetry planes.
- (ii) the molecule has nC_2 axes perpendicular to C_n axis and also has a σ_h plane.
- (iii) the molecule has nC_2 axes perpendicular to C_n axis and $n\sigma_d$ planes bisecting angles between a pair of C_2 axes.

Point group

 D_n D_{nh} D_{nd}

D_n , D_{nh} , and D_{nd} point groups are known as *dihedral groups*.

Molecules with C_n axis but without nC_2 axes

Three possibilities of the (b) type of molecules are as follows:

- (i) The molecule has no nC_2 axes perpendicular to C_n axis but σ_h plane is present.
- (ii) The molecule has no nC_2 axes perpendicular to C_n axis but has $n\sigma_v$ planes.
- (iii) the molecule has no nC_2 axes perpendicular to C_n axis and there is no symmetry planes (σ)

 C_{nh}
$$C_{nv}$$
$$C_n$$

C_n , C_{nh} , and C_{nv} point groups are known as *axial groups*.

Examine for S_n axis ($n = \text{even}$) collinear with C_n axis

- (a) S_n present
 (b) No other symmetry element present except i

Point group

 S_n
 S_2

$$S_n^{n+2} = i, \text{ if } n \text{ is even and } \frac{n}{2} \text{ is odd}$$

An appropriate dichotomous tree can infer the symmetry point group of a specific molecule systematically but that seems to be a bit cumbersome. However, the result can be arrived at faster by proceeding in a non-dichotomous manner.

The method merely involves looking for certain key symmetry elements. Three step-processes are as follows.

1. First examine for special point groups stated earlier.
2. Next procedure is as shown in Fig. 1.47.

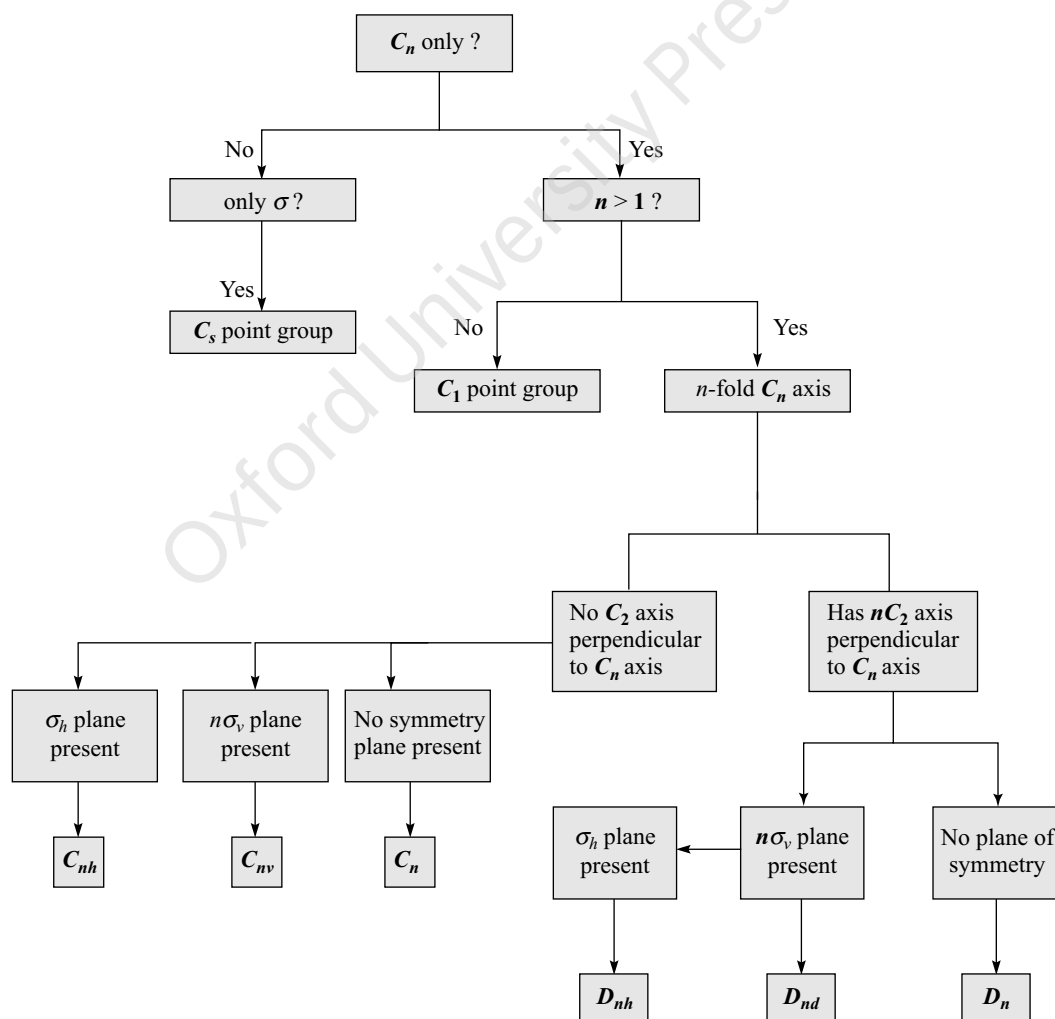


Fig. 1.47

3. Determine whether or not the molecule has the single rotation-reflection axis S_n (n is even). If such an axis is present, the molecules belong to the S_n symmetry point group.

Another method, commonly known as 'YES-NO' methodology can also be used to decide the point group of a molecule. It is shown diagrammatically in Fig. 1.48.

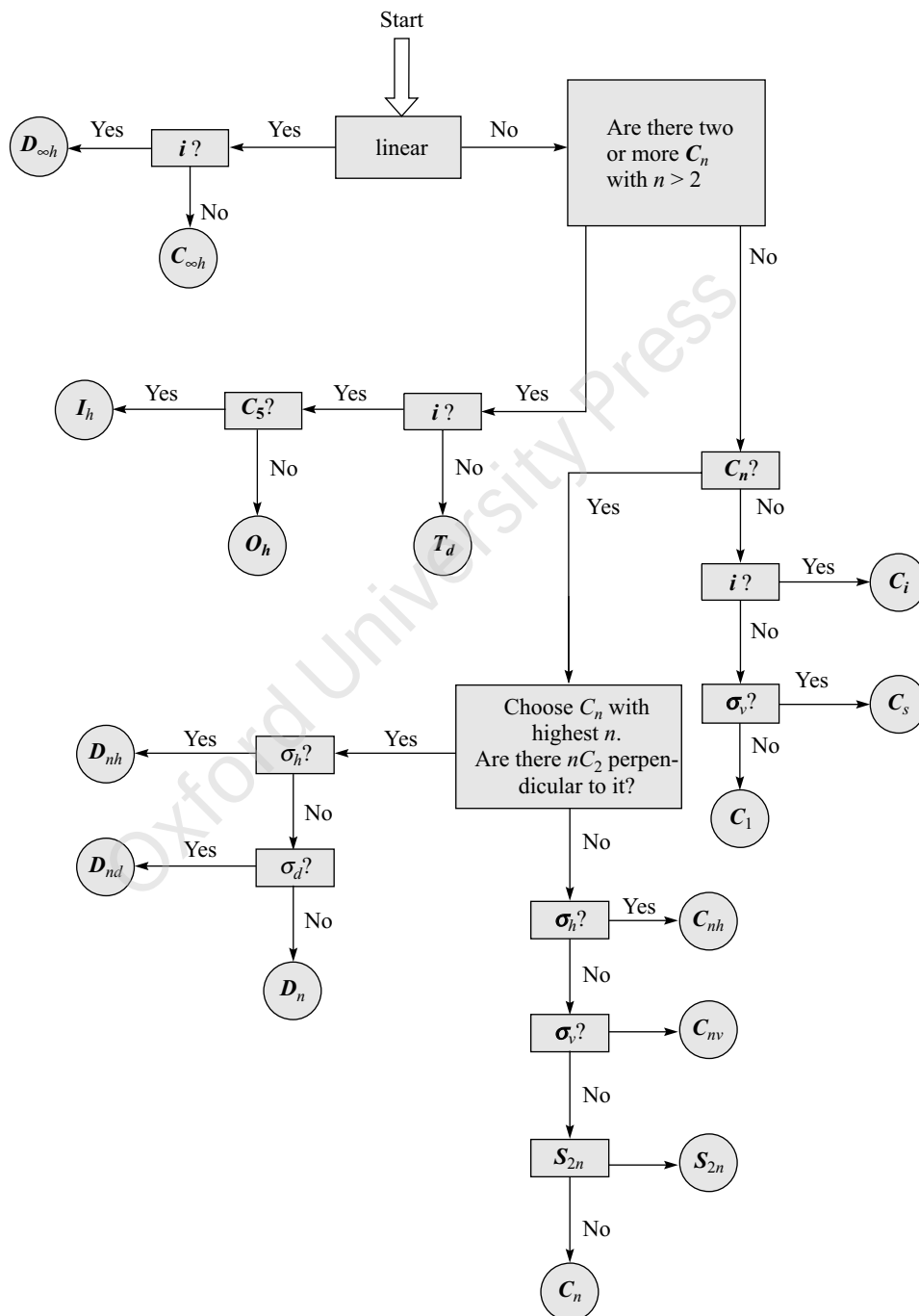


Fig. 1.48

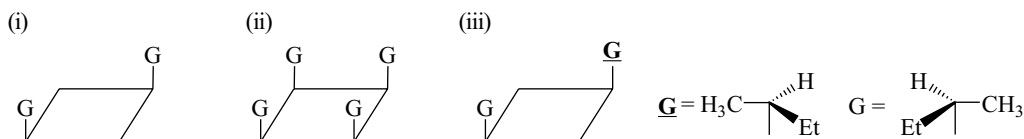
SOLVED PROBLEMS

Q.1. There are twenty-six letters in English language. How many of them are symmetric and how many of them are non-symmetric, considering them as two-dimensional?

Ans. Symmetric: A, B, C, D, E, H, I, K, M, N, O, S, T, U, V, W, X, Z, Y

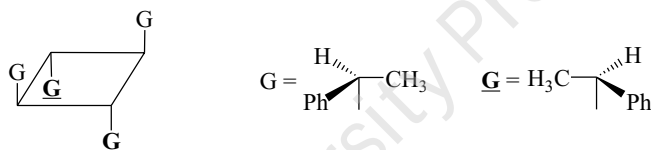
Non-symmetric: F, G, J, L, P, Q, R

Q.2. What are the elements of symmetry in the following cyclobutane derivatives where G stands for a chiral ligand and $\underline{G}$ is its enantiomorphous group? Are they chiral?

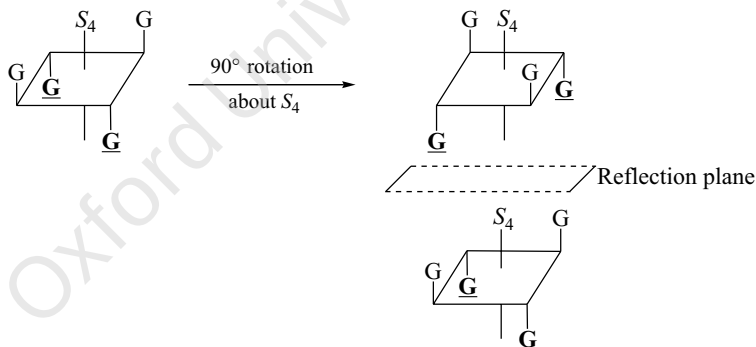


Ans. (i) C_2 axis (ii) C_4 axis (iii) σ plane, (i) and (ii) are chiral but (iii) is achiral.

Q.3. What is/are the element of symmetry in the following molecule? Is it optically active?

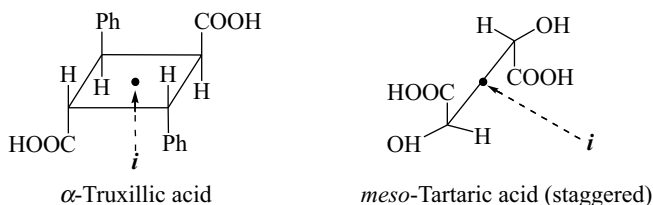


Ans. The molecule has four-fold alternating axis of symmetry and is optically inactive.



Q.4. Give the structural formulas of molecules in which the inversion centre is (i) in space in the centre of a molecule (ii) on an axis joining the two carbon atoms.

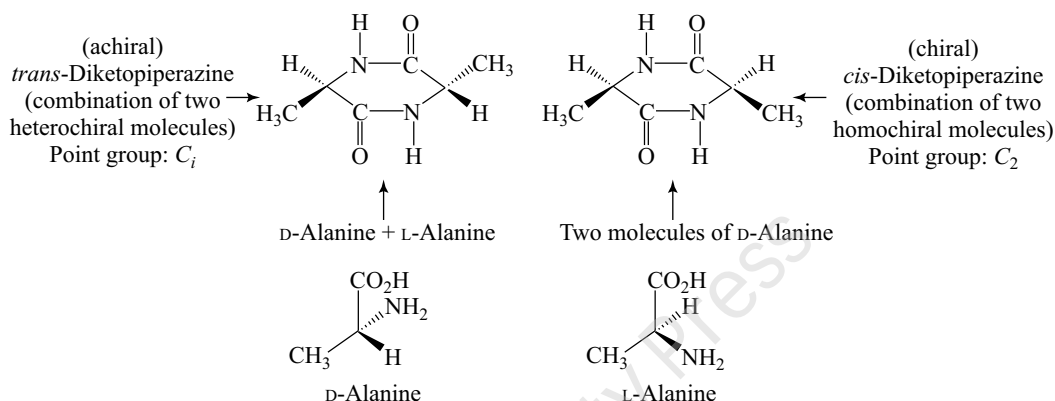
Ans. (i) α -Truxillic acid represents a molecule (planar structure) where the centre of inversion is in space.



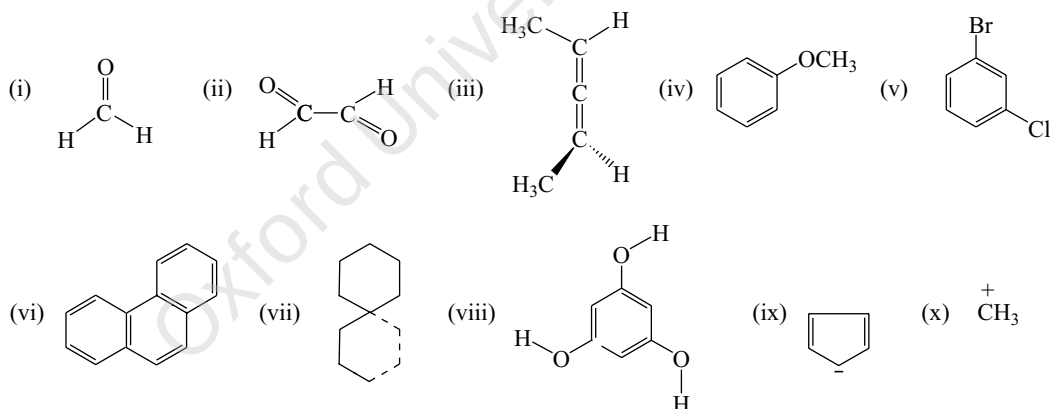
(ii) *meso*-Tartaric acid in its staggered conformation has a centre of symmetry on the bond joining C-2 and C-3 carbon atoms.

Q.5. What products are obtained when two alanine molecules undergo dimerization to form diketopiperazine derivative?

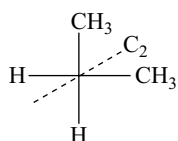
Ans. Alanine is $\text{CH}_3\text{C}^*\text{H}(\text{NH}_2)\text{COOH}$ having one chiral centre. It can exist as enantiomers, that is, D-alanine and L-alanine (see Chapter 2). If two molecules of the same enantiomer (homochiral) dimerise then a chiral *cis*-diketopiperazine is obtained having C_2 point group. If two molecules having opposite chirality (heterochiral) dimerise then achiral *trans*-diketopiperazine is obtained. Its point group is C_i .



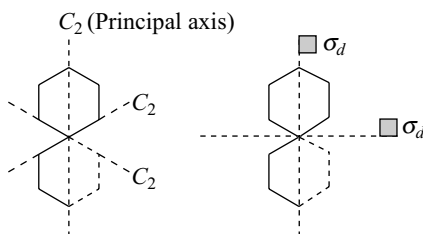
Q.6. Identify the point groups in each of the following compounds.



Ans.



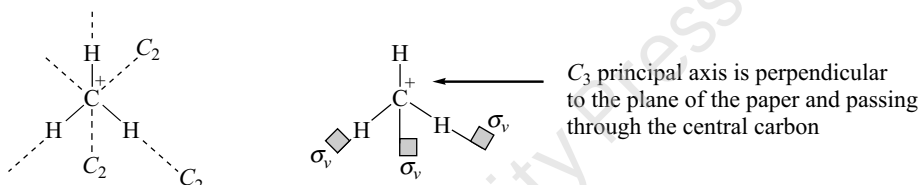
- (i) Point Group C_{2v} : it has a C_2 axis and two σ_v planes.
- (ii) Point Group C_{2h} : it has a C_2 axis and a σ_h plane (molecular plane).
- (iii) Point Group C_2 : it has only one C_2 axis. It can be shown in the corresponding Fischer projection (diagram on the left).
- (iv) Point Group C_{2v} : it has a C_2 axis and two σ_v planes. If we assume $-\text{OCH}_3$ (achiral group) as a sphere then one σ_v is vertical and the other one is the molecular plane. C_2 axis is passing through the $-\text{OCH}_3$ group and the opposite *para*-carbon.
- (v) Point Group C_s : it has only one plane of symmetry, that is, molecular plane.
- (vi) Point Group C_{2v} : it has a C_2 axis and two σ_v planes.
- (vii) Point Group D_{2d} : it has a C_2 principal proper axis, two additional C_2 axes perpendicular to principal axis and two σ_d planes intersecting the principal axis. These are shown as follows. A model will be helpful for understanding these elements of symmetry.



(viii) Point Group C_{3h} : it has a vertical C_3 proper axis, along with a σ_h plane. Molecular plane (plane of the paper) represents the σ_h plane.

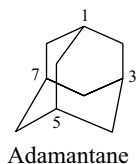
(ix) Cyclopentadienyl anion is planar and consequently it belongs to the point group D_{5h} . It has a principal C_5 proper axis, $5C_2$ axes, $5\sigma_v$ planes, and a σ_h plane.

(x) Point Group D_{3h} : $^+\text{CH}_3$ is a trigonal planar ion, therefore, it has a C_3 proper axis, three additional C_2 axes, three σ_v planes intersecting the C_3 axis, and a σ_h plane bisecting the C_3 axis.



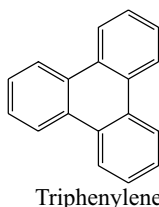
Q.7. What are the elements of symmetry in (i) adamantane and (ii) triphenylene? Mention their point group.

Ans. (i) Adamantane has the following structure:

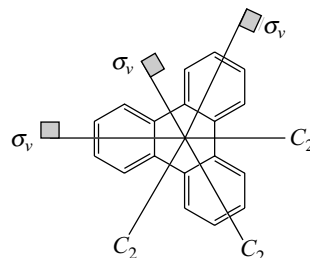


It is a strain-free molecule and is extremely stable. Hydrogen atoms at C-1, C-3, C-5, and C-7 are equivalent and, therefore, its structure has similarities with that of methane. Its elements of symmetry are three C_2 axes, four C_3 axes, six σ planes and three S_4 axes. It belongs to the point group T_d , similar to CH_4 molecule. However, unlike CH_4 , adamantane has a centre of symmetry *i*.

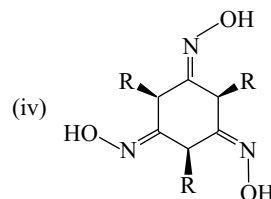
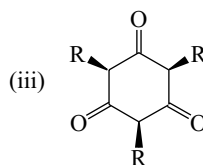
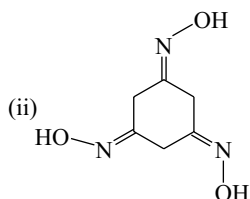
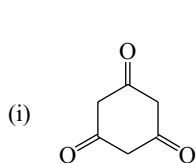
(ii) Triphenylene has the structure, as shown on left:



Its elements of symmetry are C_3 principal axis, three C_2 axes, three σ_v planes, and a σ_h plane. Its point group is D_{3h} . C_3 principal axis is passing perpendicular through the centre of the middle ring. Plane of the paper represents the plane (σ_h) which bisects the C_3 axis. These symmetry elements are shown in the diagram on the right.



Q.8. Identify the elements of symmetry of the following structures. Are they chiral? Assume the structures as rigid and planar.



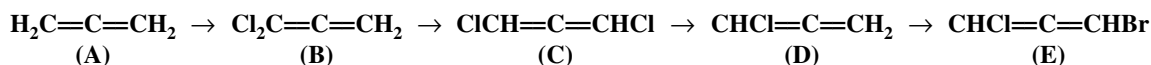
Ans. The compound (i) is a symmetrical compound having D_{3h} point group. It has C_3 proper axis along with three C_2 axes and three σ_v planes intersecting the C_3 axis. Its molecular plane (plane of the paper) is σ_h plane. Molecule is achiral.

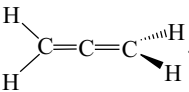
The compound (ii) belongs to the point group C_{3h} . It has a C_3 proper axis along with a σ_h plane (plane of the paper). It is also achiral.

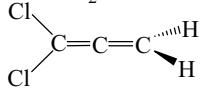
The compound (iii) having all substituents (R) in *cis*-orientation belongs to the point group C_{3v} . It has a C_3 proper axis. It also possesses three σ_v planes intersecting the C_3 axis. It has no σ_h plane. It is, therefore, an achiral molecule.

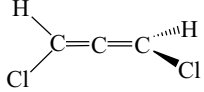
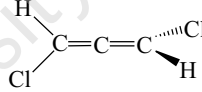
The compound (iv) belongs to the point group C_3 (C_n , $n = 3$). It is chiral.

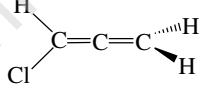
Q.9. Allene is converted sequentially into substituted allenes according to the following scheme. Find out the change in the point group in each case. How many of them are chiral?

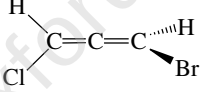
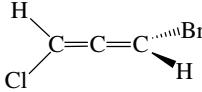


Ans. Allene (A) has the structure, . The elements of symmetry of allene are three C_2 axes, two σ_v planes, and a S_4 axis. It belongs to the point group D_{2d} (dihedral symmetry). It is an achiral molecule.

When allene is converted into $\text{Cl}_2\text{C}=\text{C}=\text{CH}_2$ (B), the desymmetrization takes place to C_{2v} point group. (B) has the structure,  and has C_2 proper axis along with two σ_v planes intersecting the C_2 axis. It is an achiral molecule.

In the compound (C),  or  the only element of symmetry is C_2 proper axis. It belongs to the point group C_n ($n = 2$). The molecule is chiral. It is a dissymmetric molecule (see Chapter 2).

The compound (D) with the structure  has only a plane of symmetry passing through H and Cl. Its point group is C_s . It is achiral.

The molecule (E),  or  has no element of symmetry except the trivial axis (C_1). Therefore, the molecule belongs to the point group C_1 . It is chiral and is asymmetric system (see Chapter 2).

Q.10. Justify the statement that AB_3 -type molecule cannot have an inversion centre (i) but a molecule AB_4 might possibly have one.

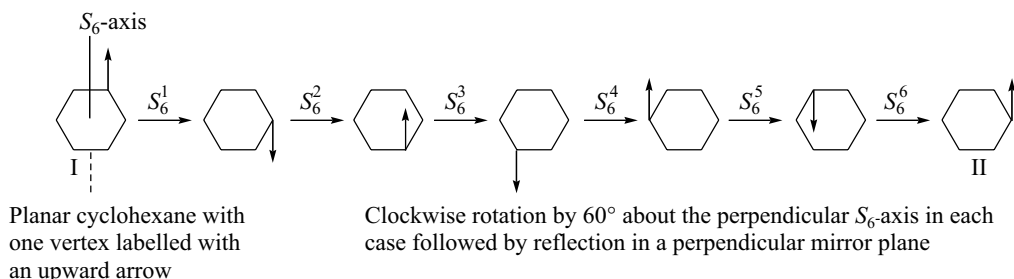
Ans. An inversion centre may be (a) in space in the centre of a molecule or (b) at a single atom in the centre of a molecule.

If the centre of inversion is in space, all types of atoms in a molecule must be present in even numbers spaced on either side of the so called centre of inversion. If it is at an atom, then that type of atom only must be present in an odd number. Since in AB_3 type molecules, neither of the above conditions is satisfied, these types of molecules have no centre of inversion. In AB_4 , A is present in odd number and B is present in even number, therefore a centre of inversion is possible through A.

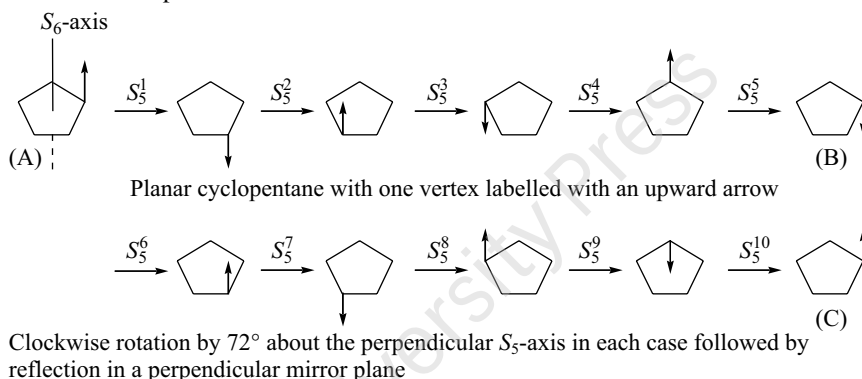
Q.11. Show by an example that when a molecule contains S_n , $S_n^n = E$ (when $n = \text{even}$) and $S_n^{2n} = E$ (when $n = \text{odd}$).

Ans. If we take cyclohexane (assuming planar structure) having one vertex (carbon atom) labelled, then we can show that $S_n^n = E$ (when $n = \text{even}$). Planar cyclohexane has a S_6 proper axis collinear with C_6 (point group D_{6h}).

Structures I and II are identical, therefore, we can conclude that when $n = \text{even}$ $S_n^n = E$ (operation of identify). In this case $S_6^6 = C_6 = E$. Now if we consider cyclopentane as a flat molecule then it has a S_5

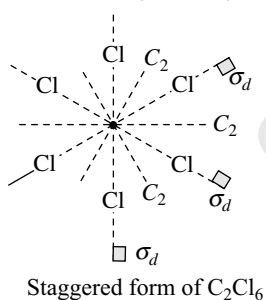


axis along with C_5 and other element of symmetry (point group: D_{5h}). In this case $C_5 \neq S_5^5$. But $C_5 = S_5^{10} = E$. That is, when n is odd, $S_n^{2n} = E$. This can be demonstrated by flat cyclopentane molecule having one vertex labelled with an upward arrow.



In the above manipulation, (A) and (B) are not identical. Therefore, $S_n^n \neq E$ (when n is odd). However, (A) and (C) are identical and therefore, it is obvious that $S_n^{2n} = E$, when n is odd.

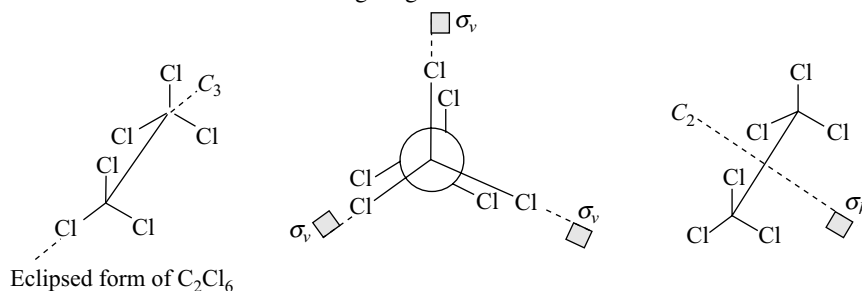
Q.12. What are the point groups of C_2Cl_6 in its staggered and eclipsed forms. Identify the elements of symmetry in each case with suitable diagram.



Ans. Staggered form of C_2Cl_6 belongs to the point group D_{3d} . Therefore, it has a C_3 principal proper axis along with three C_2 axes perpendicular to and intersecting C_3 axis. It has also three σ_d planes. These can be shown by the diagram on the left.

C_3 proper axis is perpendicular to the plane of paper passing through the axis joining the two carbon atoms. This is not shown in the diagram. Each of the planes bisects the angle between the two C_2 axes.

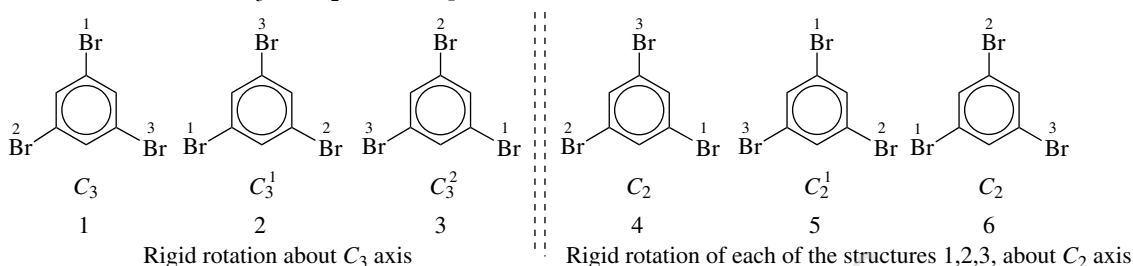
Eclipsed form of C_2Cl_6 belongs to the point group D_{3h} . Therefore, it has a C_3 principal proper axis, three C_2 axes perpendicular to C_3 axis, three σ_v planes, and a σ_h plane. These C_2 axes are perpendicular to C_3 axis. These elements of symmetry can be shown in the following diagram.



Other two C_2 axes are difficult to be shown in a two-dimensional diagram. These can be easily understood from a three-dimensional model.

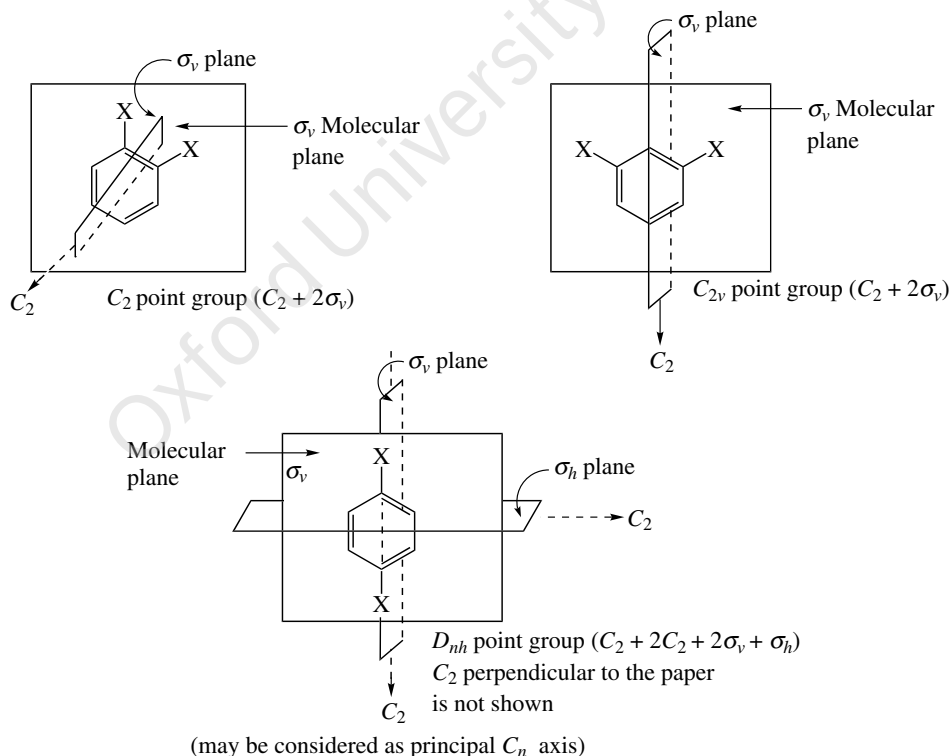
Q.13. What is the point group of 1,3,5-tribromobenzene? What is its symmetry number? Justify your answer by diagrams.

Ans. The point group of 1,3,5-tribromobenzene is D_{3h} . Therefore, it has C_3 principal proper axis, three C_2 axes intersecting the C_3 axis, three σ_v (more accurately σ_d) planes and one σ_h plane (molecular plane). Since it belongs to point group D_{nh} , its symmetry number is $2n = 2 \times 3 = 6$. These can be shown by rigid rotation about C_3 and C_2 axes as depicted below.



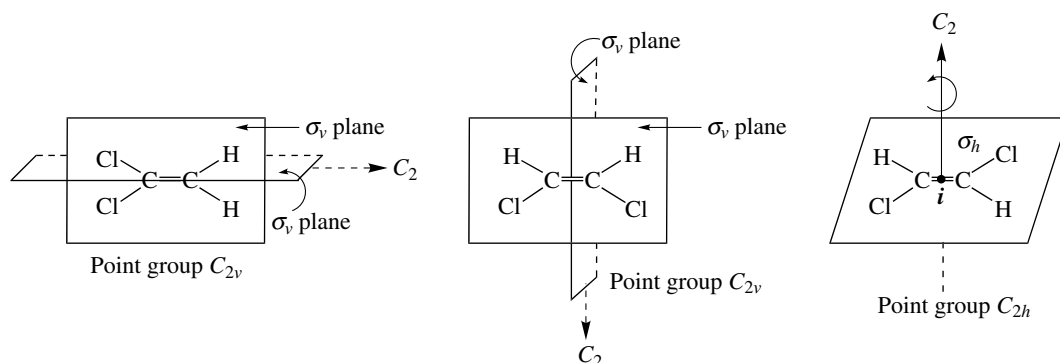
Q.14. *Ortho* and *meta* isomers of disubstituted benzene $C_6H_4X_2$ cannot be differentiated by point group determination but *para* isomer can be ----- Justify this statement.

Ans. Two isomers of $C_6H_4X_2$, *ortho*-, *meta*-belong to the same point group C_{2v} , and, therefore, they cannot be differentiated by point group determination. *para*-isomer, however, has D_{2h} point group. Point groups of these compounds are shown below.



Q.15. CH_2Cl_2 has three isomers A, B, and C. A and B have the same point group but C has a different point group. All of them are converted into a molecule of same point group when another H of CH_2Cl_2 is replaced by Cl atom. Explain.

Ans. The three isomeric compounds are (i) 1,1-dichloroethene, (ii) *cis*-1,2-dichloroethene, and (iii) *trans*-1,2-dichloroethene. The first two compounds belong to the point group C_{2v} , and the third compound has a point group C_{2h} . It has also i . Symmetry elements are shown in the following diagrams.

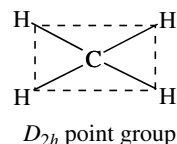
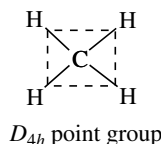
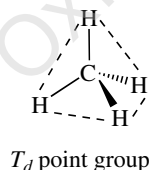


When one of the H atom of all the three compounds is replaced by another Cl, then we get the molecule, having only a plane of symmetry, that is, molecular plane (C_s point group).

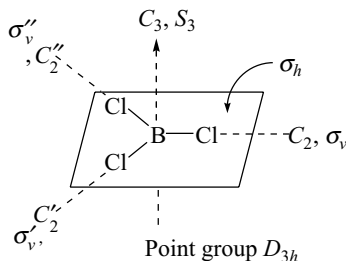
Q.16. Answer the following:

- Three students individually concluded that CH_4 has point group T_d , D_{4h} , and D_{2h} . What types of structures did they assume?
- A student reported that H_2O molecule belongs to the point group $D_{\infty h}$. What mistake did the student make?
- A point group consists of the following operations. Identify the point group. E , C_3 , C_3^2 , C_2 , C_2' , C_2'' , σ_h , S_3 , σ_v , σ_v' , σ_v'' . Give an example having that point group and show these operations diagrammatically.
- A dicarboxylic acid has the molecular formula $\text{C}_4\text{H}_4\text{O}_4$. It satisfies the symmetry operations: E , C_2 , σ_h , i . Draw the structure of the compound.
- What is meant by the point group C_{1h} ? What are its equivalent operations?

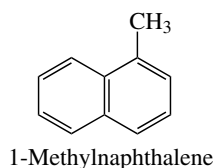
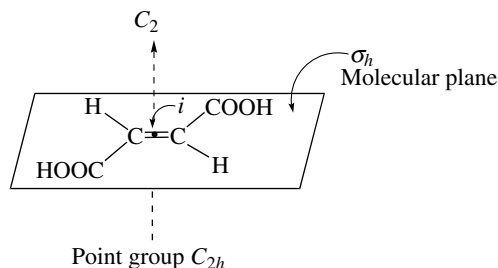
Ans. (i) The student who assigned T_d point group for CH_4 was correct because the structure of CH_4 is found to have a regular tetrahedral geometry. The student who assigned D_{4h} point group for CH_4 assumed the structure as square planar. The third student assumed the structure of CH_4 as rectangular planar and assigned the point group D_{2h} .



- The student made the mistake that H_2O molecule is linear having the structure $\text{H}-\text{O}-\text{H}$.
- These operators show that the molecule belongs to the point group D_{3h} . An example having D_{3h} point group is BCl_3 . The symmetry operations are shown in the following diagram.

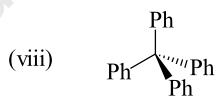
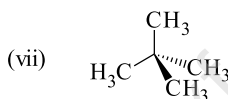
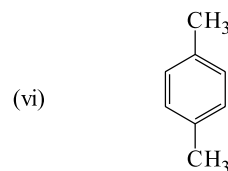
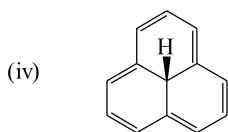
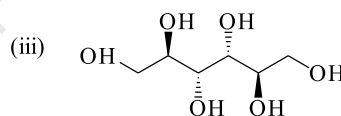
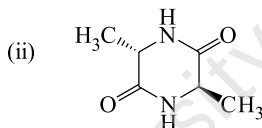
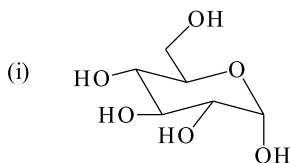


(iv) The structure of the compound is *trans*-butenedioic acid (Fumaric acid). The symmetry operations are shown below diagrammatically.



(v) The point group C_{1h} indicates that the molecule has trivial axis C_1 along with a horizontal plane of symmetry. C_{1h} is equivalent to C_s and S_1 point groups. An example of a molecule belonging to C_{1h} is 1-methylnaphthalene given on the left side.

Q.17. Find out the elements of symmetry of each of the following compounds and determine the general point group of each of them.



Ans. (i) The compound has only trivial axis C_1 . Thus the molecule belongs to the point group ' C_1 '.

(ii) The element of symmetry in the compound is centre of symmetry. Therefore, the molecule belongs to the general point group ' C_i '.

(iii) The only element of symmetry in the compound is C_2 . Therefore, its point group is C_n .

(iv) The molecule has a C_3 axis. Therefore, the molecule belongs to the general point group, ' C_n '.

(v) The compound has a C_2 axis along with a horizontal mirror plane σ_h . The general point group of the compound is ' C_{nh} '.

(vi) The molecule has one C_2 principal axis, two additional C_2 axes, perpendicular to the principal axis, and a horizontal mirror plane σ_h . Thus the molecule belongs to the general point group ' D_{nd} '.

(vii) The molecule has four C_3 principal axes and three C_2 axes. It belongs to the tetrahedral point group ' T_d '.

(viii) It is a unique compound and does not belong to the T_d (tetrahedral symmetry). It has a S_4 alternating axis of symmetry and belong to the general point group S_n ($n = \text{even}$).

(ix) It is C_{60} -fullerene. It has six C_5 principal axes amongst $10C_3$ and $15C_2$ axes. It has all rotational symmetry elements, but no mirror planes or centre of inversion. It belongs to the icosahedral point group ' I_h '.

EXERCISES

- Define the following elements of symmetry with a suitable example in each case.
 - Rotational axis of symmetry
 - Plane of symmetry
 - Centre of symmetry
 - Alternating axis of symmetry
- Which of the following molecules have inversion centres?



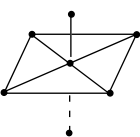
(i)



(ii)



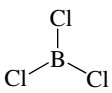
(iii)



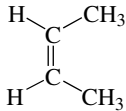
(iv)
- Give examples in favour of the statement that (a) an inversion centre may be in space in the centre of a molecule and (b) at a single atom in the centre of a molecule.
- Justify the statement that molecules of the type AB_3 cannot have an inversion centre but a molecule AB_4 might possibly have one.
- Which of the following have inversion centre? NH_3 , CH_4 , C_2H_2 , C_2H_4 , $SOCl_2$, SO_2Cl_2
- Draw neat diagrams of a tetrahedron and an octahedron and label the characteristic elements of symmetry in each case.
- Define the term 'symmetry operation'. Show diagrammatically that (i) $S_6^2 = C_3$, (ii) $S_6^3 = i$, $i^2 = E$, $\sigma^2 = E$, where the symbols have their conventional meanings in stereochemistry.
- Show with a diagram that $S_n^n = E$ (when n = even) and $S_n^n = E$ (when n = odd).
- What are elements of symmetry present in an equilateral triangle?
- List the symmetry elements of the following molecules.



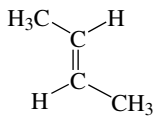
(i)



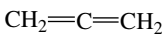
(ii)



(iii)



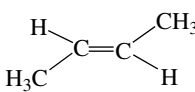
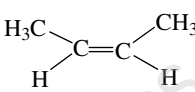
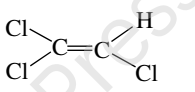
(iv)



(v)
- Write down the names and symbols of the five elements needed to completely specify molecular symmetry.
- What is meant by the term point group of symmetry of a molecule? Illustrate with examples in favour of your answer.
- Give examples of molecules having the following point groups. (i) $C_{\infty v}$, (ii) C_s , (iii) C_{nh} , (iv) C_{nv} , (v) $D_{\infty h}$.
- What is 'Dihedral symmetry'? What are the different types of dihedral symmetry that may be present in molecules? Give examples.
- Classify the following molecules into their respective point group:
 - $CH_2=CH_2$
 - Cyclohexane (boat)
 - Cyclohexane (chair)
 - CBr_4
 - SF_3
 - CO_2
 - 

(vii)
 - $POCl_3$
 - $CH_2=C=CH_2$
 - 

(x)
 - C_2H_6 (staggered and eclipsed forms)
 - HCHO
 - $CHCl_3$
 - $ClC\equiv CH$
- Classify the molecules as dissymmetric and non-dissymmetric in terms of point groups. Give suitable examples.
- Define symmetry number. What are the symmetry number of molecules possessing (i) C_3 , (ii) C_p , (iii) C_{nh} , and (iv) D_{nh} point group?
- Write *True* or *False* against each of the following statement:
 - C_1 axis is present in all objects of our universe.
 - S_2 axis and i are identical symmetry operations.
 - Molecules having only C_n axis ($n > 1$) may be optically active.
 - All planar molecules must possess C_s point group of symmetry.
 - A sphere has all possible elements of symmetry.
 - Octahedron has centre of inversion but tetrahedron has no.
 - Molecules having dihedral symmetry are always optically inactive.

- (viii) AB_3 -type molecule cannot have an inversion centre.
- (ix) A non-dissymmetric conformation with C_n must also have a σ plane.
- (x) A non-dissymmetric conformation with a σ must also have a C_n .
- (xi) Absence of σ is a necessary but not a sufficient condition for dissymmetry.
- (xii) Presence of a σ is a sufficient but not a necessary condition for reflection symmetry.
- (xiii) D_n , D_{nh} , and D_{nd} — all these point group has nC_2 axes.
- (xiv) Molecules possessing D_n and D_{nd} point groups are optically active.
- (xv) Molecules with C_s point group has also inversion centre.
- (xvi) There cannot be any geometrical shape without C_1 axis.
- (xvii) D_{nd} and D_{nh} point groups differ only by σ_h plane.
- (xviii) Molecules having only C_1 axis are asymmetric molecules.
19. Cyclopropane is converted into the following compounds:
- 1,1-dimethylcyclopropane,
 - trans*-1,2-dimethylcyclopropane,
 - cis*-1,2-dimethylcyclopropane,
 - trans*-1-ethyl-2-methylcyclopropane.
- Show the change in the point group of symmetry in each case with respect to cyclopropane and comment on the optical activity of each compound.
20. Match the compound with the correct point group from the following two lists:
- | | |
|--|--------------|
| (i) $CH_2OHCHOHCHO$ | (a) C_s |
| (ii)  | (b) C_1 |
| (iii) <i>meso</i> -Tartaric acid (staggered conformation) | (c) C_{3v} |
| (iv) $HCCl_3$ | (d) C_{2h} |
| (v)  | (e) C_{2v} |
| (vi)  | (f) D_2 |
| (vii)  (Twist boat of cyclohexane) | (g) D_{3d} |
| (viii)  (chair form of cyclohexane) | (i) D_{uh} |
| (ix)  | (j) S_2 |
| (x) $CH_3-C\equiv C-CH_3$ | (k) D_{6h} |

REFERENCES

- Atanov, Y., *Symmetry in the World of Molecules*, Mir Publishers, Moscow (1979).
- Donaldson, J.D. and S.D. Ross, *Symmetry and Stereochemistry*, Wiley, New York (1972).
- Farina, M. and C. Morandi, *High Symmetry Chiral Molecules*, *Tetrahedron*, 30, 1819 (1974).
- Hargittai, I. and M. Hargittai, *Symmetry through the Eyes of a Chemist*, VCH Publishers, New York (1987).
- Heilborn, E. and J.D. Dunitz, *Reflection on Symmetry*, VCH Publishers, New York (1993).
- Jaffe, H.H. and M. Orchin, *Symmetry in Chemistry*, John Wiley & Sons, New York (1974).
- Kettle, S.A.F., *Symmetry and Structure*, Wiley, New York (1985).
- Salthouse, J.A., M.J. Ware, *Point Group Character Tables and Related Data*, Cambridge University Press (1972).
- Shubnikov, A.V. and V.A. Koptsik, *Symmetry in Science and Art*, Plenum Press, New York (1974).
- Tarasov, L., *This Amazingly Symmetrical World*, Mir Publishers, Moscow (1986).
- Vincent, A., *Molecular Symmetry and Group Theory*, John Wiley & Sons, New York (1977).