

Elements of Symmetry

What do you mean by symmetry? It is nothing but an idea through which man can create order, periodicity, beauty and perfection. The ancient Greek philosopher Plato (430 BC) believed that universe consists of four symmetry elements which are the earth, the water, the fire and the air. According to him earth is cubical, water is icosahedron, fire is tetrahedron and air is octahedron. From the concept of symmetry we normally think about a molecule or body is symmetric or not-symmetric with respect of some character such as a point, a line and or a plane.

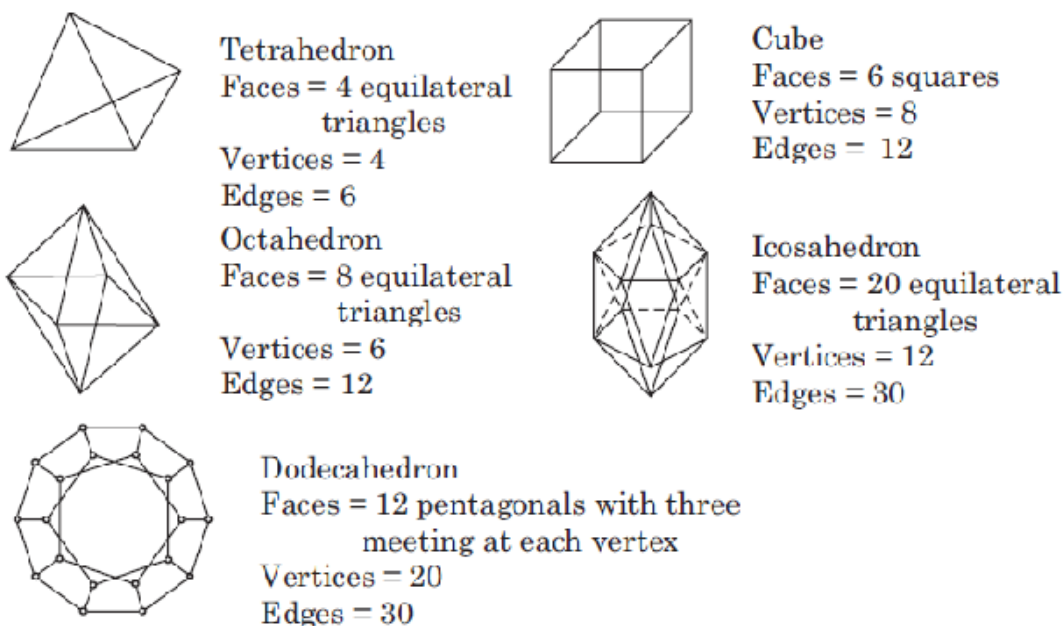


Fig. Five regular plato's symmetrical body

In the context of molecular symmetry, a **symmetry operation** is a permutation of atoms such that the molecule or crystal is transformed into a state indistinguishable from the starting state. Two basic facts follow from this definition, which emphasize its usefulness.

1. Physical properties must be invariant with respect to symmetry operations.
2. Symmetry operations can be collected together in groups which are isomorphous to permutation groups.

Symmetry Operation: A transformation in three-dimensional space that preserves the size and shape of a molecule, and which brings it into an orientation in three dimensional space physically indistinguishable from the original one, is called a

symmetry operation. A symmetry operation carries every point in the object into an **equivalent point or the identical point**.

A **symmetry element** is a point, a line and or a plane of reference about which symmetry operations can take place. In particular, symmetry elements can be identities, mirror planes, axes of rotation (both proper and improper), and centers of inversion. A symmetry element corresponds to a symmetry operation that generates the same representation of an object.

Symmetry element is classified in for categories and they are

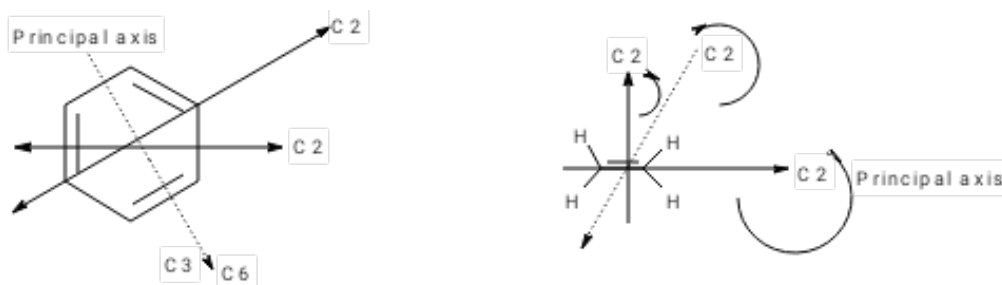
1. Simple axis of Symmetry (C_n)
2. Plane of Symmetry (σ)
3. Center of Symmetry or Center of Inversion (i)
4. Rotational reflexional axis of Symmetry (S_n)

1. Simple axis of Symmetry or Rotational Axis of symmetry (C_n):

Simple axis of a molecule is an imaginary axis passing through the molecule in such a way that if the molecule rotates about this axis through an angle of $360^\circ/n$, results in an indistinguishable structure with the original molecule. It is denoted by C_n (*Latin word Circulate*) and called rotational or proper or simple axis of symmetry. The subscript n denotes the fold or order of rotation and it is determined by:

$$n = \frac{360^\circ}{\text{angle(smallest) of rotation to give an indistinguishable structure with the original one}}$$

The value of n can never be a fraction because in that case every C_n operation will not give equivalent structure. E.g.



Before going to the next topic we have to decide the **principal axis**.

1. If a molecule possesses C_n axes with different n values then the C_n axis having maximum value of n (fold/order) is called the principal axis i.e. highest fold axis will be called as principal axis.
2. If there are several C_n axes with same value of n (when there is absence of different order of axes), then the principal axis will be one which passes through the maximum number of atoms of the molecule.

For example in benzene the principal axis is C_6 (C_6 is the highest fold axis between C_6 , C_3 and C_2 though C_2 is passing through the maximum no. of atom) mentioned in the figure and in ethane the principal axis is C_2 (as all the axes are C_2) which is mentioned in the figure.

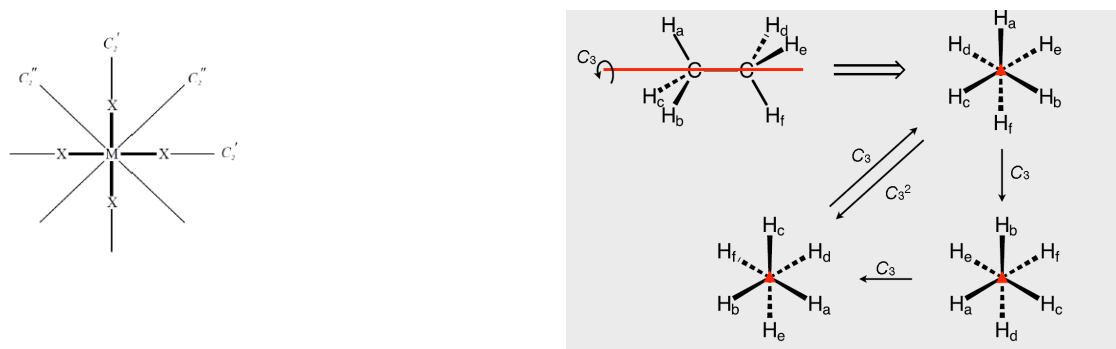


Fig. Some example of axis of symmetry.

General Relationships for C_n

$$C_n^n = E$$

$$C_{2n}^n = C_2 \quad (n = 2, 4, 6, 8 \dots \text{etc.})$$

$$C_n^m = C_{n/m} \quad (n/m = 2, 3, 4, 5 \dots \text{etc.})$$

$$C_n^{n-1} = C_{n-1}$$

$$C_n^{n+m} = C_n^m \quad (m < n)$$

- Every n -fold rotational axis has $n-1$ associated operations (excluding $C_n^n = E$).
- Remember, the rotational operation C_n^m is preferably identified as the simpler $C_{n/m}$ operation where m/n is an integer value.

2. Plane of Symmetry (σ):

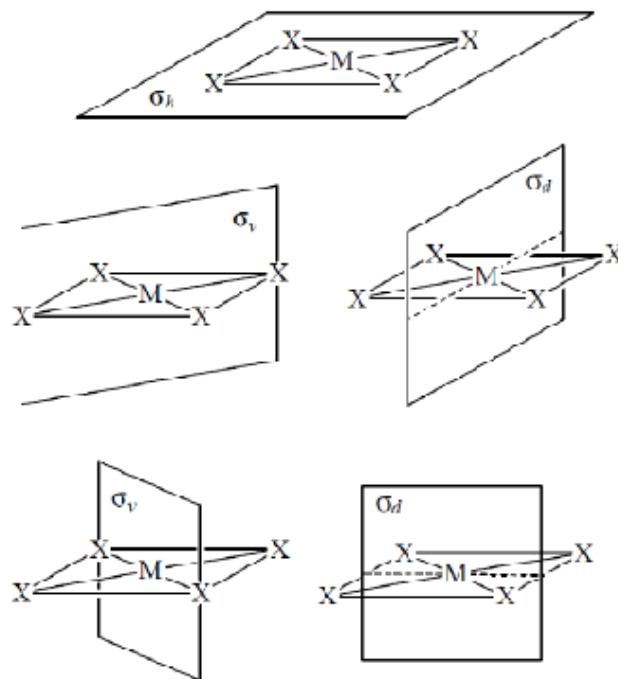
The plane of symmetry is an imaginary plane which divides the molecule in two equal halves which are mirror image to each other. The plane is also called mirror plane or σ -plane and the operation is called σ -operation. The designation sigma (σ) comes from the German word spiegel, meaning mirror. *It is an imaginary bisecting plane within a molecule such that if a mirror placed through that plane after reflection encounter an equivalent (identical) atom and or group on the other side.* The structure of dichloromethane and cis dichloroethene possessing mirror planes showing in below.



It should be noted that every planer molecule has a plane of symmetry namely molecular plane. Plane of symmetry are classified in three categories such as Horizontal plane of symmetry(σ_h), Vertical plane of symmetry(σ_v) and Dihedral or diagonal plane of symmetry(σ_d)

Horizontal, Vertical, and Dihedral Mirror Planes

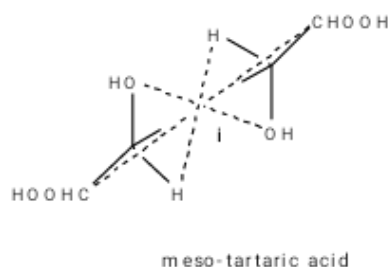
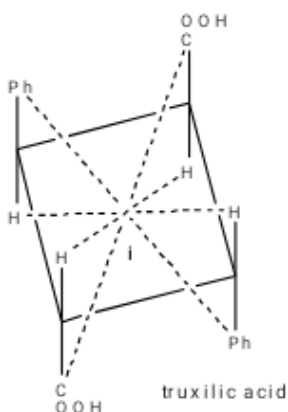
- A σ_h plane is defined as perpendicular to the principal axis of rotation.
- If no principal axis of rotation exists, σ_h is defined as the plane of the molecule.
- σ_v and σ_d planes are defined so as to contain a principal axis of rotation and to be perpendicular to a σ_h plane.
- When both σ_v and σ_d planes occur in the same system, the distinction between the types is made by defining σ_v to contain the greater number of atoms or to contain a principal axis of a reference Cartesian coordinate system (x or y axis).
- Any σ_d planes typically will contain bond angle bisectors.
- The five mirror planes of a square planar molecule MX_4 are grouped into three classes (σ_h , $2\sigma_v$, $2\sigma_d$).



3. The Inversion Operation/Centre of Symmetry (i):

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 to an equal distance by a straight line on the opposite end, a like atom or part of the molecule is encountered. Centre of symmetry is also called as centre of inversion and symbolized as *i*.

This can be explained by α -truxillic acid, staggered *meso*-tartaric acid, etc.



- The operation of inversion is defined relative to the central point within the molecule, through which all symmetry elements must pass,

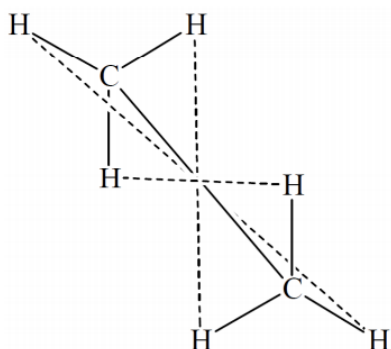
e.g., typically typically the origin of the Cartesian Cartesian coordinate coordinate system ($x,y,z = 0,0,0$).

- If inversion symmetry exists, for every point (x,y,z) there is an equivalent point $(-x,-y,-z)$.

- Molecules or ions that have inversion symmetry are said to be centrosymmetric.

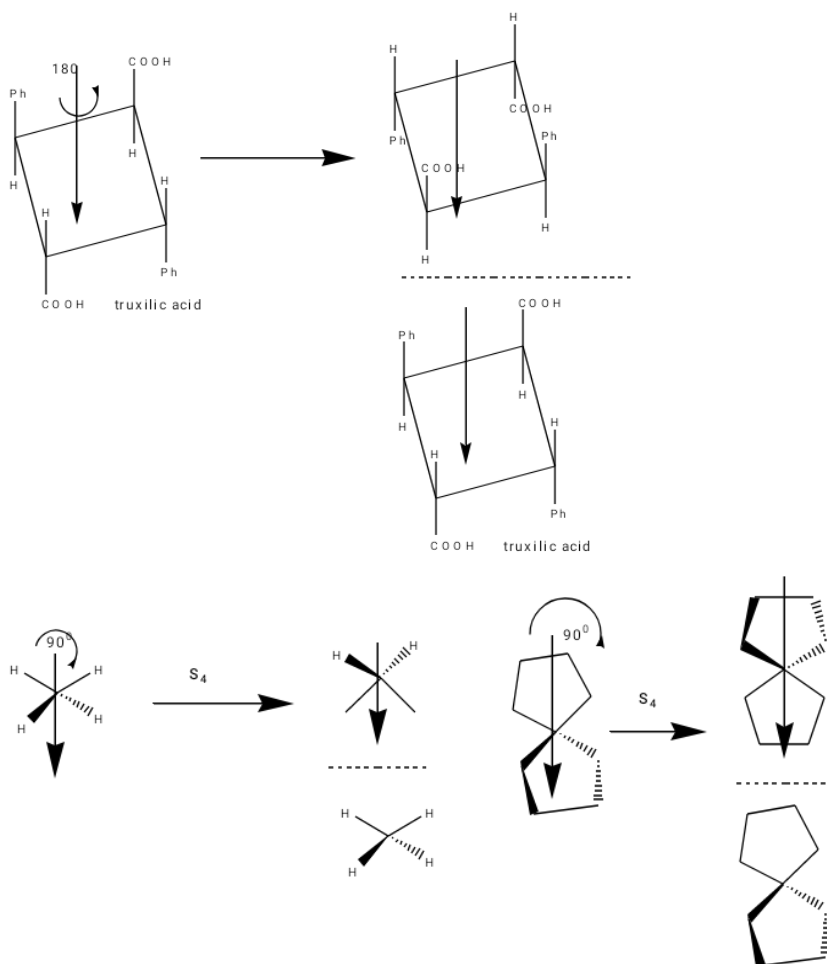
- Each inversion center has only one operation associated with it, since $i^2 = E$

Ethane in the staggered configuration. The inversion center is at the midpoint along the C-C bond. Hydrogen atoms related by inversion are connected by dotted lines, which intersect at the inversion center. The two carbon atoms are also related by inversion.



4. Alternating axis of symmetry/ Rotational reflexional axis of Symmetry (S_n)

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 perpendicular plane to this axis produces an indistinguishable structure with the original. Alternating axis of symmetry is designated as S_n , it is also known rotational reflexional axis of symmetry. This symmetry is known as improper axis of symmetry. This can be explained by This can be explained by α -truxillic acid (S_2), staggered *meso*-tartaric acid (S_2), methane (S_4) etc.



The improper rotation operation S_n is also known as the rotation-reflection operation and, as its name suggests, is a compound operation.

- Rotation-reflection consists of a proper rotation followed by reflection in a plane perpendicular to the axis of rotation.
- n refers to the improper rotation $2\pi/n = 360^\circ/n$.
- S_n exists if the movements C_n followed by σ_h (or vice versa) bring the object to an equivalent position.
- If both C_n and σ_h exist, then S_n must exist. e.g., S_4 collinear with C_4 in planar MX_4 .
- Neither C_n nor σ_h need exist for S_n to exist. e.g., S_4 collinear with C_2 in tetrahedral MX_4 .

The Identity Operation (E)

- The simplest of all symmetry operations is identity, given the symbol E.
- Every object possesses identity. If it possesses no other symmetry, the object is said to be asymmetric.
- As an operation, identity does nothing to the molecule. It exists for every object, because the object itself exists.
- The need for such an operation arises from the mathematical requirements of group theory.
- In addition addition, identity identity is often the result of carrying carrying out a particular operation operation successively successively a certain number of times, i.e., if you keep doing

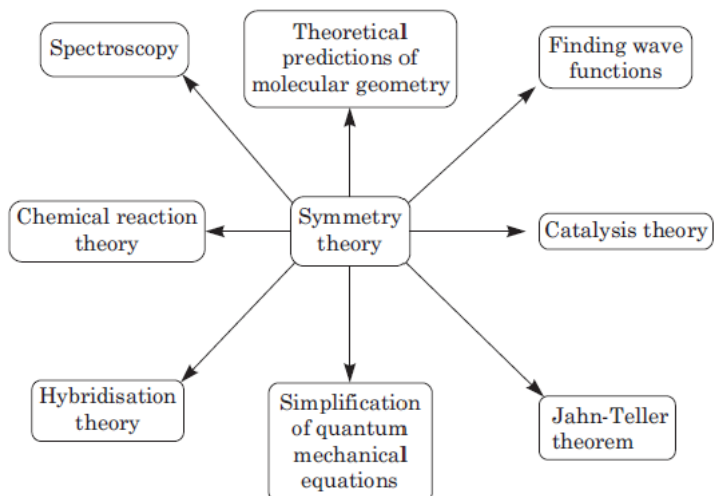
the same operation repeatedly, eventually you may bring the object back to the identical (not simply equivalent) orientation from which was started.

- When identifying the result of multiple or compound symmetry operations they are designated by their most direct single equivalent.
- Thus, if a series of repeated operations carries the object back to its starting point, the result would be identified simply as identity

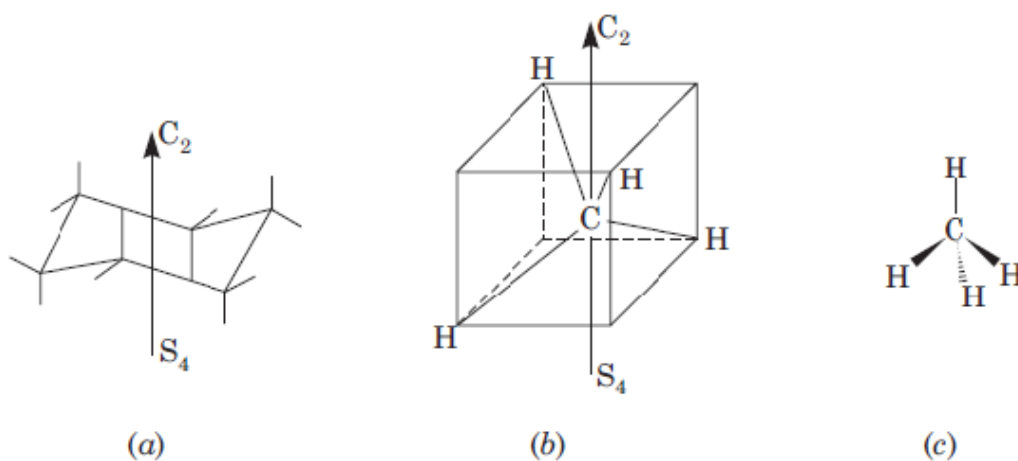
Symmetry Elements and Operations

element	operation	Symbol
symmetry plane	reflection through plane	σ
inversion center	inversion: every point x,y,z translated to $-x,-y,-z$	i
proper axis	rotation about axis by $360/n$ degrees	C_n
improper axis	1. rotation by $360/n$ degrees 2. reflection through plane perpendicular to rotation axis	S_n

<i>Symmetry Elements</i>		<i>Symmetry Operation</i>	
<i>Symbol</i>	<i>Description</i>	<i>Symbol</i>	<i>Description</i>
E (or I)	Identity	\hat{E} (\hat{I})	No change
C_n	n -fold axis of symmetry	\hat{C}_n	One or several rotations about the axis by an angle $\theta = \frac{2\pi}{n}$
σ	Plane of symmetry	$\hat{\sigma}$	Reflection in a plane
i	Centre of symmetry, or inversion centre	\hat{i}	Inversion of all atoms through a centre (i), or Reflection through the centre
S_n	n -fold rotation-reflection axis of symmetry or improper rotation	\hat{S}_n	Rotation through an angle of $\theta = \frac{2\pi}{n}$ followed by reflection in a plane perpendicular to the rotation axis (S_n).

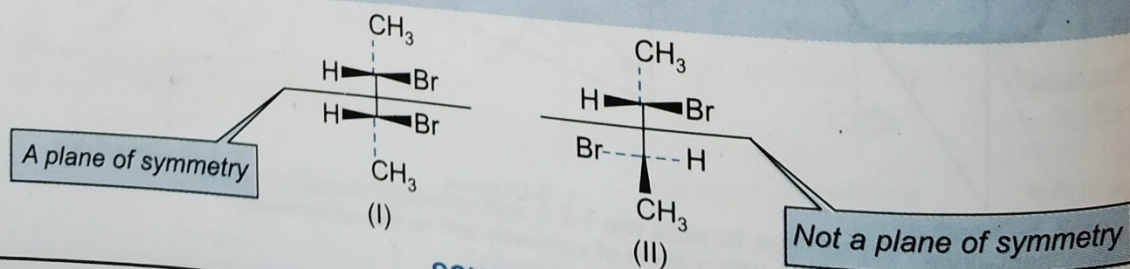


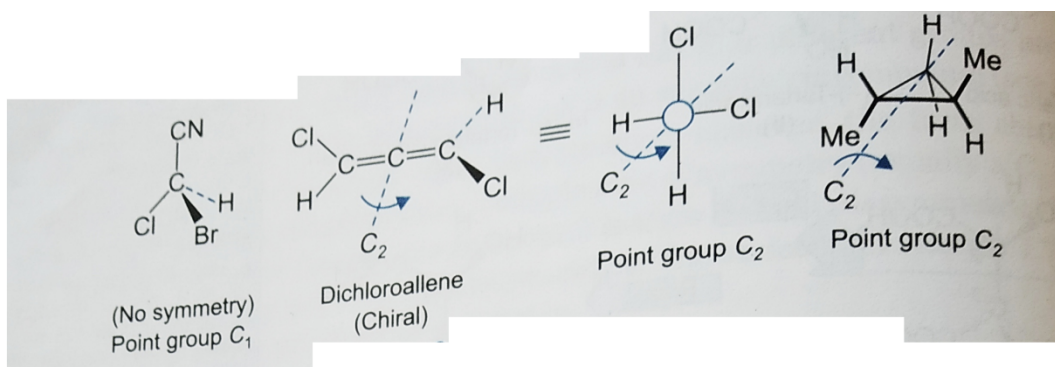
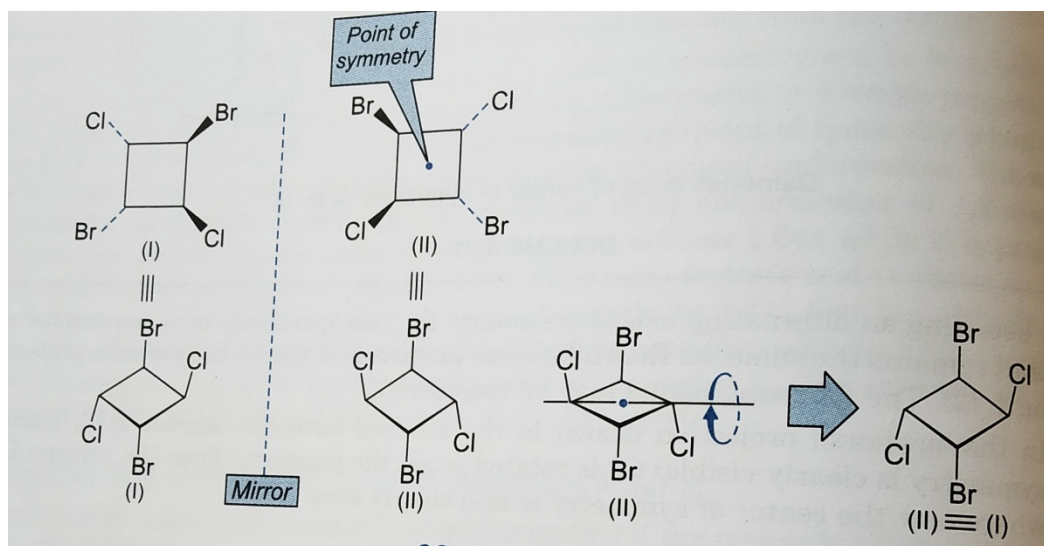
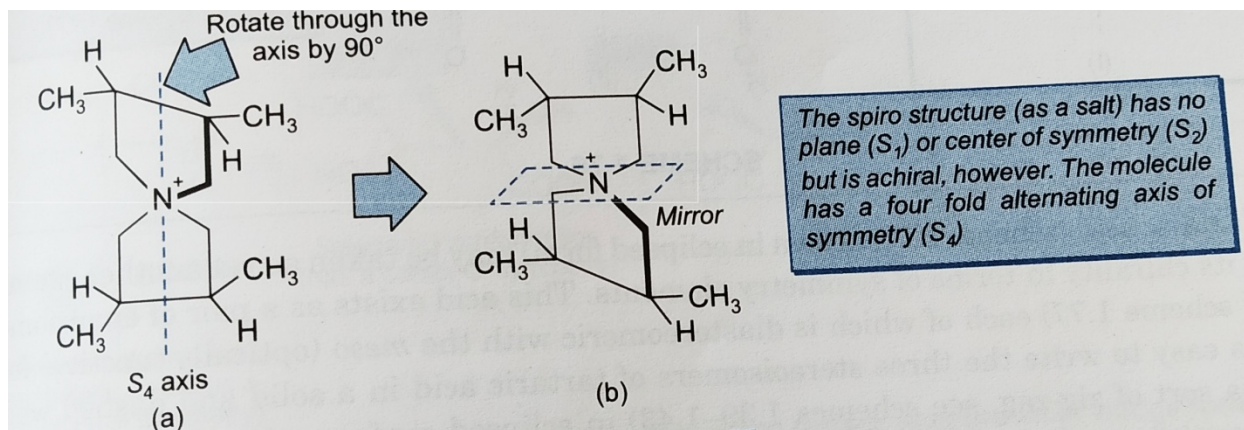
. The flow sheet diagram summarising the applications of symmetry theory in chemistry.

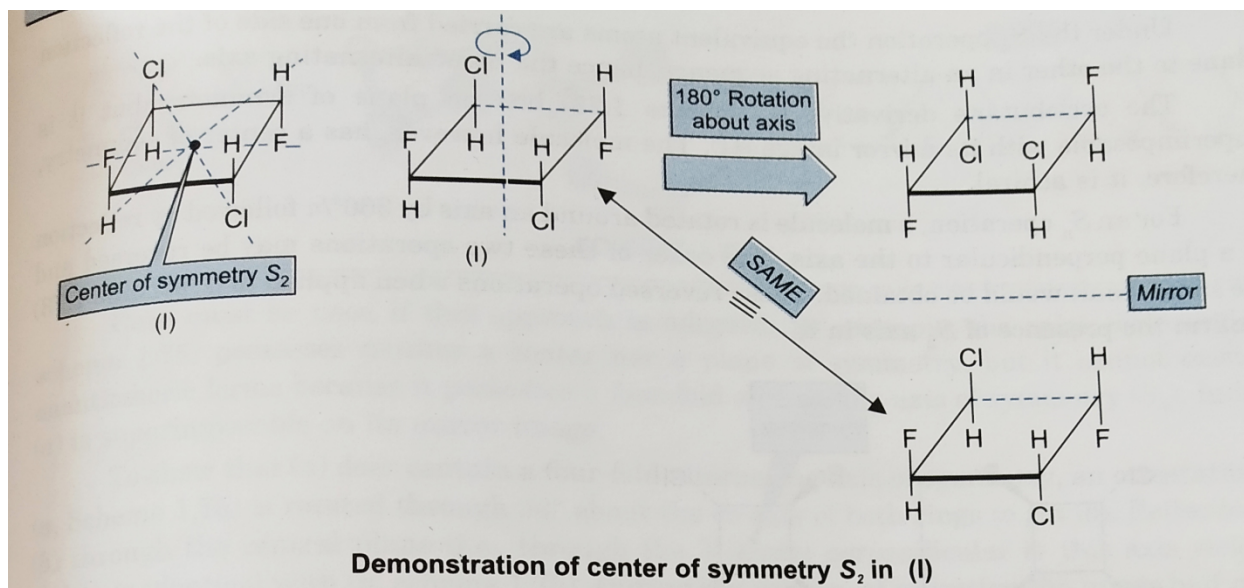


A useful Mental Exercise with Meso 2, 3-dibromobutane

One can detect a plane of symmetry in the eclipsed Fischer projection (I, drawn with more stereochemical details) but not in its staggered conformation (II, written in the related style).

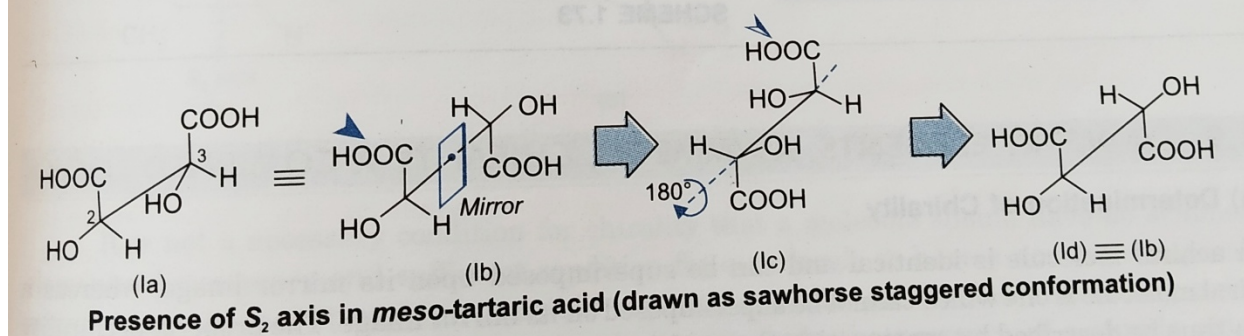






For detecting an alternating axis of symmetry, the two operations may be reversed and the net result remains the same, as shown for *meso* tartaric acid drawn in sawhorse projection (Ia, scheme 1.72). The following points may be considered:

- In the sawhorse projection drawn in the eclipsed form (Ia, scheme 1.72, plane of symmetry is clearly visible) C_3 is rotated to get the staggered form (Ib, scheme 1.72) where now the center of symmetry is also clearly seen.



Point Groups:

Molecules having specific rigid structures can be subjected to symmetry operations that can be performed on elements of symmetry, i.e., E , σ , C_n , i , S_n . All these five operations are called point symmetry operations because such symmetry operations one point, the centre of mass always remain unchanged. By the term **Point Group**, we mean a short hand notation for specifying the symmetry class of a molecule. The criteria for a set of operations to constitute a point group are as follows:

- The product of two members of the group and the square of any member is also

a member of the group. For example,

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

- b. One of the symmetry operations must be the operation of identities E, which commutes with all other operations and leave them unaltered.

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

- c. The combination of operation must obey association law,

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

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

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

- d. Every member of the group must have an inverse i.e., if A is a member, then A^{-1} must also be a member, where $AA^{-1} = E$, if

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

Symmetry operations do not necessarily commute, i.e., AB does not always equal to BA.

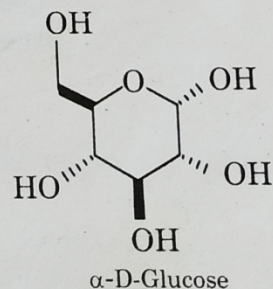
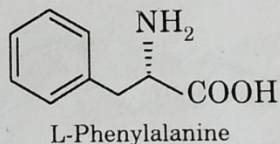
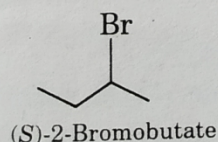
Order of a point group represents the number of different operations that can be performed in a group. For example, a molecule having C_4 , there are four possible operations that can be performed on this symmetry element leading to indistinguishable – super-imposable orientation.

They are $C_4^1, C_4^2, C_4^3, C_4^4$, therefore, the order of point group is 4.

Specifying the symmetry class of molecule are discussed below:

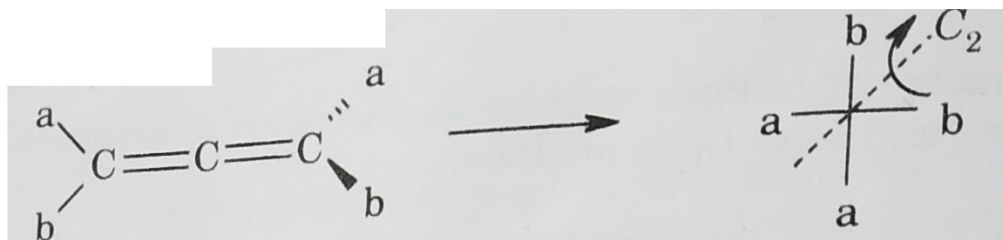
(a) C_1 Point Group:

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 Cabcd belongs to this point group. A few structures with C_1 point group are given below.

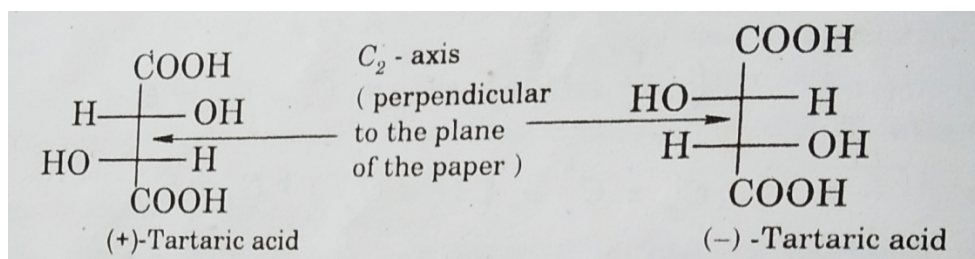


(b). C_n Point group:

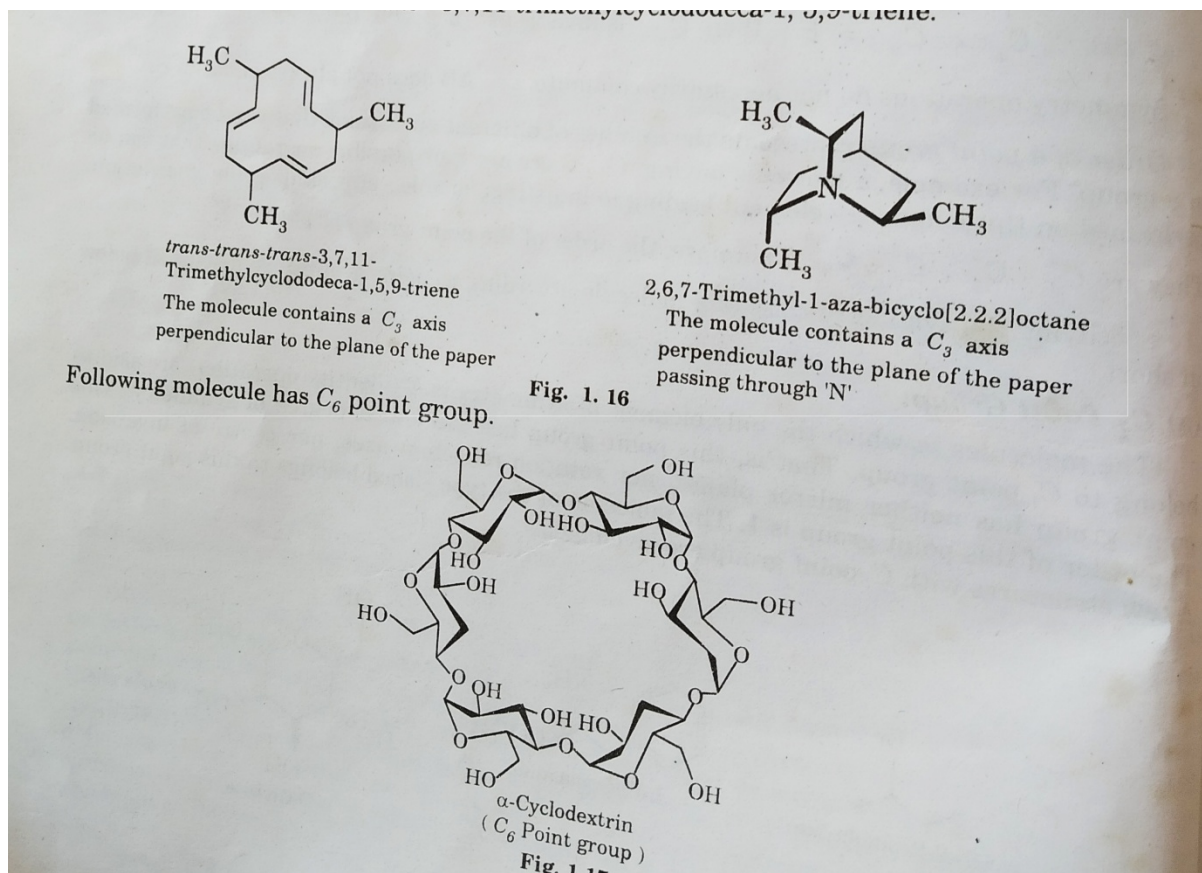
In this case the only element of symmetry in the concerned molecule is C_n axis ($n > 1$). Point group C_2 is of very common occurrence among the organic molecules. For example allene shown below have a C_2 Point group.



Active tartaric acid also have C_2 point group

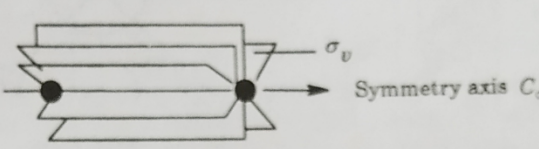


Others examples are



(c) $C_{\infty v}$ Point group:

Linear molecules having symmetry axis (C_{∞}) 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 *canical symmetry*.



σ_v
Symmetry axis C_{∞}

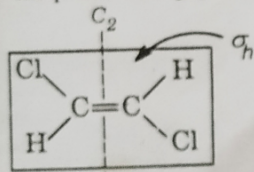
Molecule with $C_{\infty h}$ symmetry group. The Fig. shown has no σ_h perpendicular to C_{∞}

Fig. 1.18

(d) C_{nh} Point group:

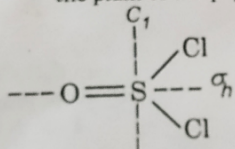
Molecules having C_n ($n > 1$) and a single σ_h as elements of symmetry are said to have C_{nh} point group. For example, *trans*-1,2-dichloroethylene has a C_2 axis and σ_h in molecular plane. Therefore, it has C_{2h} point group

C_2 -axis perpendicular to the plain of the paper

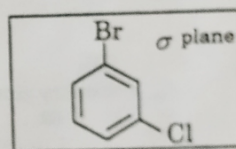


Molecule with point group C_{2h}

Perpendicular to the plain of the paper

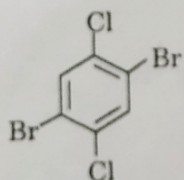


Molecule with point group C_{1h}

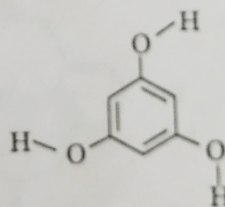


Molecule with point group C_{1h}

← Molecular plane



Molecule with point group C_{2h}

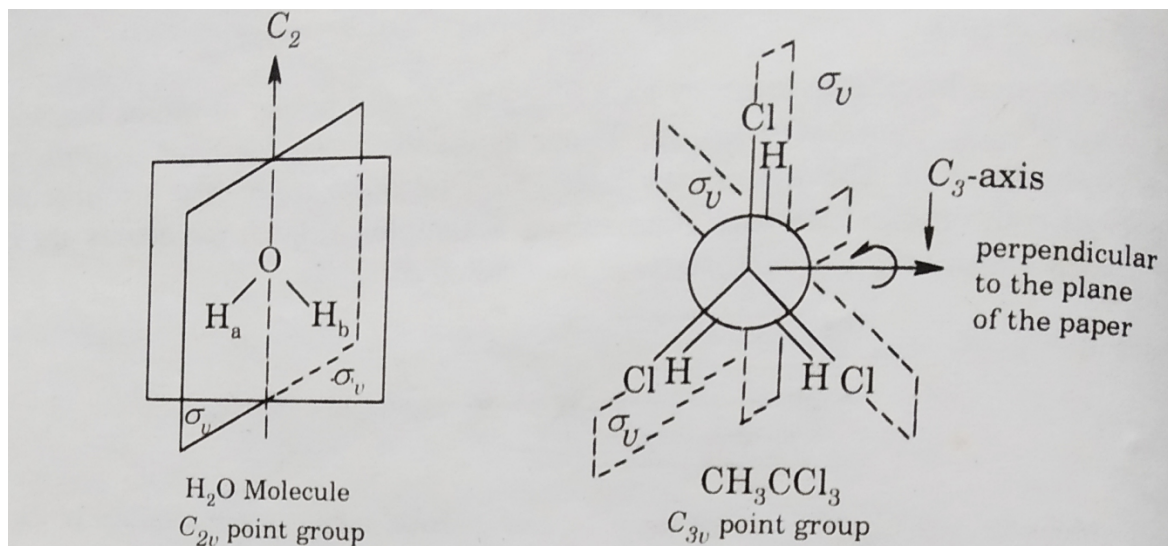


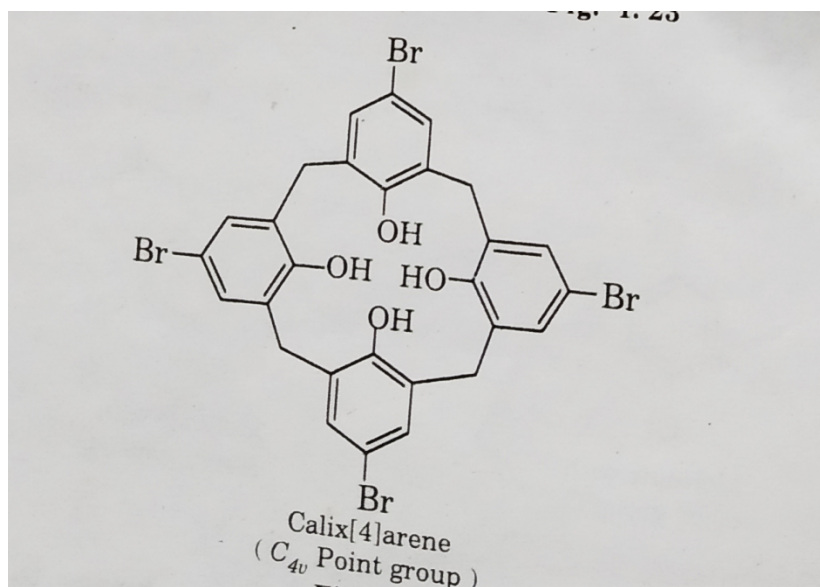
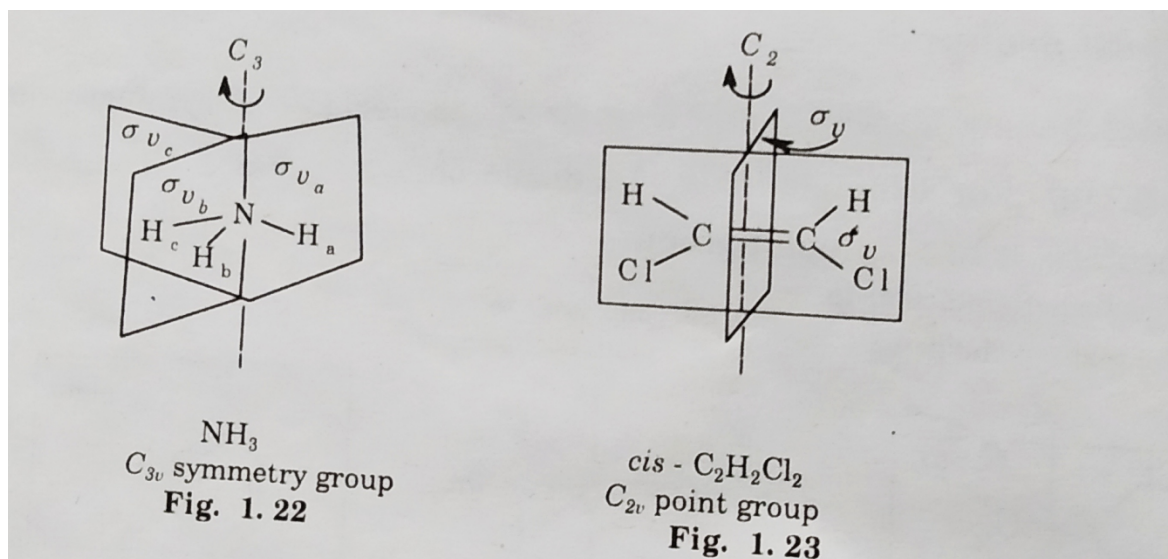
Molecule with point group C_{2h}

The molecule SOCl_2 and *m*- $\text{C}_6\text{H}_4\text{ClBr}$, shown above C_{1h} point group C_{1h} equivalent to S_1 .

(e). C_{nv} Point group:

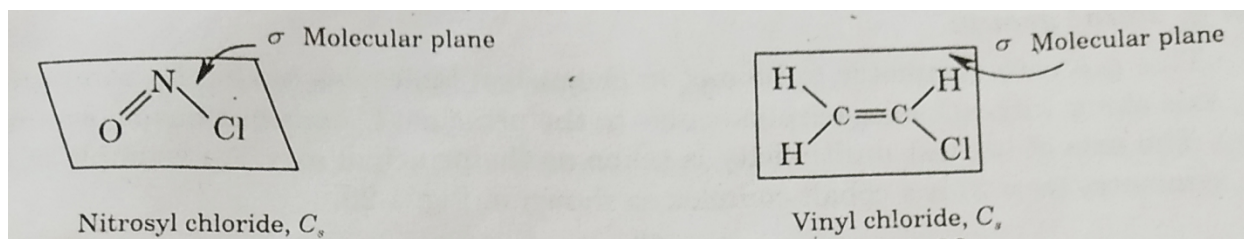
C_{nv} point group is a combination of n -fold symmetry axis C_n and n symmetry plane (σ_v). *cis*- $\text{C}_2\text{H}_2\text{Cl}_2$ belong to the C_{2v} point group while PCl_5 , NH_3 , CHCl_3 , etc., belong to C_{3v} point Group.





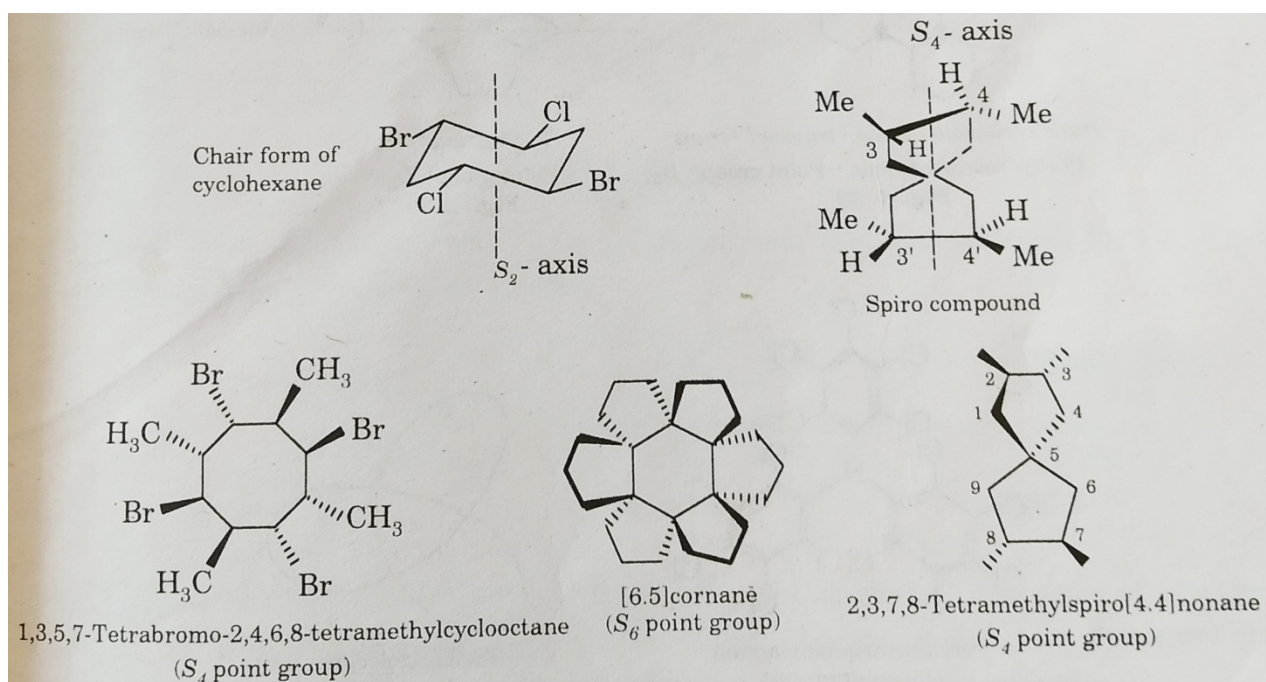
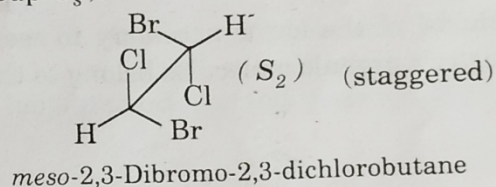
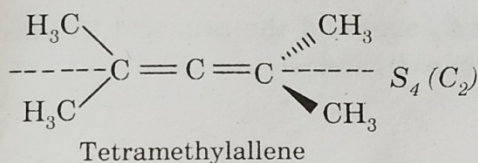
(f). C_s point group:

Molecule having a single plane of symmetry (σ) belong to C_s point group. For example, NOCl , $\text{CH}_2=\text{CHCl}$, etc., have only one plane of symmetry which is coplanar with their molecular plane. Molecule belongs to C_s point can't have any C_n ($n > 1$).



(g) 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 $n = 4x + 2$ ($x = 0, 1, 2, \text{etc.}$), 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 ($n = \text{odd}$). S_2 point group is equivalent to C_i and S_1 is equal to σ plane (point group C_s).



Dihedral Symmetry:

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

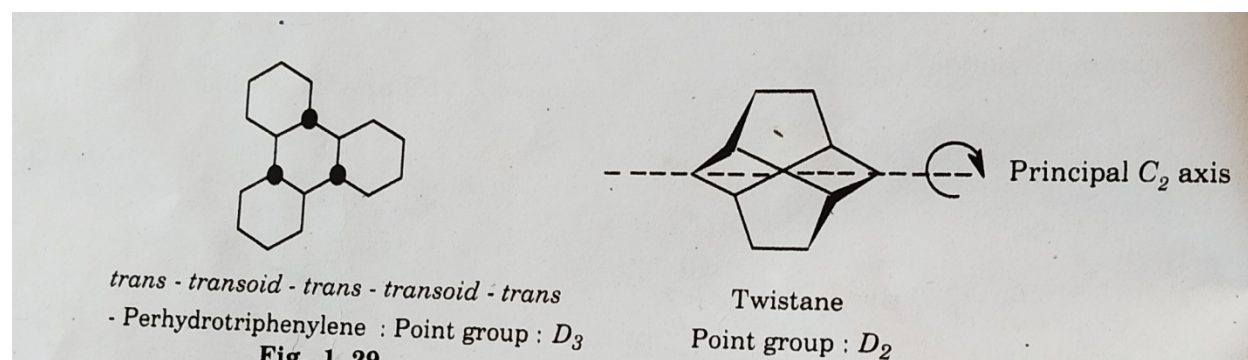
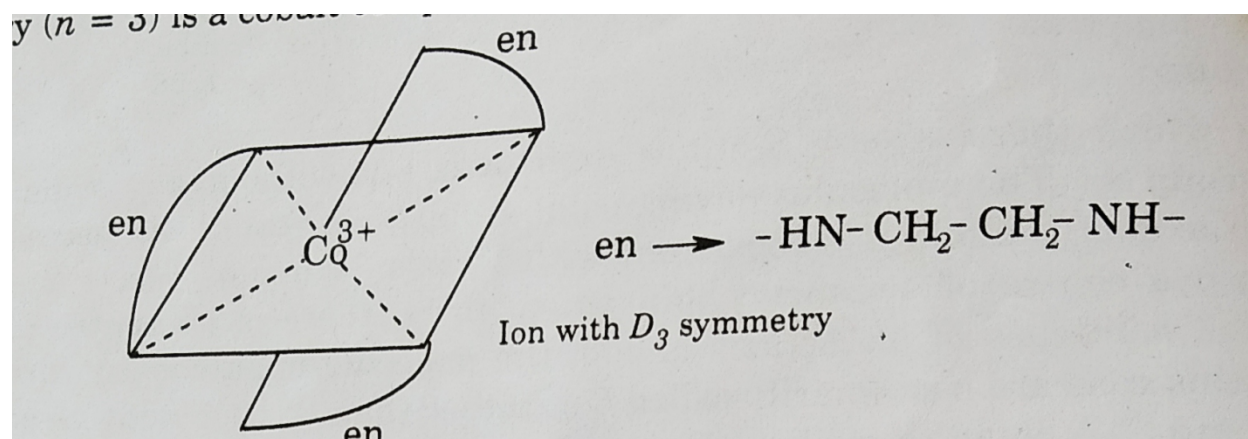
Dihedral symmetry includes three different point groups. They are D_n , D_{nh} and D_{nd} , Characteristics of these groups are stated below.

(a). D_n Point Group:

This is a rare symmetry element met in chemistry. Molecules having D_n point group

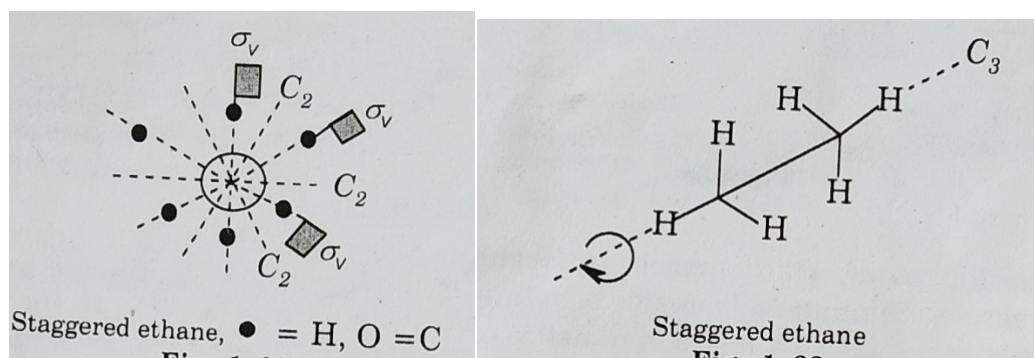
possess C_n axis along with nC_2 axes perpendicular to the principal C_n axis but has no symmetry planes (σ). The axis of highest multiplicity is taken as the principal axis.

Examples are below:



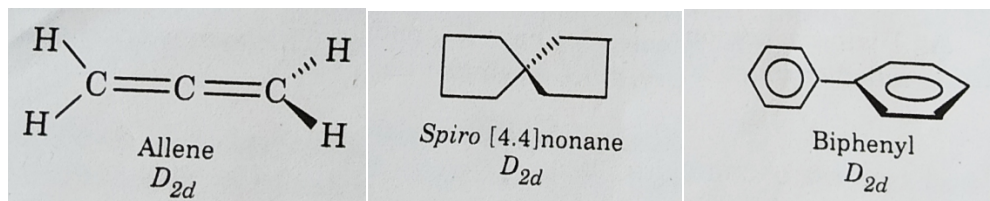
(b). D_{nd} Point group:

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 ($d = \text{diagonal}$). Here σ_v plane bisects the angle between the two C_2 axes, staggered ethane belongs to D_{3d} point group.



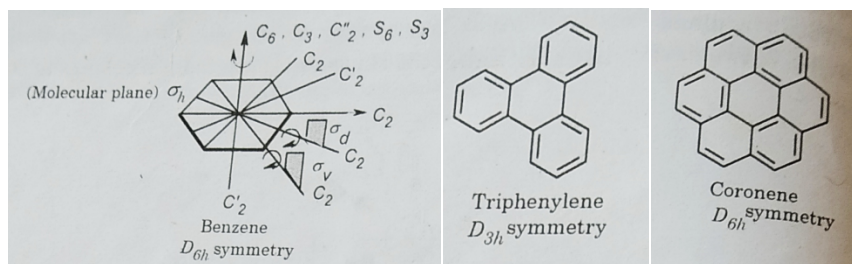
Allene, certain spiranes and biphenyl in which rings are perpendicular, have D_{2d} point

group,



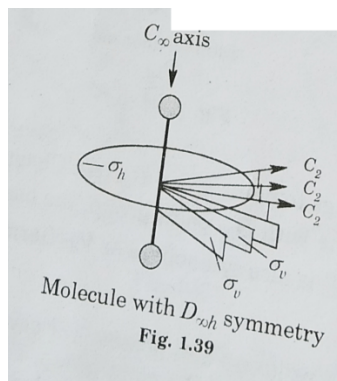
(c). D_{nh} Point group:

Molecules with C_n Symmetry axis in addition to perpendicular nC_2 axes and $n\sigma_v$ planes in addition with σ_h plane are known to have D_{nh} point group. Here σ_h plane perpendicular to the principal axis C_n , For example ethylene has D_{2h} and benzene has D_{6h} point group.



(d) $D_{\infty h}$ Point group:

In a 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, Cl-Cl, H-C≡C-H, O=C=O etc., have $D_{\infty h}$ point group.



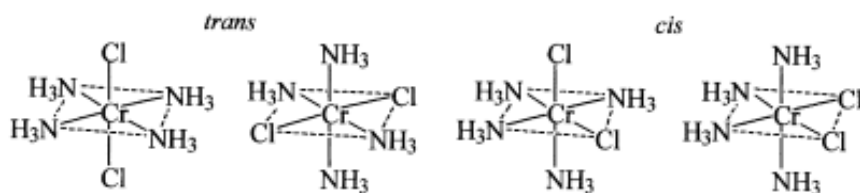
Few question:

1. Deduce the symmetry point groups of all the isomers of $[\text{CrCl}_2(\text{NH}_3)_4]^+$ and assign a

precise stereodescriptor for each isomer.

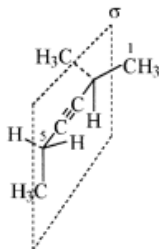
Ans. Both diastereomers of $[\text{CrCl}_2(\text{NH}_3)_4]^+$ are shown below, these are usually differentiated by the stereodescriptors *cis* and *trans*. The *trans* isomer belongs to the symmetry point group D_{4h} . The symmetry elements are the main fourfold axis of symmetry C_4 , a horizontal plane of symmetry σ_h (perpendicular to the C_4 axis), four C_2 axes also perpendicular to the C_4 axis and four planes of symmetry σ_v the intersection of which is the main axis of symmetry. The *cis* isomer belongs to the symmetry point group C_{2v} . The associated symmetry elements are a C_2 axis and two vertical planes of symmetry σ_v intersecting at the C_2 axis. Verify this using the flow chart in the appendix.

Since the descriptors *cis* and *trans* are not generally applicable for octahedral coordination compounds, systematic descriptors based on the CIP system should be used in their place. These consist of the polyhedral symbol, in this example OC-6 (OC for octahedral and 6 for the coordination number), together with the configuration index. For octahedral compounds the latter consists of two digits. The first indicates the priority number of the coordinated atom (ligand) *trans* to the highest ranking coordinated atom (ligand). In the *cis* isomer this is 2, and 1 in the *trans* isomer. The second digit is determined in the same way for the plane perpendicular to the reference axis (main axis) of the octahedron. The *cis* isomer has thus the descriptor OC-6-22. The *trans* isomer is (OC-6-12)-tetraamminedichloridochromium(III).



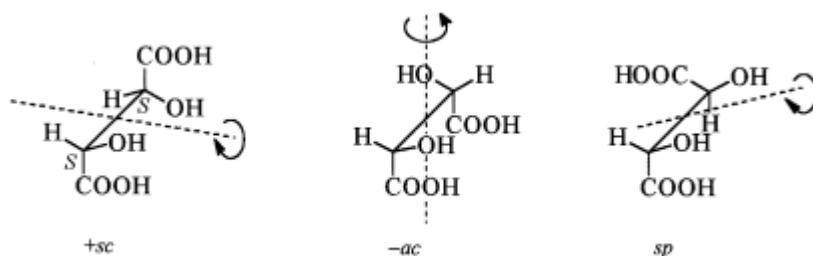
2. To which symmetry point group does 2-methylhex-3-yne belong?

Ans. Only a plane of symmetry σ is present in 2-methylhex-3-yne, thus it belongs to the point group C_s . The methyl group on carbon 5 has free rotation and can lie in the plane of symmetry.



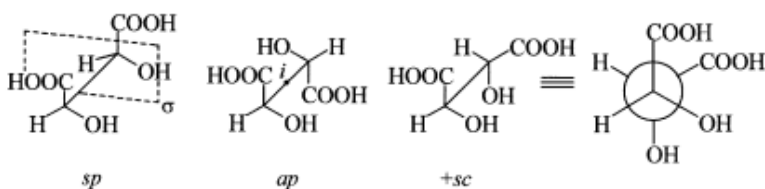
3. Deduce the symmetry point group of (S,S)-tartaric acid in the +synclinal conformation.

Ans. (S,S)-Tartaric acid has a single symmetry element, a C_2 axis, and therefore belongs to the symmetry point group C_2 . On rotation through 180° the pairs of carbon centres 1 and 4, and 2 and 3 are transformed into each other. This is also the case if the molecule adopts another conformation as illustrated by the two examples shown below



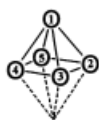
4. Which symmetry elements are present in meso-tartaric acid?

Ans. In order to ascertain which symmetry elements are present in meso-tartaric acid, it is necessary to look at the various conformations of the molecule. The symmetrical highest energy conformer, i.e. the synperiplanar conformer (sp), has a plane of symmetry in which both enantiomorphous halves of the molecule are reflections of each other. No other symmetry elements are present in this conformation (point group C_s). In the ap conformation of meso-tartaric acid the only symmetry element present is a centre of symmetry (disregarding the fact that the centre of symmetry is equivalent to any of the infinite number of S_2 axes). The symmetry point group is therefore C_i . All other conformations, e.g. the +synclinal conformation (+sc) of meso-tartaric acid shown below, are chiral and do not possess any symmetry elements and therefore belong to the point group C_1 .

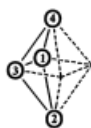


5. Determine the symmetry elements present in the following boranes and hence assign their symmetry point groups. The numbered circles in the polyhedra represent the boron atoms with the corresponding number of attached hydrogen atoms. (177)

a) B_5H_9



b) B_4H_{10}



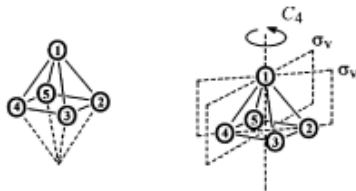
c) B_6H_{10}



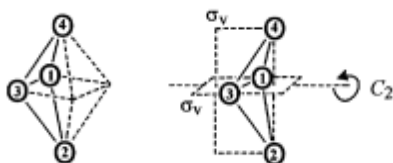
d) B_5H_{11}



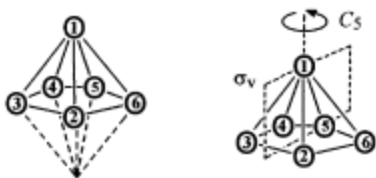
Ans. a) B_5H_9 has a square pyramidal structure. The compound belongs to the symmetry point group C_{4v} . It has one C_4 axis and four planes of symmetry σ_v two of which pass through opposite corners and two of which bisect opposite edges of the square plane.



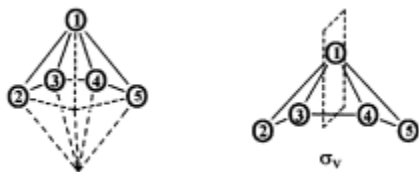
b) B_4H_{10} belongs to the symmetry point group C_{2v} . It has one C_2 axis and two planes of symmetry σ_v



c) B_6H_{10} has a pentagonal pyramidal structure. The compound belongs to the symmetry point group C_{5v} . It has one C_5 axis of symmetry and five vertical planes of symmetry σ_v whose line of intersection is the C_5 axis.



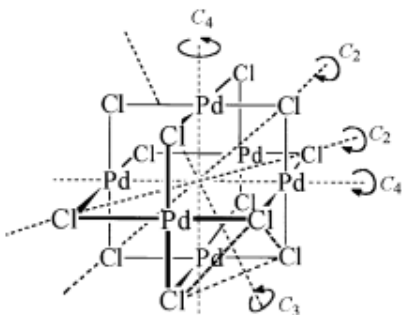
d) B_5H_{11} possesses only a plane of symmetry σ and therefore belongs to the symmetry point group C_s



6. Deduce the symmetry point group of $[(PdCl_2)_6]$.

Ans. By means of the flow chart given in the appendix the symmetry point group can be easily established. As the molecule is not linear, the first question to be answered is what is the order of the axis of symmetry of the highest order? This is a four-fold axis. Next we must determine whether this is the only C_4 axis or if other C_4 axes are present. In this case there are two other C_4

axes which each pass through two oppositely positioned palladium atoms. Since there is no C_5 axis, the structure must be inspected to see whether there are any C_3 axes. It is now meaningful to look at the chlorine atoms in the molecule. A total of four three-fold axes of symmetry pass through the middle of triangles formed from three chlorine atoms or three palladium atoms, respectively. Since the question of four-fold axes has already been answered, it only remains to see whether a centre of symmetry is present. This is the case and therefore $[(PdCl_2)_6]$ has the symmetry point group O_h . There are, in addition to the symmetry elements already established above, six C_2 axes passing through opposite pairs of chlorine atoms. There are also three planes of symmetry each containing four palladium atoms and six planes of symmetry diagonal to these planes each containing two palladium atoms and two chlorine atoms. There are also three S_4 axes coinciding with the C_4 axes and four S_6 axes coinciding with the C_3 axes. Note that the palladium atoms are located at the corners of an octahedron the edges of which have a bridging chlorine atom.



Exercise

Full exercise of S. Sengupta.

Reference: S. sengupta