

MOLECULAR SYMMETRY

All molecules may be characterised and categorised by their symmetry.

An object is symmetrical if some movement or operation leaves the object in a position indistinguishable from its original position.

Symmetry operation: Operations that leave objects looking the same.

Symmetry element: Corresponding elements – are the points, lines, and planes with respect to which symmetry operation is performed.

There are only 5 unique symmetry elements.

Symmetry of a molecule defined by all the symmetry elements inherent within the molecule.

All molecules characterised by 32 different combinations of symmetry elements: *point groups*.

There are two naming systems commonly used when describing symmetry elements

1. The Schoenflies notation used extensively by spectroscopists
2. The Hermann-Mauguin or international notation preferred by crystallographers

The Symmetry Elements

Identity ($C_1 \equiv E$ or 1)

Rotation by 360° around any randomly chosen axes through the molecule returns it to original position.

Any direction in any object is a C_1 axis; rotation by 360° restores original orientation.

Schoenflies: C is the symbol given to a rotational axis
1 indicates rotation by 360°

Hermann-Mauguin: 1 for 1-fold rotation

Operation: act of rotating molecule through 360°

Element: axis of symmetry (i.e. the rotation axis).

Rotation axes (C_n or n)

Rotations through angles other than 360° .

Sphere has infinite number of possible rotation angles and axes, all other objects/molecules have reduced rotational symmetry.

Operation: act of rotation

Element: rotation axis

Symbol for a symmetry element for which the operation is a rotation of $360^\circ/n$

Schoenflies: C_n

Hermann–Mauguin: n .

The molecule has an n -fold axis of symmetry.

An object may possess several rotation axes and in such a case the one (or more) with the greatest value of n is called the **principal axes of rotation**.

Mirror planes (σ or m)

Mirror reflection through a plane.

Operation: act of reflection

Element: mirror plane

Schoenflies notation:

Horizontal mirror plane (σ_h): plane perpendicular to the principal rotation axis

Vertical mirror plane (σ_v): plane includes principal rotation axis

Diagonal mirror plane (σ_d): plane includes principal rotation axis and bisects the angle between a pair of 2-fold rotation axes that are normal (perpendicular) to principal rotation axis.

Schoenflies: σ_h , σ_v , σ_d

Hermann–Mauguin: m

Centres of inversion (centre of symmetry, i or $\bar{1}$)

Operation: inversion through this point

Element: point

Straight line drawn through centre of inversion from any point of the molecule will meet an equivalent point at an equal distance beyond the centre.

Schoenflies: i

Hermann–Mauguin: $\bar{1}$

Molecules possessing a centre of inversion are **centrosymmetric**

Axes of rotary inversion (improper rotation S_n or \bar{n})

Involves a combination of elements and operations

Schoenflies: S_n

Element: axis of rotatory reflection

The operation is a combination of rotation by $360^\circ/n$ (C_n) followed by reflection in a plane normal (σ_h) to the S_n axis.

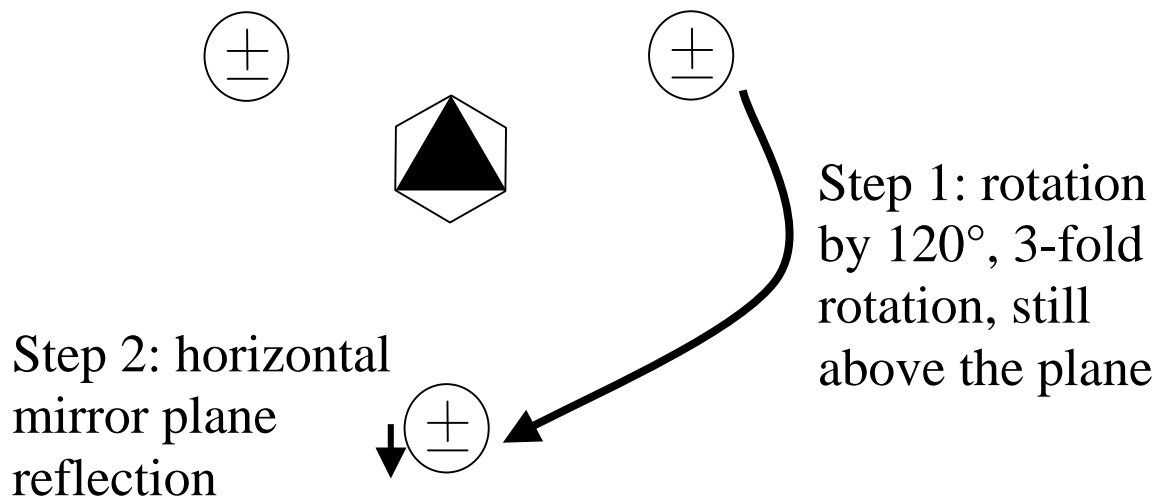
Molecule does not need to have either a C_n or a σ_h symmetry element

S_3

Start with point above the plane of the paper (+), rotate by 120° and then reflect in the horizontal mirror plane.

One application of S_3 generates a point rotated 120° and below the plane of the paper (-).

Successive applications (S_3 applied to each newly generated point) give a total of 6 points.

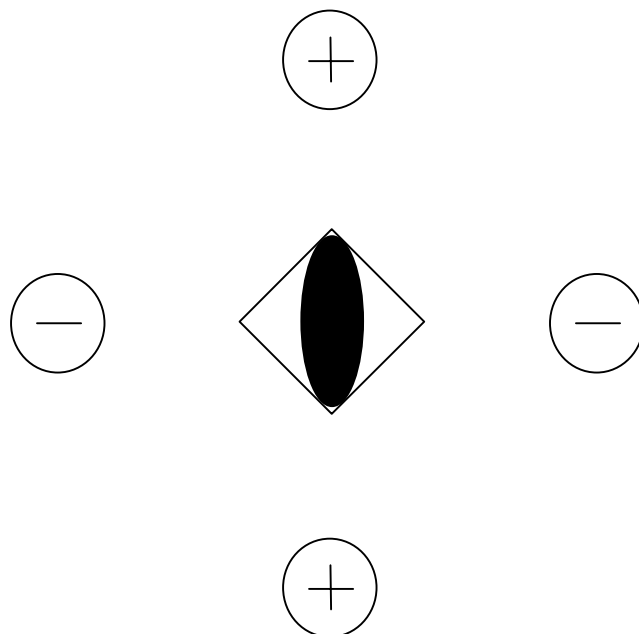


S_4

Start with a point above the plane of the paper (+)

One application of S_4 generates a point rotated 90° and below the plane of the paper (-).

Successive applications of S_4 give a total of 4 points.



Hermann-Mauguin: \bar{n}

Element: axis of rotatory inversion.

The operation is a combination of rotation by $360^\circ/n$ (n) followed by inversion through a point ($\bar{1}$).

Molecule does not need to have either a n or a $\bar{1}$ symmetry element

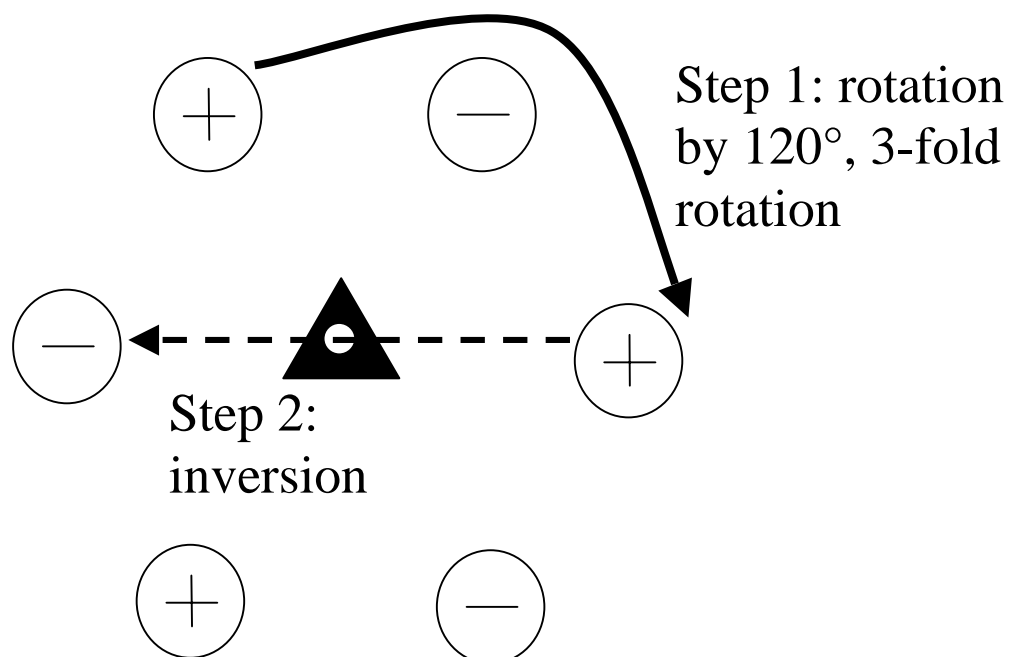
$\bar{3}$

Start with point above the plane of the paper (+), rotate by 120° and then invert through centre of symmetry.

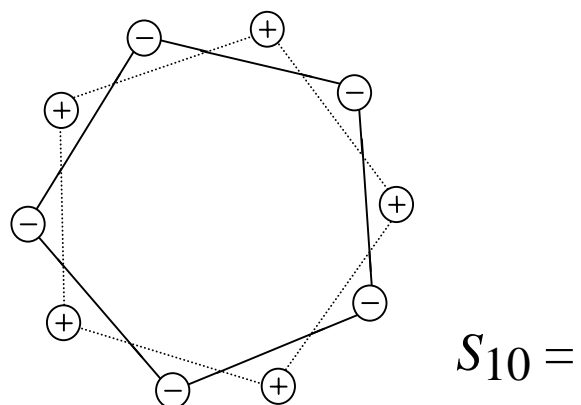
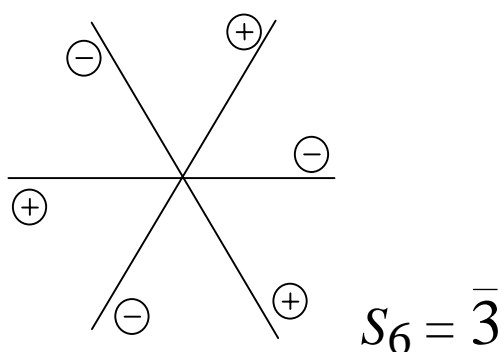
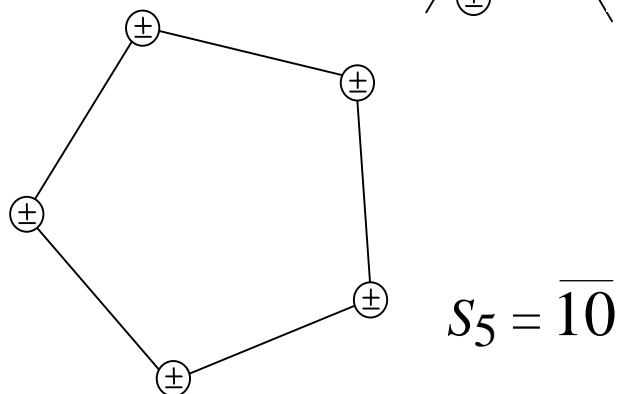
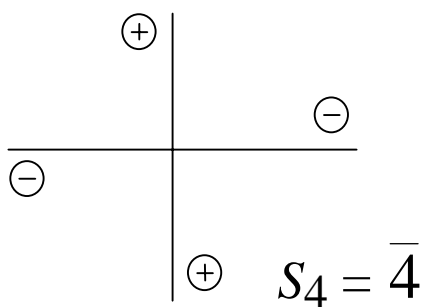
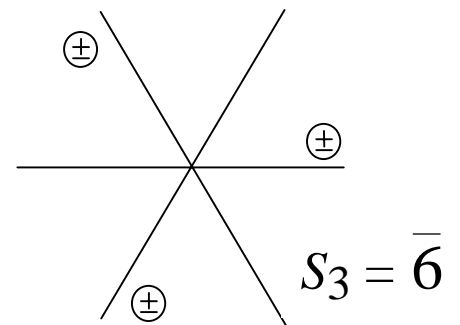
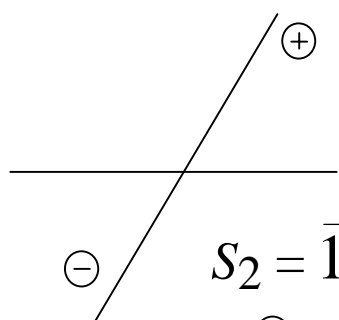
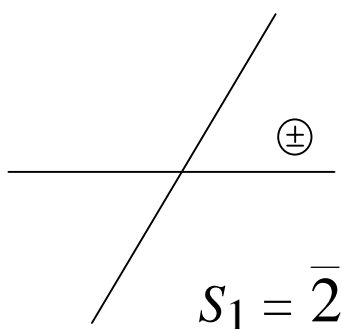
One application of $\bar{3}$ generates a point rotated -60° and below the plane of the paper (-).

Successive applications (S_3 applied to each newly generated point) give a total of 6 points.

Note that the sequence of events and final pattern is very different for a $\bar{3}$ vs. a S_3 operation.



- S_n and \bar{n} are different unless n is a multiple of 4.
- When n is odd $S_n = (\overline{2n})$ and $\bar{n} = S_{2n}$
- $S_1 = \bar{2} = \sigma (= m)$, $S_3 = \bar{6}$, $S_5 = \overline{10} \dots$
- $\bar{1} = S_2 = i$, $\bar{3} = S_6$, $\bar{5} = S_{10} \dots$
- The symbol σ (or m) is always used in place of S_1 (or $\bar{2}$)
- i is always used in place of S_2
- When n is odd, S_n implies the presence of both C_n and σ_h , and \bar{n} implies the presence of both n and $\bar{1}$.



ELEMENTS OF POINT SYMMETRY

<i>Type of element</i>	<i>Description of operation</i>	<i>Schoenflies</i>
Identity	Rotation of 360° about any axis. All objects and geometric figures possess this element	$E = C_\infty$
Rotation axis	Counterclockwise rotation of $360^\circ/n$ about axis	C_1, C_2, C_3, \dots
Mirror plane	Reflection through a plane	$\sigma (\sigma_h, \sigma_v)$
Centre of inversion (centre of symmetry)	All points inverted through a centre of symmetry	i
<i>Improper rotation axis</i> (<i>rotatory reflection axis</i>)	Rotation of $360^\circ/n$ followed by reflection in a plane perpendicular to the axis	S_1, S_2, S_3, \dots
<i>Improper rotation axis</i> (<i>rotatory inversion axis</i>)	Rotation of $360^\circ/n$ followed by inversion through a point on the axis	

Combinations of symmetry elements

Most molecules will possess more than one symmetry element.

To describe the symmetry of a molecule must identify each element and their orientation.

Each molecule is completely described by a minimum number of symmetry operations.

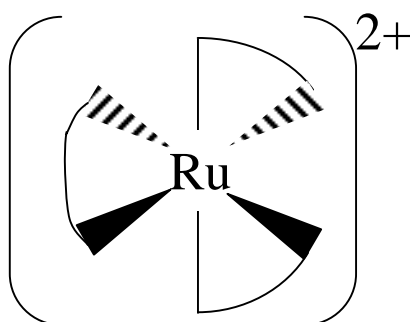
Asymmetry: Molecule possesses no symmetry operations except the identity.

Molecule is optically active, cannot be superimposed on its mirror image.

Dissymmetry: Molecules possess one additional symmetry operation; a proper axis of rotation (C_n or n).

Dissymmetrical molecules can still exhibit optical activity.

General condition for optical activity: molecules contain no alternating axis of symmetry of any order (i.e. no S_n axis).



The symmetry classification of molecules

- List symmetry elements
- Collect together molecules with the same list of elements

Group: any set or collection of elements which together with some well defined combining operation obey a certain set of rules

Rules which elements of a group must obey:

- Combination of any two elements of the group must produce an element which is also a member of the group.
- Group must contain the identity element.

The 32 crystallographic point group

C_i	$\bar{1}$								
C_s	m								
C_1	1	C_2	2	C_3	3	C_4	4	C_6	6
		C_{2v}	2mm	C_{3v}	3m	C_{4v}	4mm	C_{6v}	6mm
		C_{2h}	2/m	C_{3h}	$\bar{6}$	C_{4h}	4/m	C_{6h}	6/m
		D_2	222	D_3	32	D_4	422	D_6	622
		D_{2h}	mmm	D_{3h}	$\bar{6}2m$	D_{4h}	4/mmm	D_{6h}	6/mmm
		D_{2d}	$\bar{4}2m$	D_{3d}	$\bar{3}m$	D_{4d}	$\bar{4}/m$	D_{6d}	$\bar{3}$
T	23	T_d	$\bar{4}3m$	T_h	m3				
O	432	O_h	m3m						

Molecule

Linear?

Y

N

$D_{\infty h}$

Y

$i?$

N

$C_{\infty v}$

Y

Two or more $C_n, n > 2?$

Y

$i?$

N

T_d

I_h

Y

$C_5?$

N

O_h

N

‡ Select C_n with highest n ; then, are there $nC_2 \perp$ to C_n ?

D_{nh}

Y

$\sigma_h?$

N

Y

‡

Y

$C_n?$

N

D_{nd}

Y

$n\sigma_d$

N

C_{nh}

Y

$\sigma_h?$

N

C_s

Y

$\sigma?$

N

D_n

C_{nv}

Y

$n\sigma_v$

N

C_i

Y

$i?$

N

S_{2n}

Y

$S_{2n}?$

N

C_n

C_1

The groups C_1 , C_i and C_s

C_1 : no element other than the identity

C_i : identity and inversion alone

C_s : identity and a mirror plane alone

The groups C_n , C_{nv} and C_{nh}

C_n : n -fold rotation axis

C_{nv} : identity, C_n axis plus n vertical mirror planes σ_v

C_{nh} : identity and an n -fold rotation principal axis plus a horizontal mirror plane σ_h

Presence of certain symmetry elements may be implied by the presence of others; thus in C_{2h} , the operations C_2 and σ_h jointly imply the presence of a centre of inversion.

The groups D_n , D_{nh} and D_{nd}

D_n : n -fold principal axis and n two-fold axes perpendicular to C_n

D_{nh} : molecule also possesses a horizontal mirror plane

D_{nd} : in addition to the elements of D_n possesses n dihedral mirror planes σ_d

The groups S_n

S_n : Molecules not already classified possessing one S_n axis

Molecules belonging to S_n with $n > 4$ are rare

$S_2 \equiv C_i$

The cubic groups

T_d and O_h : groups of the regular tetrahedron (e.g. CH_4) and regular octahedron (e.g. SF_6), respectively.

T or O : object possesses the rotational symmetry of the tetrahedron or the octahedron, but none of their planes of reflection

T_h : based on T but also contains a centre of inversion

The full rotation group

R_3 : consists of an infinite number of rotation axes with all possible values of n . A sphere and an atom belong to R_3 , but no molecule does.