MSc S1-16P1CHET04 -QUANTUM CHEMISTRY AND GROUP THEORY

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Topic – Symmetry Elements and Symmetry Operations

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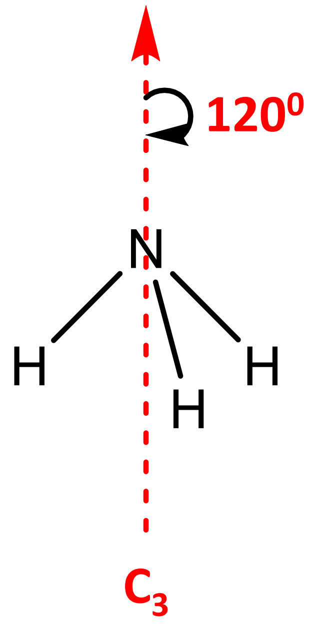
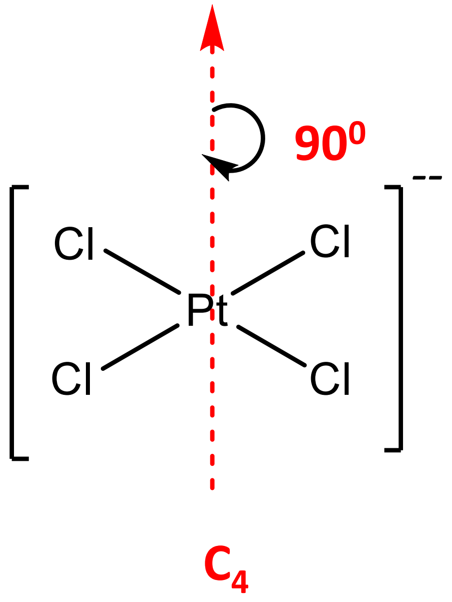
OPERATIONS

Part I

GROUP THEORY

AND CHEMISTRY





GROUP THEORY AND CHEMISTRY

- Group Theory is a purely mathematical concept
- Most of the fundamentals of group theory were developed by the French mathematician Evariste Galois (1811 – 1832) in the early 19th century
- The principles of Group theory are used by Chemists and Physicists for the analysis of symmetry properties, structure, bonding and molecular spectra of compounds

Symmetry Elements and Symmetry Operations

- A **symmetry element** is a **geometric entity** such as **a line, a plane or a point** about which one can perform an operation of rotation, reflection or inversion

- A **symmetry operation** is a **movement of a molecule/object** such that the resulting configuration is **indistinguishable** from the original.

  - During any symmetry operation at least one point in the molecule should remain unchanged. This point is the center of gravity of the molecule

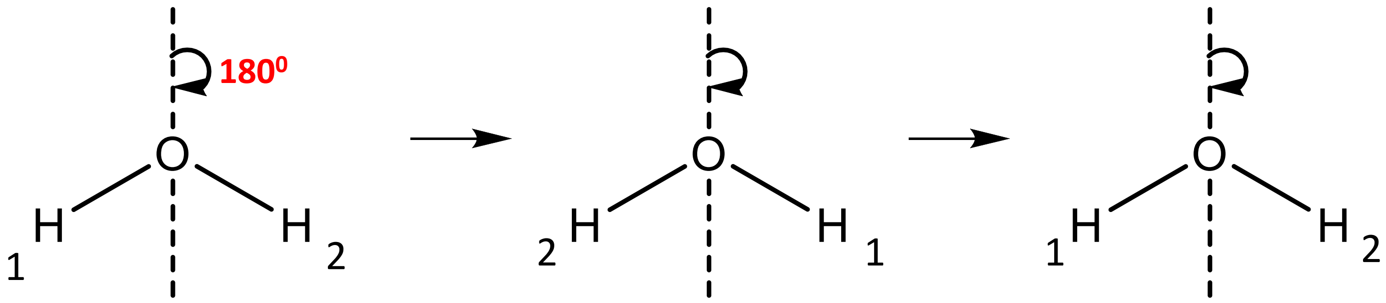
  - During translation (bodily movement from one point to another) the center of gravity of the molecule is changed

  - Therefore, a molecule should never be translated during a symmetry operation

- A symmetry operation will transform a molecule into an equivalent or identical configuration

Illustration

Suppose, H_2O molecule is rotated about an axis passing through the oxygen atom and bisecting the H-O-H bond angle, through 180^0



I **II** **III**

The configurations I and II are equivalent

The configurations II and III are equivalent

The configurations I and III are identical

The configurations I, II and III are indistinguishable. Therefore this operation is a symmetry operation

The **symmetry element** is **the imaginary line (axis)** and

the **symmetry operation** is the **rotation of the molecule about this axis through 180^0**

There are only 5 basic operations in nature which will leave the center of gravity of a molecule unchanged

SYMMETRY ELEMENT	SYMMETRY OPERATION
1. Identity E	Doing nothing
2. Proper rotation axis C_n	Rotation about the axis through some angle
3. Mirror plane or Plane of symmetry σ	Reflection about the plane
4. Inversion center or Center of symmetry i	Inversion. Inversion is reflection about a point
5. Improper rotation axis S_n	Rotation about an axis through some angle followed by a reflection in a plane perpendicular to the rotation axis

IDENTITY E

- This operation does nothing. It is the simplest of all the symmetry operations
- This is the only element/operation possessed by all molecules
- Both the symmetry element and the symmetry operation are denoted by the same symbol, E
- If this operation is carried out n times it is denoted as E^n where n is 1,2 ,3, 4, ….. And $E^n = E$ whether n is odd or even.
- $E^2 = EE = E$
- The identity element E can generate only one operation

Proper rotation axis C_n

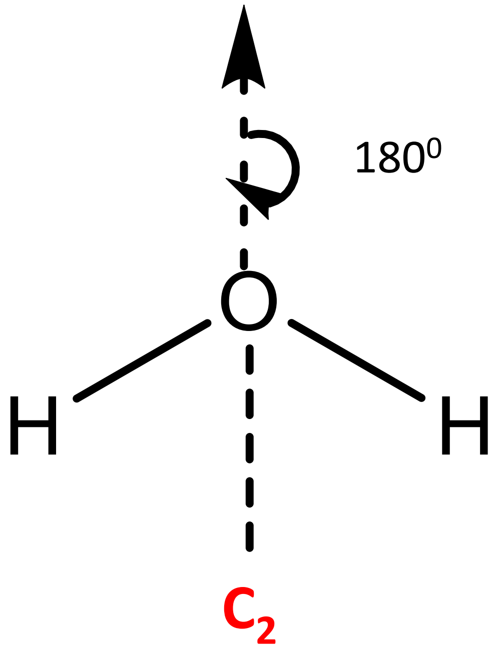
- If the rotation of a molecule about an axis through some angle results in a configuration which is indistinguishable from the original, then the molecule is said to possess a proper rotation axis. It is denoted by the symbol **C_n.**
- C stands for cyclic
- n = $\frac{360^0}{\theta}$ where θ is the angle through which the molecule is rotated
- C_n is called a n- fold rotation axis and n is the order of the axis

- H_2O molecule has to be rotated through 180^0 about the axis passing through the O atom and bisecting the H-O-H bond angle to get an indistinguishable orientation. So the symmetry axis is a $360^0/180^0 = 2$ fold rotation axis and is denoted as C_2

Θ in degree ^{0}	$n = \frac{360^0}{\theta}$	Symbol of the proper rotation axis
180	2	C_2
120	3	C_3
90	4	C_4
72	5	C_5
60	6	C_6

Identifying the proper rotation axis in some common molecules

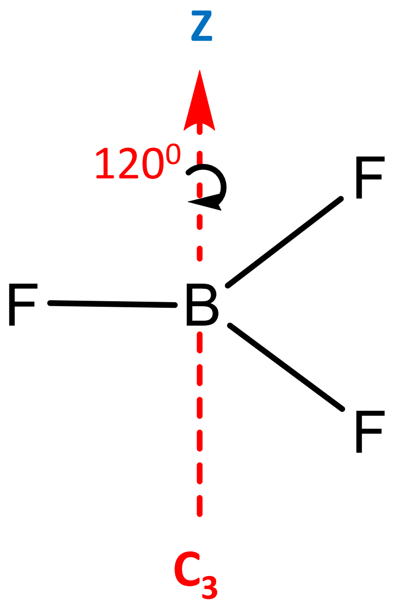
Water H_2O Angular Shape



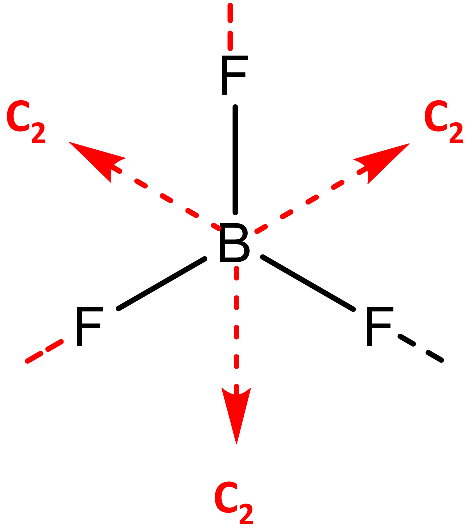
There is only one C_2 axis

The C_2 axis is in the plane of the molecule

Boron tri fluoride BF_3 (Shape : Planar triangular –The B and the three F atoms are in the same plane – the molecular plane)



The C_3 axis passes through the B atom and perpendicular to the plane of the molecule



Each C_2 axis passes through the B atom and one of the F atoms. The three C_2 axes are in the molecular plane

One C_3 axis and Three C_2 axes

The higher order C_3 axis is called the principal axis

The unique principal axis is always taken as the z-axis

In BF_3 molecule, the C_3 axis is the z-axis and the molecular plane which is perpendicular to the principal axis (Z) is the *xy* plane

In fact, in all planar molecules, with a unique principal axis, the principal axis is the z-axis and the molecular plane is *xy* plane

Ammonia NH_3

The NH_3molecule has **pyramidal shape** with the N atom at the apex

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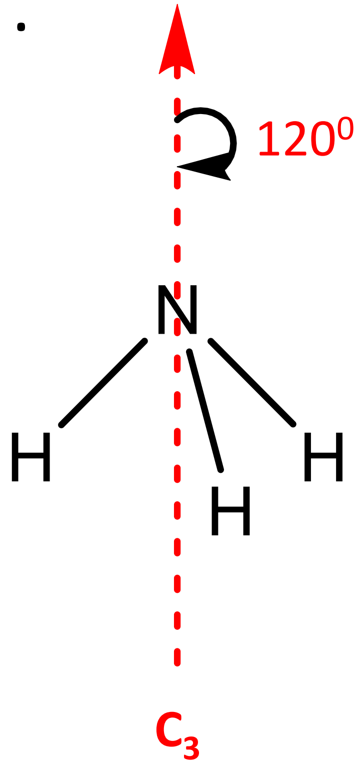
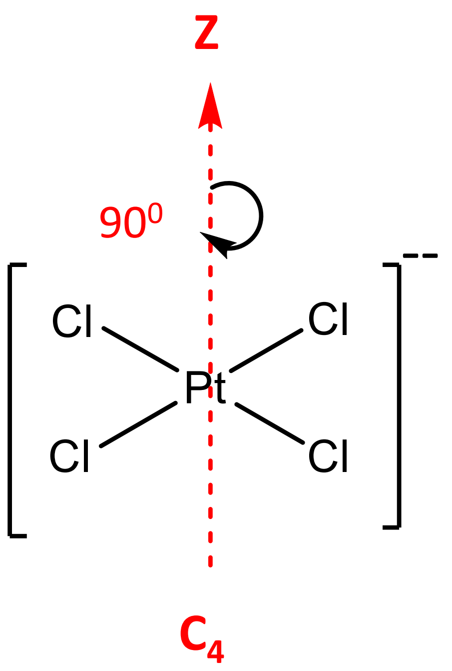
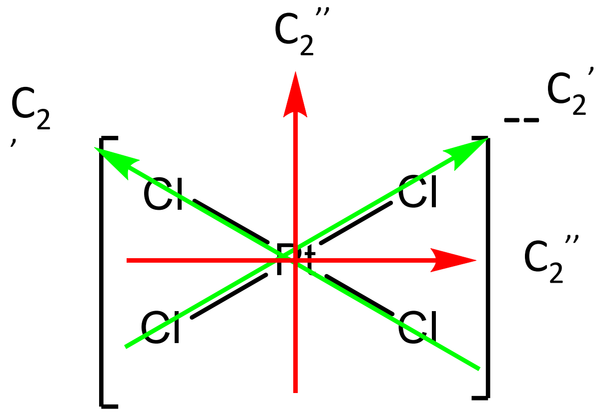


There is only one C_3 axis .

The C_3 axis passes through the N atom and the center of the triangular base formed by the 3 H atoms

$PtCl_4^{--}$ ion   The shape of this ion is square planar





The four C_2 axes

One C_4 axis

Four C_2 axes separated into 2 sets

Two C_2' axes

Two C_2'' axes

The four C_2 axes are in the plane of the molecule

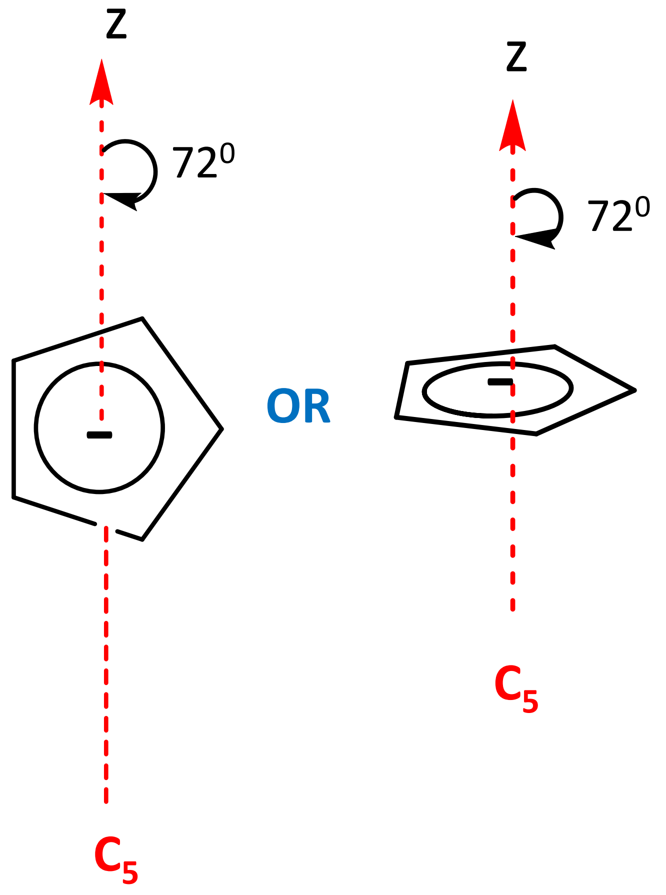
The C_4 axis passes through the Pt atom and perpendicular to the plane of the ion

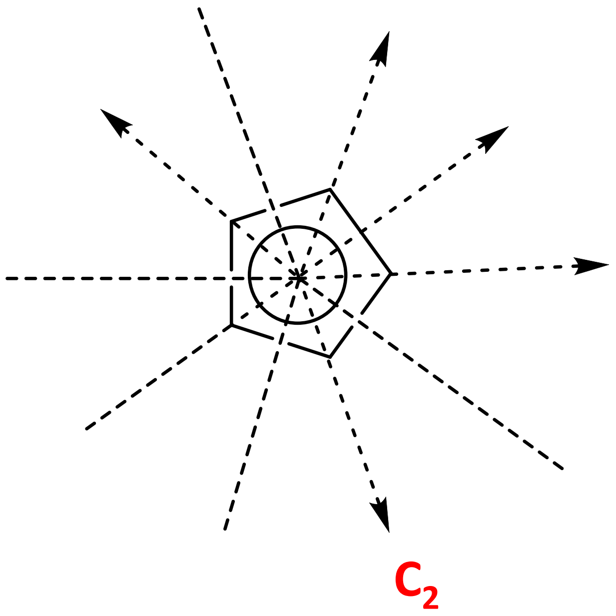
The C_2' axis passes through the Pt atom and two diagonal Cl atoms

The C_2'' axis passes through the Pt atom and bisects the Cl-Pt-Cl bond angle

Cyclo penta dienyl anion $C_5H_5^-$

Shape of the ion: **Pentagonal Planar**



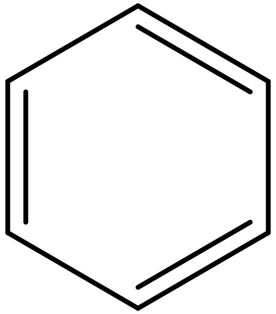


One C_5 axis perpendicular To the molecular plane

Five C_2 axes, all in the molecular plane

Benzene C_6H_6

Shape : Hexagonal planar



One C_6 axis

Six C_2 axes

Three C_2 axis of one type C_2'

Three C_2 axis of another type C_2''

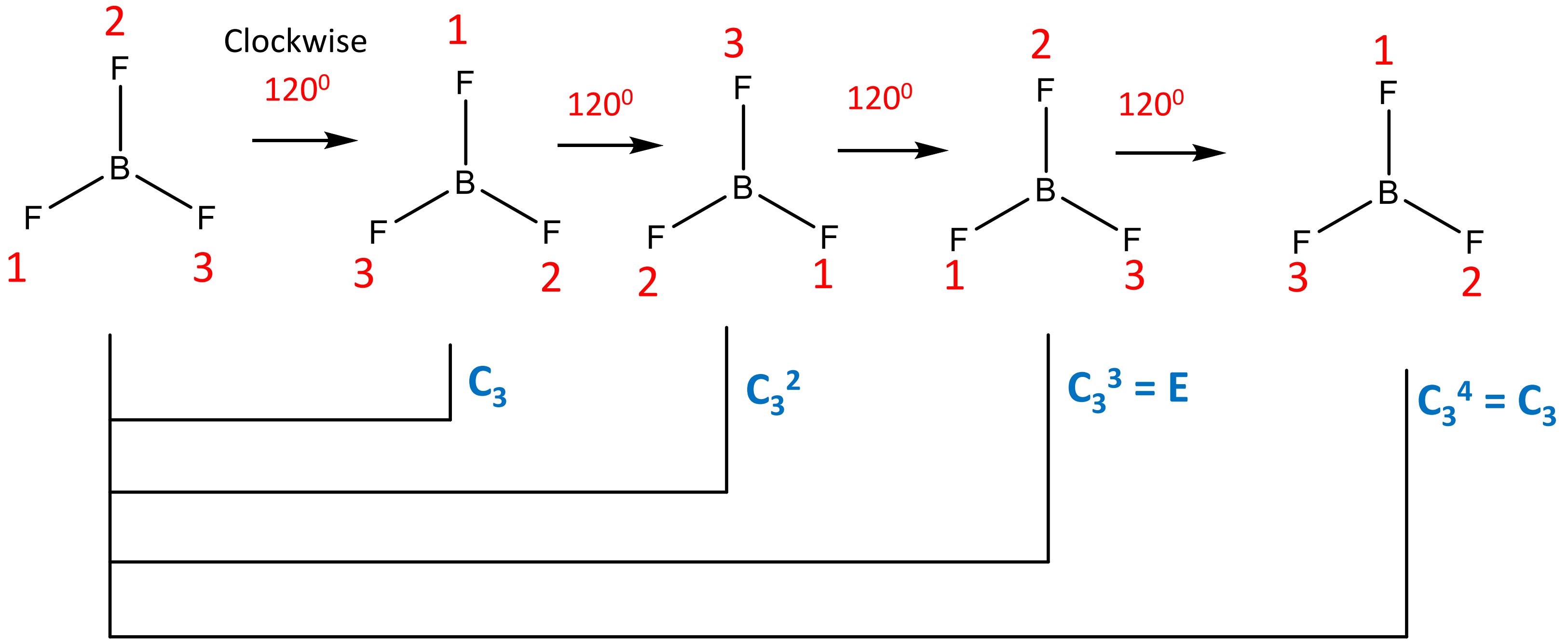
Visualize these proper rotation axes of Benzene molecule

Symmetry operations associated with various Symmetry elements

- An important note:
- In the application of group theory to molecular symmetry, the elements of the 'group' are the symmetry operations and not the symmetry elements.
- So it is very important to be familiar with the symmetry operations associated with each symmetry element
- **We have already seen that identity E can generate only one operation**

Symmetry operations associated with Proper rotation axis C_n

- **Consider the following symmetry operations**



It is also evident that

$C_3^4 = C_3$

$C_3^5 = C_3^2$

$C_3^6 = C_3^3 = E$

and so on

We find that C_3 and C_3^2 are unique operations but $C_3^3 = E$

Therefore, the 3 operations generated by C_3 axis are C_3 , C_3^2 and E

- In general, a C_n axis can generate n operations namely C_n, C_n^2, C_n^3 … C_n^n

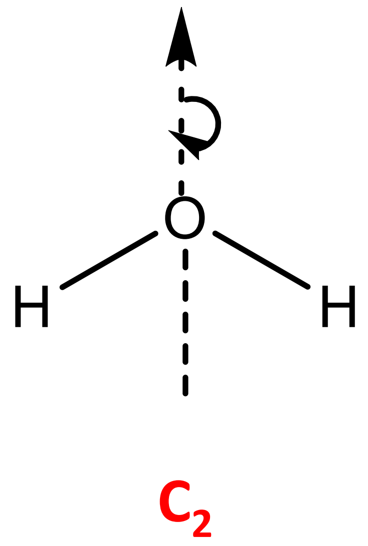
- Also $C_n^n = E$ whether n is odd or even.

$C_n^{n+1} = C_n$

$C_n^{n+2} = C_n^2$ and so on

Operations generated by some common C_n axes

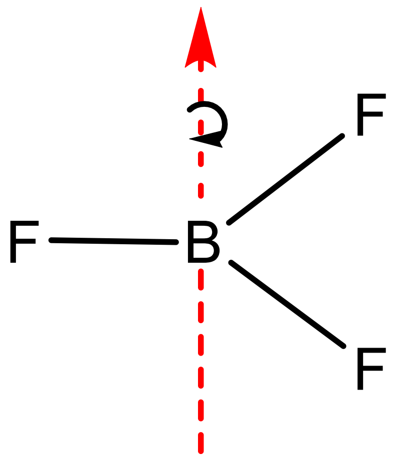
C_2 axis



2 Operations

$$C_2 \text{ and } C_2^2 = E$$

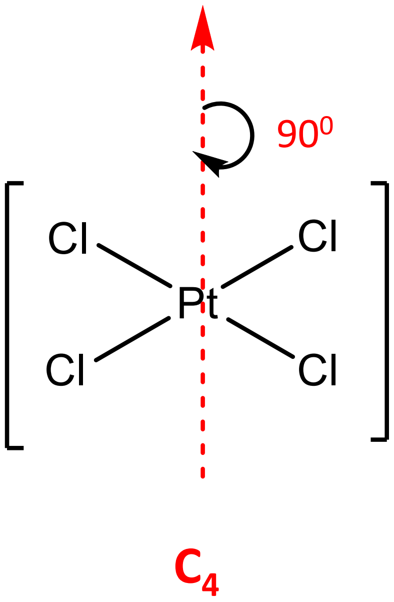
C_3 axis



3 Operations

C_3 , C_3^2 and C_3^3 = E

C_4 axis



4 Operations

$$C_4\,,\ C_4^{\,2}\,,\ C_4^{\,3}\ \text{and}\ C_4^{\,4} = E$$

$C_4^{\,2}$ stands for rotation through 90^0 twice (90x2) which is same as rotation through 180^0 once. That is C_2

$$C_4^{\,2} = C_2$$

Therefore, the four operations of a C_4 axis are

$$\boxed{C_4\,,\ C_2\,,\ C_4^{\,3}\ \text{and}\ C_4^{\,4} = E}$$

VERIFY THIS DIAGRAMMATICALLY.

HINT: In the diagram, number the four Cl atoms, carry out $C_4^{\,2}$ and C_2 operations separately and compare the two resulting configurations

The four operations of a C_4 axis are

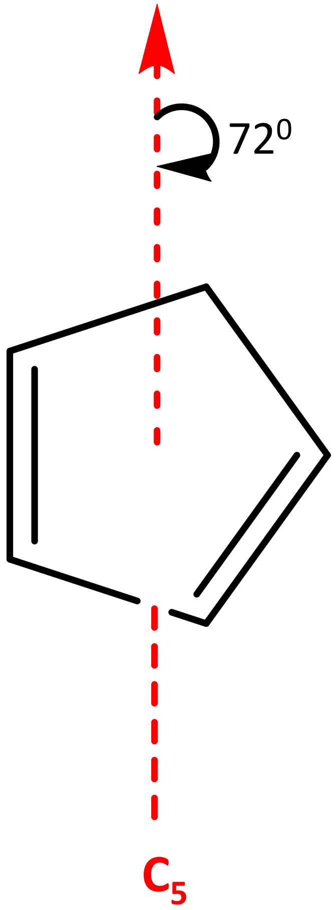
C_4 , C_2 , C_4^3 and $C_4^4 = E$

Of these 4 operations, C_2 and E are operations of a C_2 axis

That means the C_4 axis is also a C_2 axis

In other words, the C_4 axis is coincident with a C_2 axis

C_5 axis



5 Operations

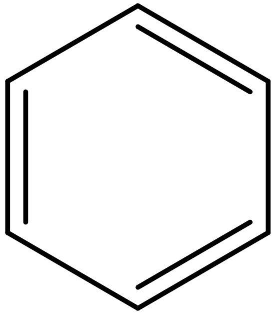
C_5, C_5^2, C_5^3, C_5^4 and $C_5^5 = E$

These operations cannot be written in any other way

C_6 axis

6 Operations

$$C_6,\ C_6^2,\ C_6^3,\ C_6^4,\ C_6^5 \text{ and } C_6^6 = E$$



Some of these operations may be written in other simpler forms

C_6^2 stands for rotation through 60^0 twice (60x2) which is same as rotation through 120^0 once. That is C_3

$$C_6^2 = C_3$$

C_6^3 stands for rotation through 60^0 three times (60x3) which is same as rotation through 180^0 once. That is C_2

$$C_6^3 = C_2$$

C_6^4 stands for rotation through 60^0 four times (60x4) which is same as rotation through 240^0 once or rotation through 120^0 twice (120x2) That is C_3^2

$$C_6^4 = C_3^2$$

Therefore, the six operations of a C_6 axis are

$$C_6,\ C_3,\ C_2,\ C_3^2,\ C_6^5 \text{ and } C_6^6 = E$$

VERIFY THIS DIAGRAMMATICALLY.

The six operations of a C_6 axis are

C_6 , C_3 , C_2, C_3^2, C_6^5 and $C_6^6 = E$

Of these 6 operations, C_3 , C_3^2 and E are operations of a C_3 axis

That means the C_6 axis is also a C_3 axis

In other words, the C_6 axis is coincident with a C_3 axis

In general, if an even order C_n axis exists, then a $C_{n/2}$ axis should exist independently

Note that the C_6 axis is also coincident with a C_2 axis