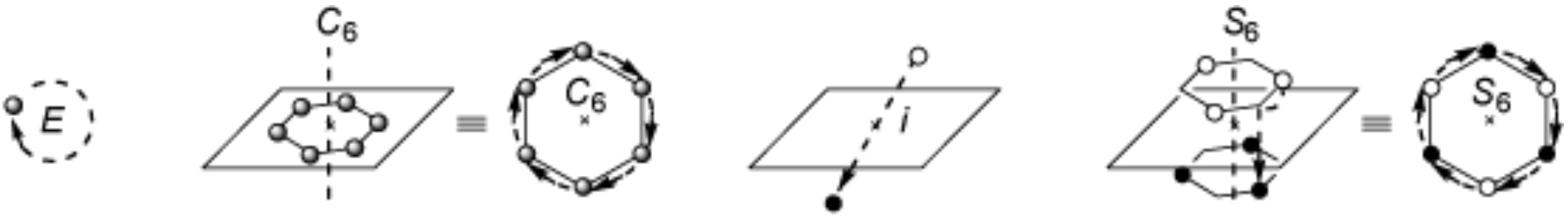
POINT GROUPS

MFT Chapter 4

Symmetry operations

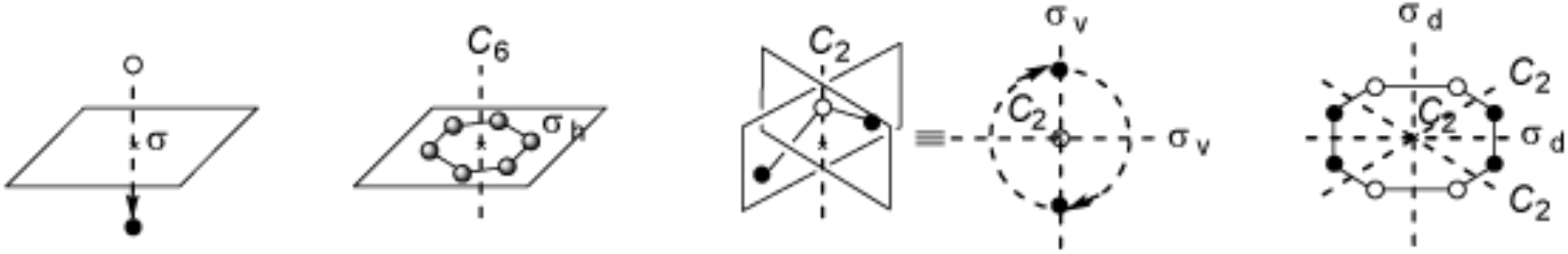


identity
E

n-fold rotation axis
C_n

center of inversion
i

n-fold improper rotation
S_n



mirror plane
σ

mirror plane
σ_h

mirror plane
σ_v

mirror plane
σ_d

Point groups

- Every molecule has a set of symmetry operations associated with it (even if it is only E!)
- The complete set of symmetry operations that describe a molecule is called a Point Group

- Within a Point group, every possible product of two operations in the set is also an operation in the set

- Example: H_2O

Point groups

FOUR RULES:

1) A•B = C (multiplying two operations yields a third operation in the group)
2) Multiplication is associative (A•B)C = A(B•C)
3) There is an operation such that E•X = X•E =X (i.e. the identity)
4) Any operation (R) must have a reciprocal/ inverse operation (R^{-1}) such that $R \bullet R^{-1} = E$

Schoenfleis Notation

- This notation is a systematic way to name point groups
- The notation often reflects the notation for symmetry operations contained in the group
- We will use a step-by-step method to identify the point groups of molecules and objects

Steps to identify a point group

1) Does the molecule belong to special groups with very **low or high symmetry**?
2) If not, what is the principal rotation axis (**C_n** with highest n)?
3) Are there **C_2 axes perpendicular** to the principal rotation axis?
4) Is there a **σ_h** perpendicular to the principal rotation axis?
5) Are there mirror planes that contain the prinicpal rotation axis (**σ_v** or **σ_d**)?
6) Is there a collinear **S_{2n}** axis with the principal C_n axis?

1) Does the molecule belong to special groups with very **low or high symmetry**?

TABLE 4.2 Groups of Low Symmetry

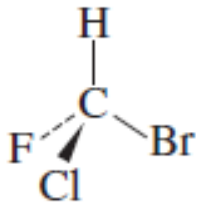
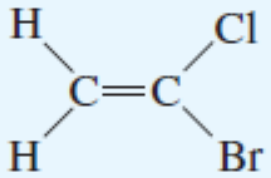
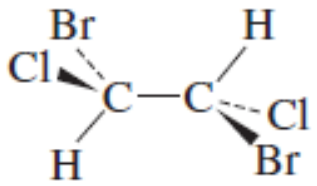
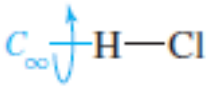
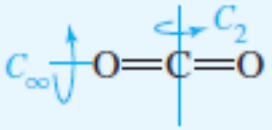
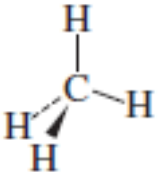
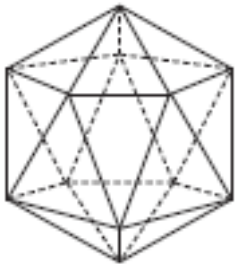
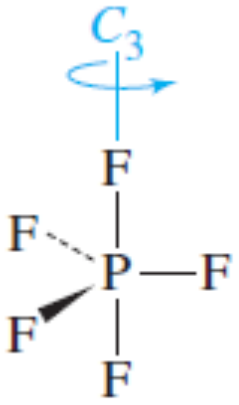
Group	Symmetry	Examples	
C_1	No symmetry other than the identity operation	CHFClBr	
C_s	Only one mirror plane	$H_2C{=}CClBr$	
C_i	Only an inversion center; few molecular examples	HClBrC—CHClBr (staggered conformation)	

TABLE 4.3 Groups of High Symmetry

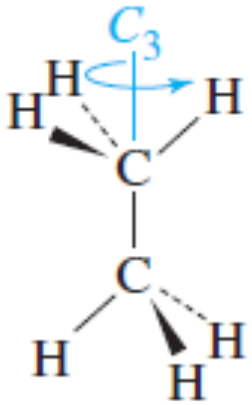
Group	Description	Examples
$C_{\infty v}$	These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They do not have a center of inversion.	
$D_{\infty h}$	These molecules are linear, with an infinite number of rotations and an infinite number of reflection planes containing the rotation axis. They also have perpendicular C_2 axes, a perpendicular reflection plane, and an inversion center.	
T_d	Most (but not all) molecules in this point group have the familiar tetrahedral geometry. They have four C_3 axes, three C_2 axes, three S_4 axes, and six σ_d planes. They have no C_4 axes.	
O_h	These molecules include those of octahedral structure, although some other geometrical forms, such as the cube, share the same set of symmetry operations. Among their 48 symmetry operations are four C_3 rotations, three C_4 rotations, and an inversion.	
I_h	Icosahedral structures are best recognized by their six C_5 axes, as well as many other symmetry operations—120 in all.	 $B_{12}H_{12}^{2-}$ with BH at each vertex of an icosahedron

2) If not, what is the principal rotation axis (**C_n** with highest n)?

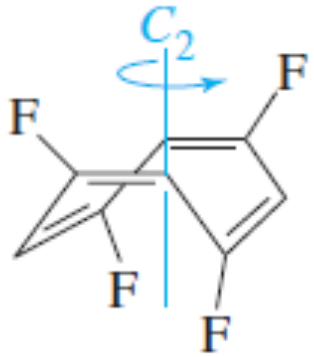
The *n* in C_n will determine the subscript in the Point Group name



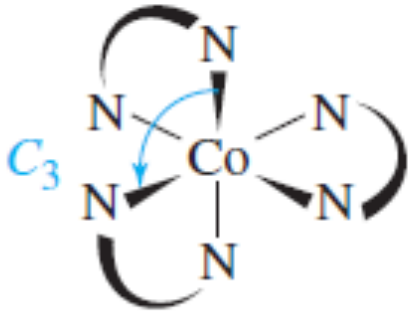
PF_5



H_3CCH_3



1,3,5,7-tetrafluoro-cyclooctatetraene



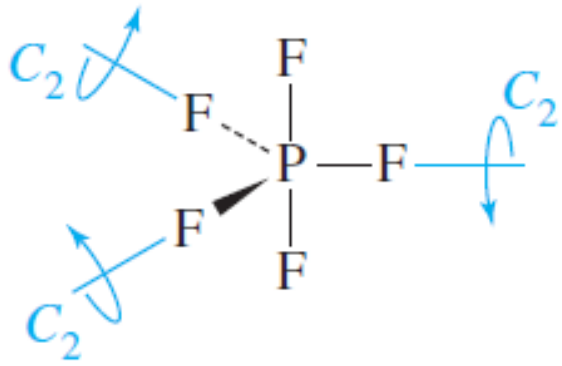
C_3 perpendicular to the plane of the page

$[Co(en)_3]^{3+}$

3) Are there **C_2 axes perpendicular** to the principal rotation axis?

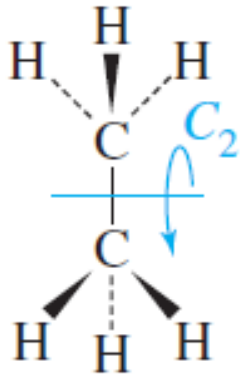
If yes, the point group name will contain ‘D’

If no, the point group name will contain ‘C’



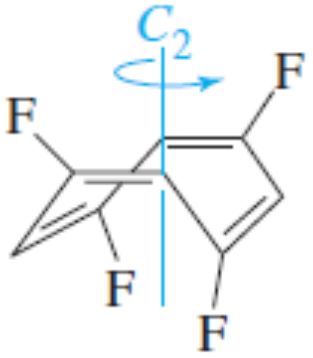
PF_5

Yes



H_3CCH_3

Yes



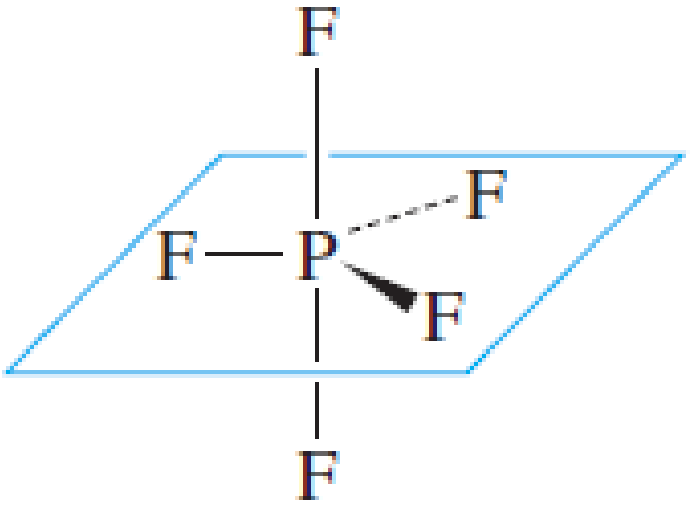
1,3,5,7-tetrafluoro-cyclooctatetraene

No

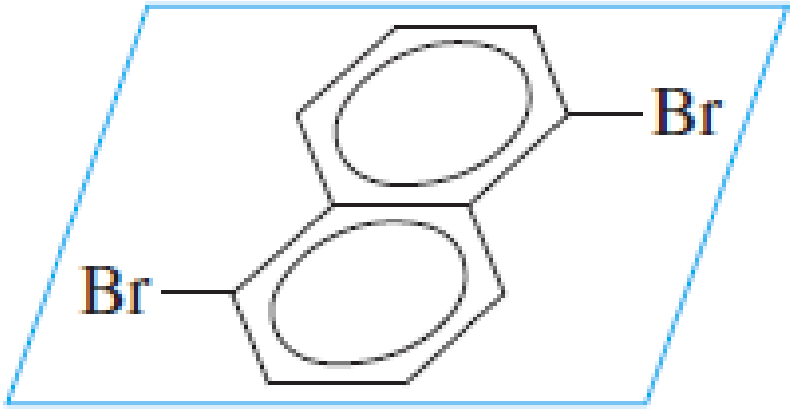
4) Is there a σ_h perpendicular to the principal rotation axis?

If yes, the point group name will contain a subscript ‘h’

If no, move on to next step.



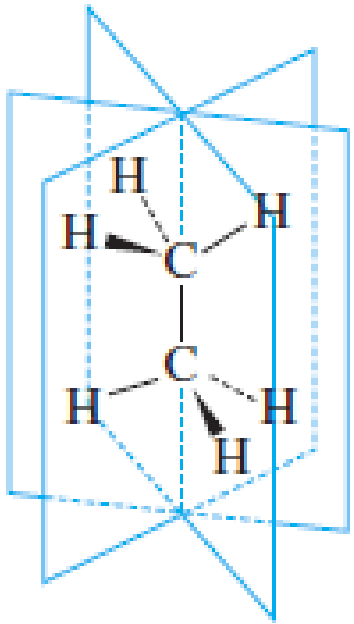
PF_5
Yes
D_{3h}



1,5-dibromonaphthalene
Yes
C_{2h}

5) Are there mirror planes that contain the prinicpal rotation axis (σ_v or σ_d)?

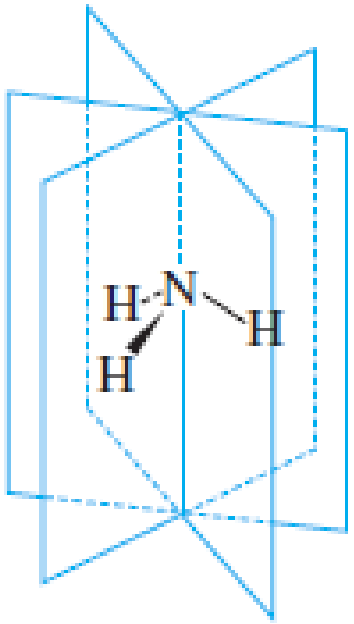
If yes, either a D_{nd} or C_{nv} group



H_3CCH_3

Yes

D_{3d}



NH_3

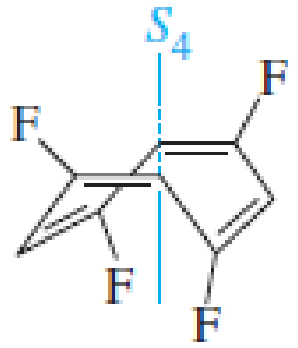
Yes

C_{3v}

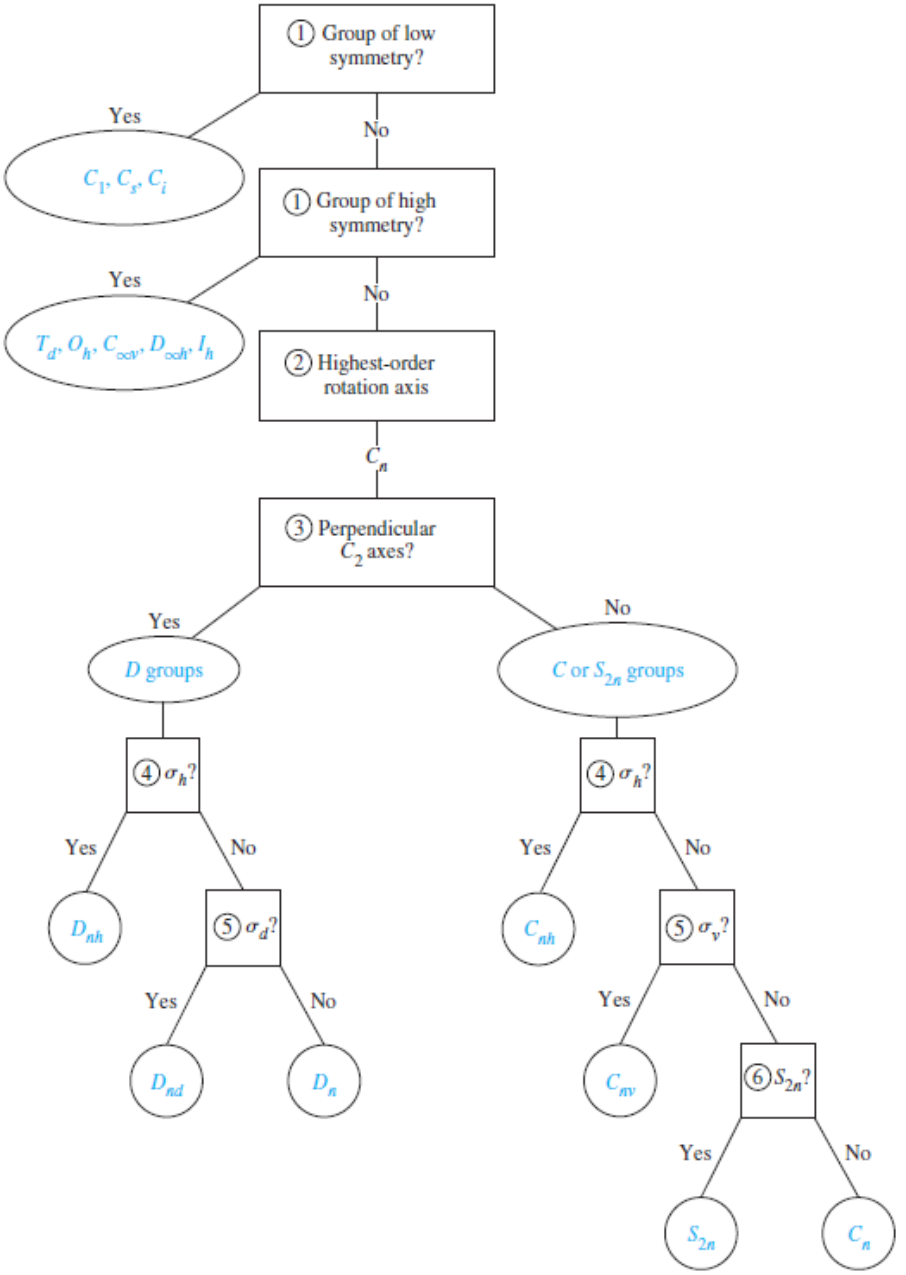
If no, either a D_n group or C_n/S_{2n}

6) Is there a collinear $\mathbf{S_{2n}}$ axis with the principal C_n axis?

If yes, then S_{2n} group
If no, then C_n group

S_{2n} ?
H_2O_2
No C_2
 1,3,5,7,-tetrafluoro-cyclooctatetraene
Yes S_4

Point group flow chart



Point group short cuts