Molecular Symmetry – Point groups

Symmetry props. of molecules closely tied to many properties

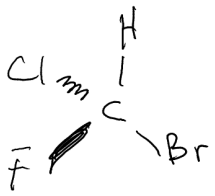
① Electronic Structure + MO Structure
② Reactivity
③ Molecular Vibrations + EAS

We characterize symmetry of molecules by placing them into point groups

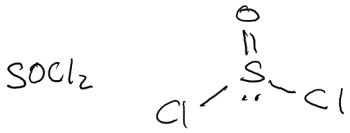
↳ Point Group – defines a collection of symmetry elements

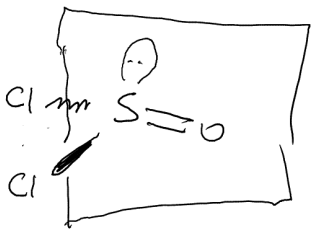
↳ point at which at which all symmetry elements intersect

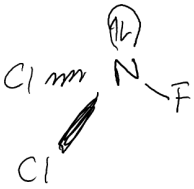
C_1 (E) No Symmetry



C_s (σ) one mirror plane exists

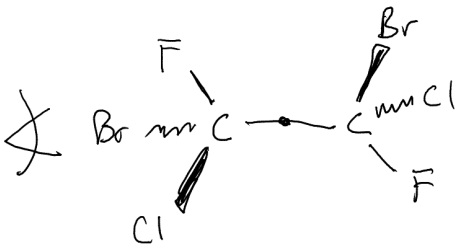




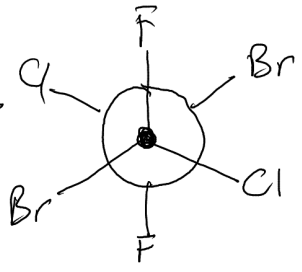


C_i (i) inversion center

dichlorodifluoroethane



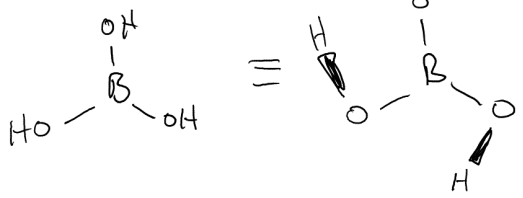
≡

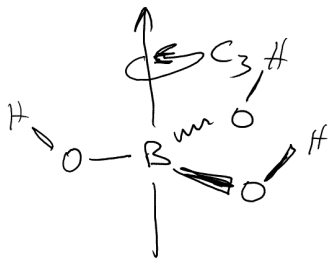


Newman Projection

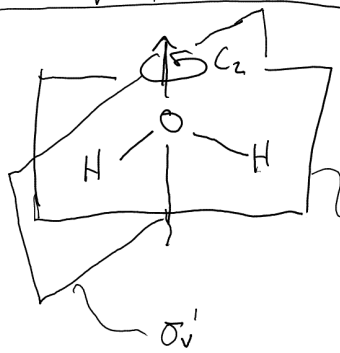
C_n Rotation Axis

$B(OH)_3$





C_{nv} Rotation Axis ($n \times \sigma_v$)



$2 \times \sigma_v$

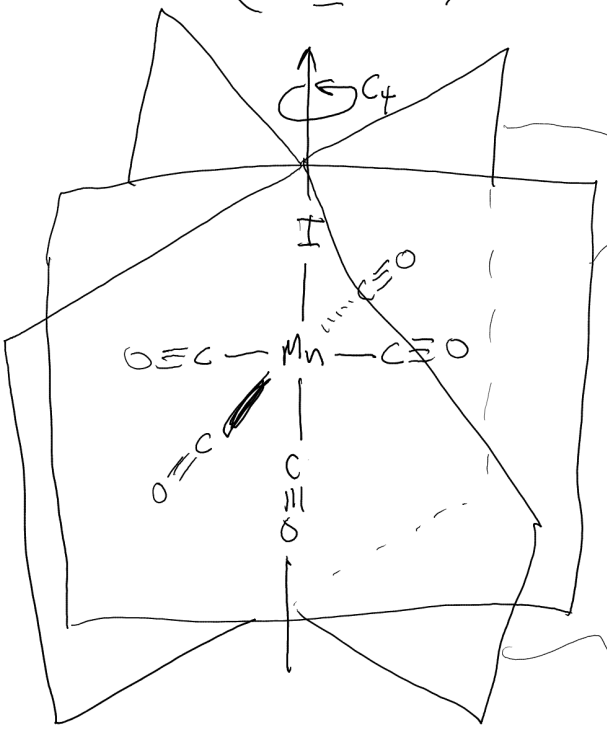
vertical mirror plane contains C_n

horizontal mirror plane $\perp C_n$

σ_h

σ_v (contains the most atoms 3)

σ_v' (contains fewer atoms 1)



4 vertical mirror planes

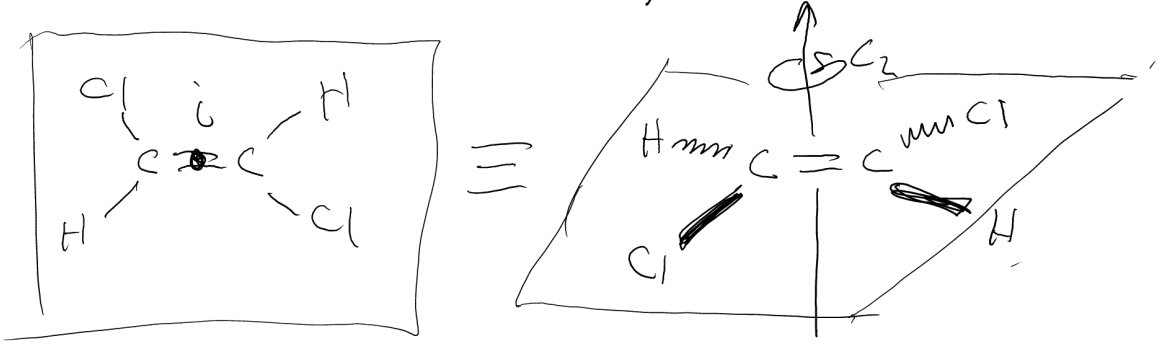
σ_v (8 atoms)

σ_v (8 atoms

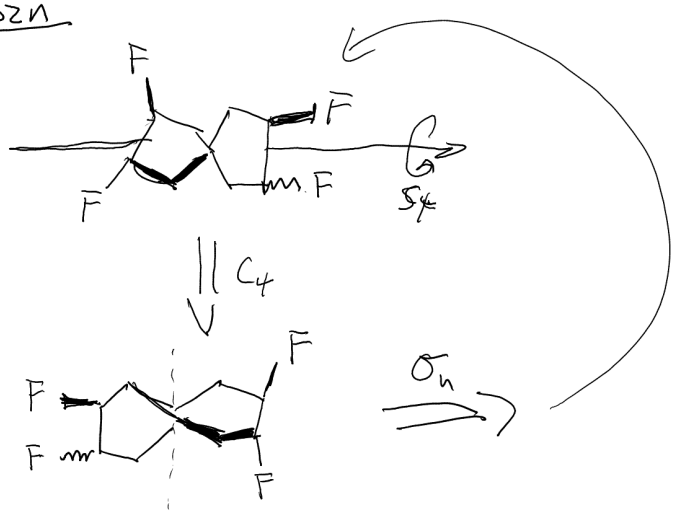
σ_v' (4 atoms) $\equiv \sigma_d$

$C_2 + \sigma_h \rightarrow S_2$

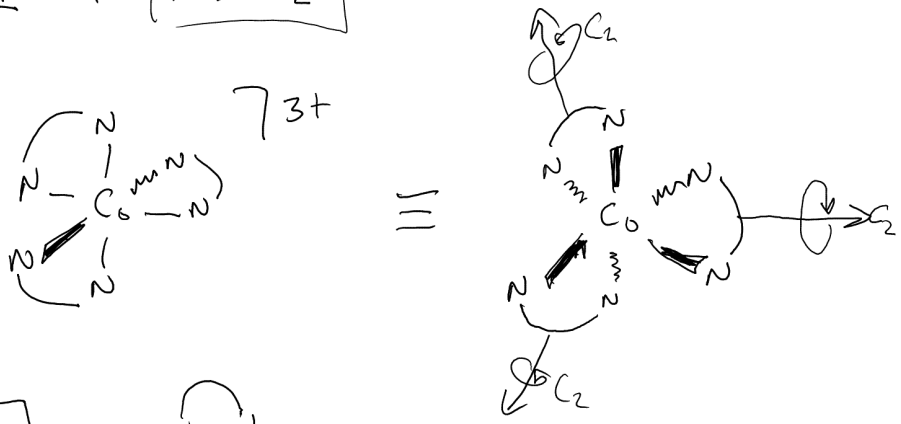
C_{nh} $C_n + \sigma_h$ ($\perp$ to C_n)

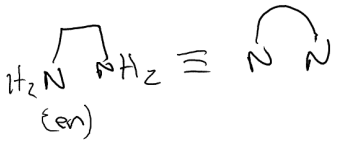


S_{2n}



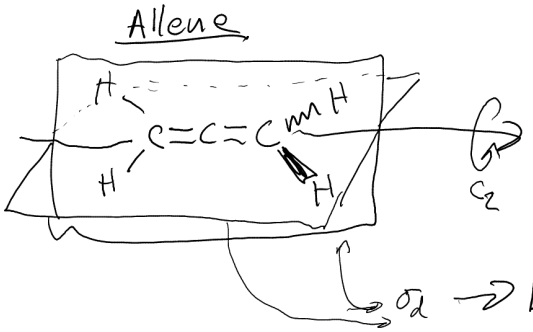
D_n C_n $n \perp C_2$

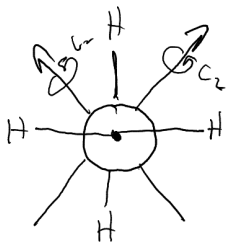




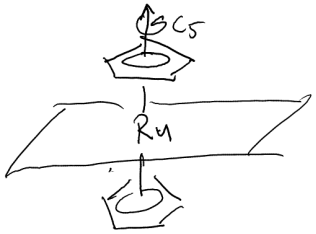
D_{nd} C_n $n \perp C_2$ $n\sigma_d$

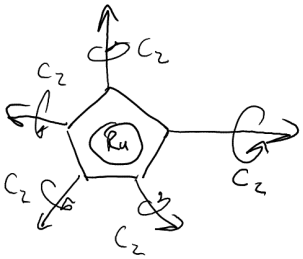
Allene





D_{nh} C_n, $n \perp C_2$, σ_h



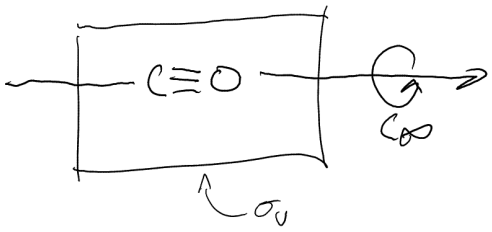


 ≡ 6e⁻ Aromatic System

Ferrocene

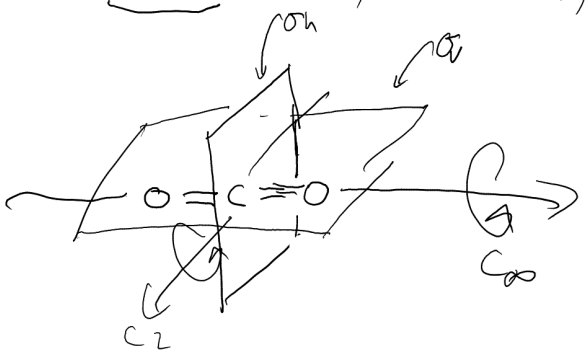
Points of higher Symmetry

$C_{\infty v}$ C_∞, σ_v



C_∞ generates ∞ σ_v

$D_{\infty h}$ C_∞, $\infty \perp C_2$, σ_h, $\infty \sigma_v$



* Any linear molecule w/ an inversion center

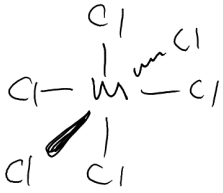
T_d = tetrahedral

$8C_3$, $3C_2$, $6S_4$, $6\sigma_d$

O_h = Octahedral

$8C_3$, $6C_4$, $3C_2$

$6S_4$, $8S_6$, $3\sigma_h$, $6\sigma_d$



I_h = Icosahedral

O, T, I

TABLE 4.2 Groups of Low Symmetry

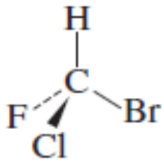
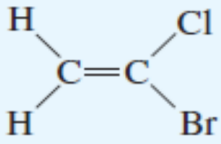
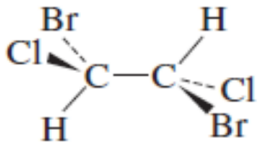
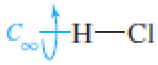
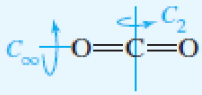
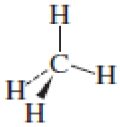
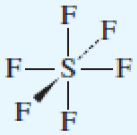
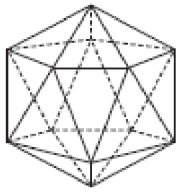
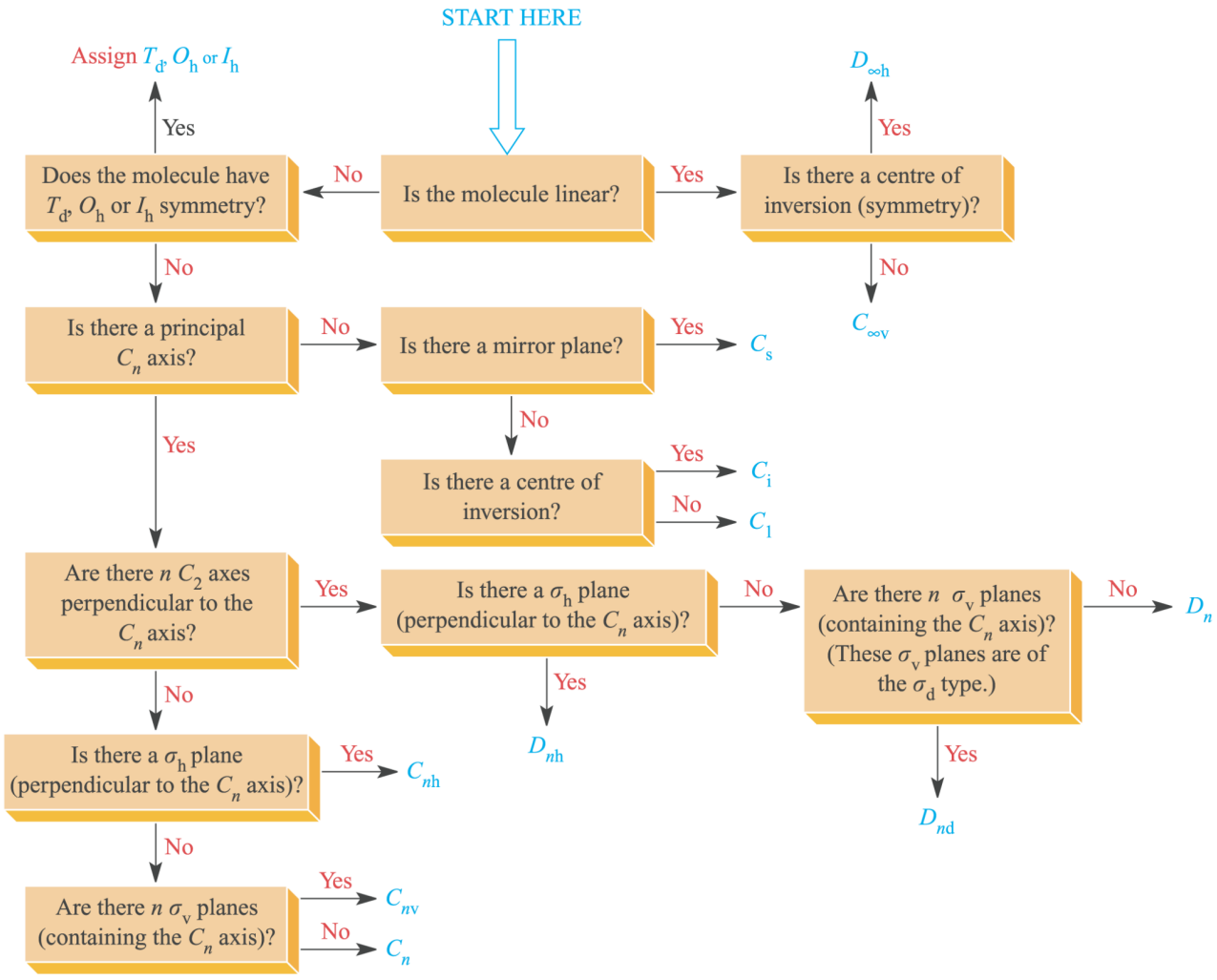
Group	Symmetry	Examples	
C_1	No symmetry other than the identity operation	CHFClBr	
C_s	Only one mirror plane	$H_2C{=}CClBr$	
C_i	Only an inversion center; few molecular examples	HClBrC—CHClBr (staggered conformation)	

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

In addition, there are four other groups, *T*, T_h, *O*, and *I*, which are rarely seen in nature. These groups are discussed at the end of this section.


START HERE
Is the molecule linear?
No
Yes
Does the molecule have T_d, O_h or I_h symmetry?
Yes
Assign T_d, O_h or I_h
Is there a centre of inversion (symmetry)?
Yes
$D_{\infty h}$
No
$C_{\infty v}$
Is there a principal C_n axis?
No
Is there a mirror plane?
Yes
C_s
No
Is there a centre of inversion?
Yes
C_i
No
C_1
Yes
Are there n C_2 axes perpendicular to the C_n axis?
Yes
Is there a σ_h plane (perpendicular to the C_n axis)?
No
Are there n σ_v planes (containing the C_n axis)? (These σ_v planes are of the σ_d type.)
No
D_n
Yes
D_{nh}
Yes
D_{nd}
No
Is there a σ_h plane (perpendicular to the C_n axis)?
Yes
C_{nh}
No
Are there n σ_v planes (containing the C_n axis)?
Yes
C_{nv}
No
C_n

Point group	Characteristic symmetry elements	Comments
C_s	E, one σ plane	
C_i	E, inversion centre	
C_n	E, one (principal) n-fold axis	
C_{nv}	E, one (principal) n-fold axis, n σ_v planes	
C_{nh}	E, one (principal) n-fold axis, one σ_h plane, one S_n-fold axis which is coincident with the C_n axis	The S_n axis necessarily follows from the C_n axis and σ_h plane For $n = 2$, 4 or 6, there is also an inversion centre
D_{nh}	E, one (principal) n-fold axis, n C_2 axes, one σ_h plane, n σ_v planes, one S_n-fold axis	The S_n axis necessarily follows from the C_n axis and σ_h plane For $n = 2$, 4 or 6, there is also an inversion centre
D_{nd}	E, one (principal) n-fold axis, n C_2 axes, n σ_v planes, one S_{2n}-fold axis	For $n = 3$ or 5, there is also an inversion centre
T_d		Tetrahedral
O_h		Octahedral
I_h		Icosahedral

http://symmetry.otterbein.edu/tutorial/pointgroups.html

http://www.reciprocalnet.org/edumodules/symmetry/pointgroups/index.html