Point Groups of Molecules

☞ Chemists in general and spectroscopists in particular use the Schönflies notation; crystallographers use the Hermann-Mauguin notation.

Examples

Schönflies	Hermann-Mauguin
C_1	1
C_s	m
C_2	2
C_{2v}	mm
D_2	222
D_{3h}	$(3/m)mm$

Common Point Groups and Their Principal Operations

Nonrotational Groups	
Symbol	Operations
C_1	E (asymmetric)
C_s	E, σ_h
C_i	E, i

Single-axis Groups	
Symbol	Operations ($n = 2, 3, \ldots, \infty$)
C_n	$E, C_n, \ldots, C_n^{n-1}$
C_{nv}	$E, C_n, \ldots, C_n^{n-1}, n\sigma_v$ ($n/2$ σ_v and $n/2$ σ_d if n even)
C_{nh}	$E, C_n, \ldots, C_n^{n-1}, \sigma_h$
S_{2n}	$E, S_{2n}, \ldots, S_{2n}^{2n-1}$
$C_{\infty v}$	$E, C_\infty, \infty\sigma_v$ (noncentrosymmetric linear)

Dihedral Groups	
Symbol	Operations ($n = 2, 3, \ldots, \infty$)
D_n	$E, C_n, \ldots, C_n^{n-1}, nC_2(\perp C_n)$
D_{nd}	$E, C_n, \ldots, C_n^{n-1}, S_{2n}, \ldots, S_{2n}^{2n-1}, nC_2(\perp C_n), n\sigma_d$
D_{nh}	$E, C_n, \ldots, C_n^{n-1}, nC_2(\perp C_n), \sigma_h, n\sigma_v$
$D_{\infty h}$	$E, C_\infty, S_\infty, \infty C_2(\perp C_\infty), \infty\sigma_v, i$ (centrosymmetric linear)

Common Point Groups and Their Principal Operations - Continued

Cubic Groups	
Symbol	Operations
T_d	E, $4C_3$, $4C_3^2$, $3C_2$, $3S_4$, $3S_4^3$, $6\sigma_d$ (tetrahedron)
O_h	E, $4C_3$, $4C_3^2$, $6C_2$, $3C_4$, $3C_4^3$, $3C_2(= C_4^2)$, i, $3S_4$, $3S_4^3$,$4S_6$, $4S_6^5$, $3\sigma_h$, $6\sigma_d$ (octahedron)
I_h	E, $6C_5$, $6C_5^2$, $6C_5^3$, $6C_5^4$, $10C_3$, $10C_3^2$, $15C_2$, i, $6S_{10}$, $6S_{10}^3$, $6S_{10}^7$, $6S_{10}^9$, $10S_6$, $10S_6^5$, 15σ (icosahedron, dodecahedron)

Cyclic Groups

☞ A cyclic group of order h is generated by taking a single element X through all its powers to $X^h = E$.

$$G = \{X, X^2, \ldots, X^h = E\}$$

✓ All cyclic groups are Abelian.

☞ The C_n and S_{2n} groups are cyclic groups; e.g.,

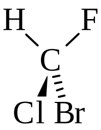
$$C_4 = \{C_4, C_2, C_4^3, E\}$$

$$S_4 = \{S_4, C_2, S_4^3, E\}$$

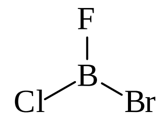
☞ The multiplication tables of cyclic groups "scroll" from row to row and column to column; e.g.,

C_4	E	C_4	C_2	C_4^3
E	E	C_4	C_2	C_4^3
C_4	C_4	C_2	C_4^3	E
C_2	C_2	C_4^3	E	C_4
C_4^3	C_4^3	E	C_4	C_2

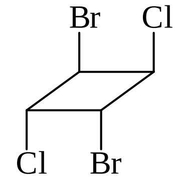
Examples of molecules with various point group symmetries



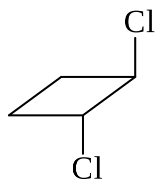
C_1



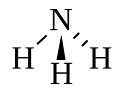
C_s



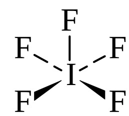
C_i



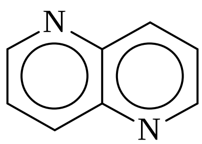
C_2



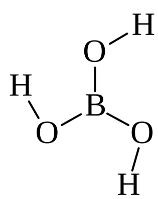
C_{3v}



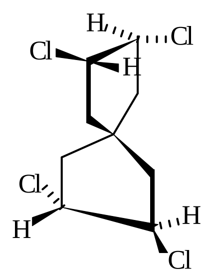
C_{4v}



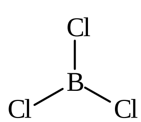
C_{2h}



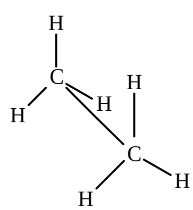
C_{3h}



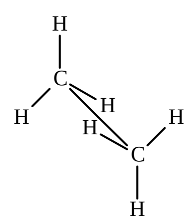
S_4



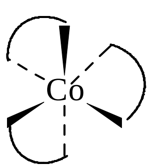
D_{3h}



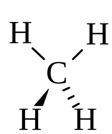
D_{3h}



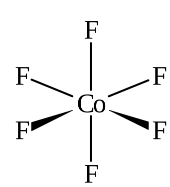
D_{3d}



D_3

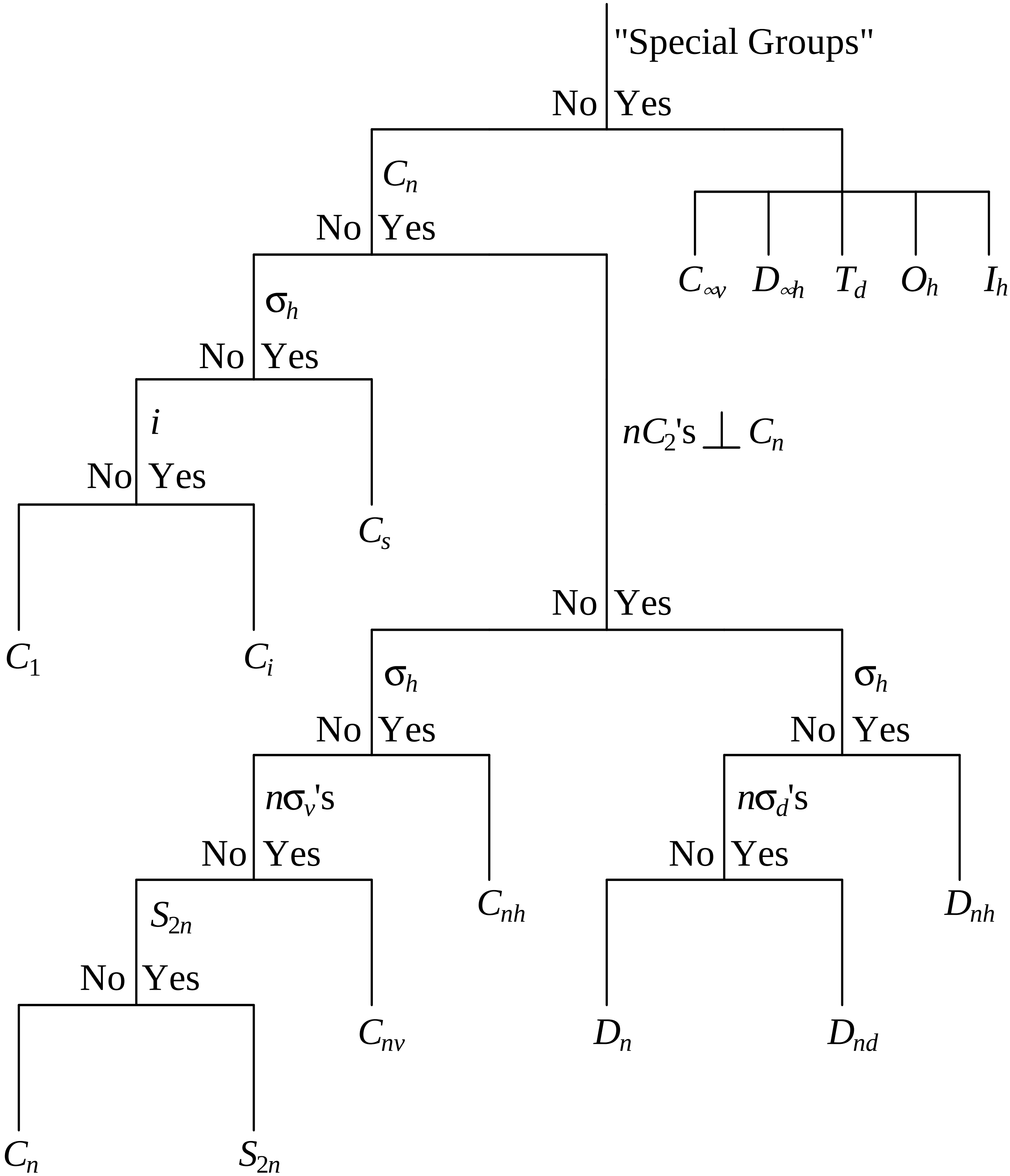


T_d

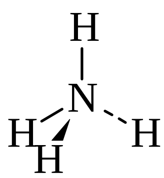


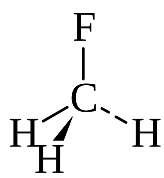
O_h

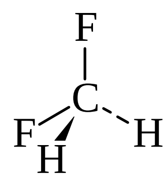
Flow Chart for Point Group Determination

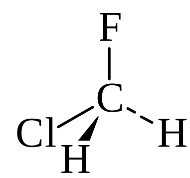


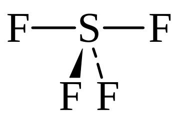
Examples for Point Group Classification

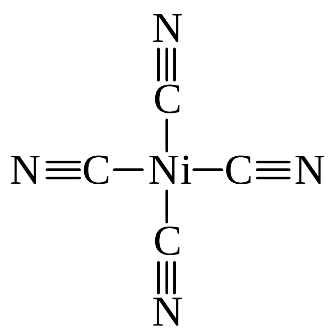


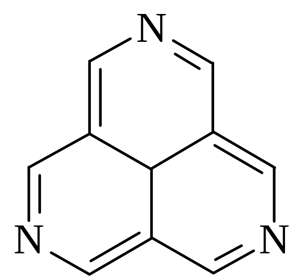


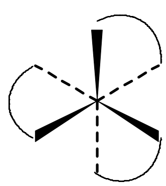


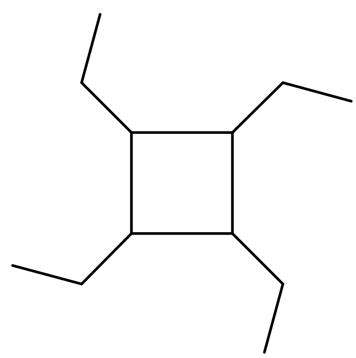




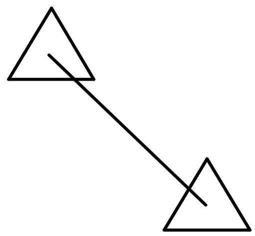




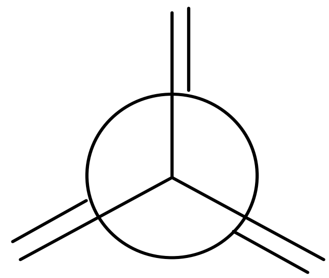


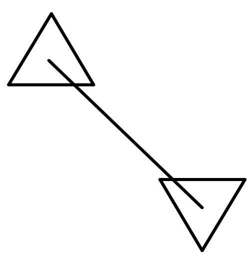


Representation of the Conformations of Ethane

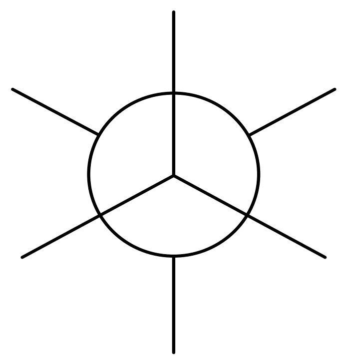


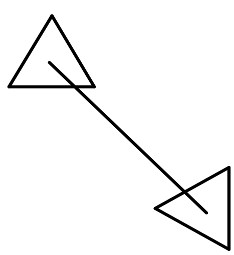
D_{3h}



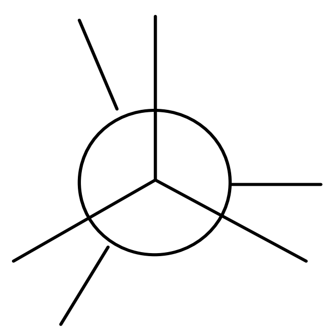


D_{3d}





D_3



Optical Activity and Symmetry

☞ **Chiral** molecules can exist as enantiomers, which will rotate plane-polarized light in opposite directions.

☞ Chiral molecules are **dissymmetric**, but not necessarily asymmetric (point group C_1).

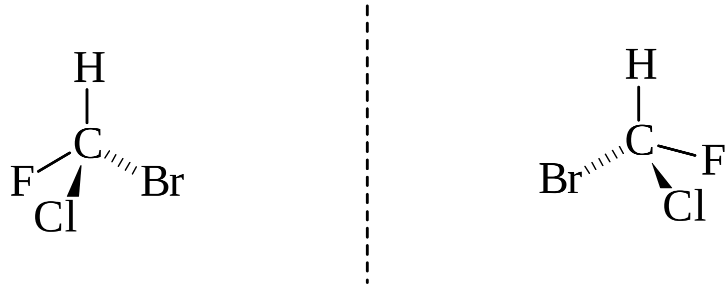
- ✓ Asymmetric molecules are just the least symmetric among all dissymetric molecules.

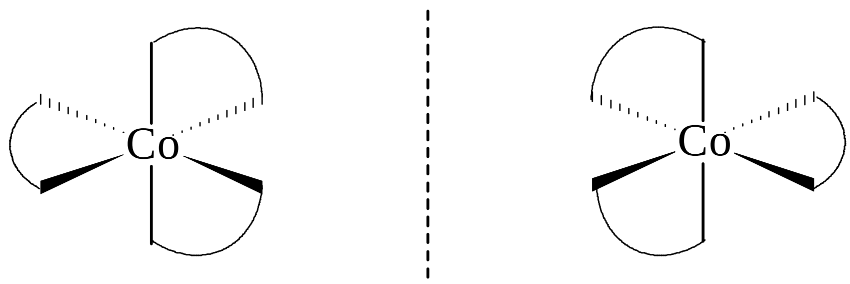
☞ Dissymetric molecules can have no other symmetry but proper rotations (C_n).

☞ Chiral molecules belong to one of the following point groups:

$$C_1, C_n, D_n \ (T, O, I)$$

Enantiomers of Dissymetric Species

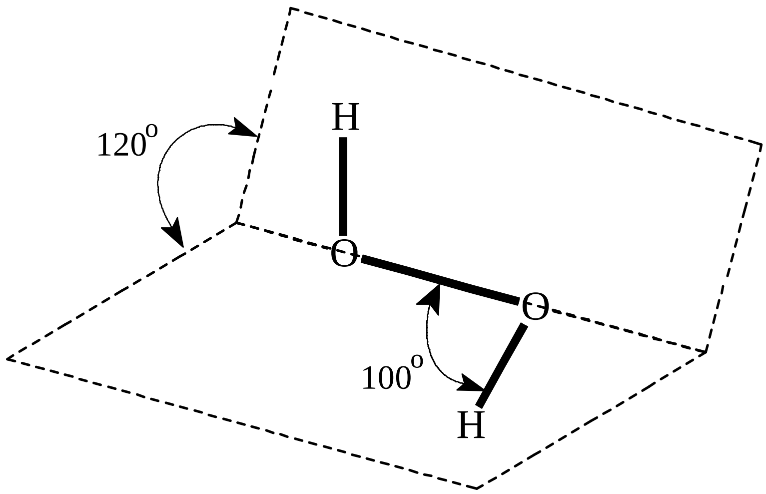




☞ CHFClBr (point group C_1) is asymmetric, but $[Co(en)_3]^{3+}$ (point group D_3) is not.

Non-Chiral Dissymetric Molecules

☞ Sometimes, theoretically possible enantiomeric pairs do not exist, due to stereochemical non-rigidity.



Structure of hydrogen peroxide (point group C_2)