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}	$(3/m)mm$

Table 1.1 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, ..., ∞)
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, ..., ∞)
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)

Table 1.1 - 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

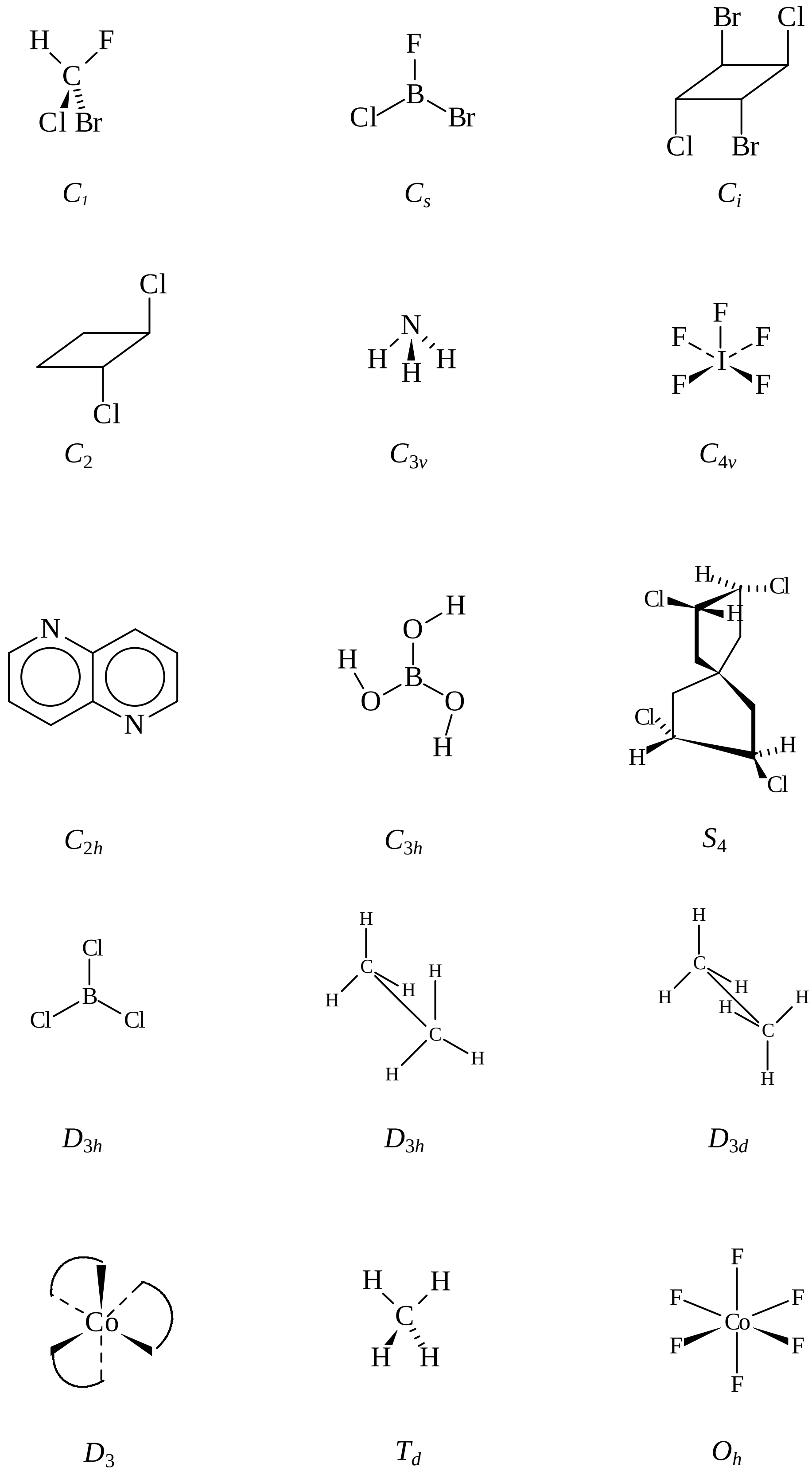


Fig. 1.14 Examples of molecules with various point group symmetries.

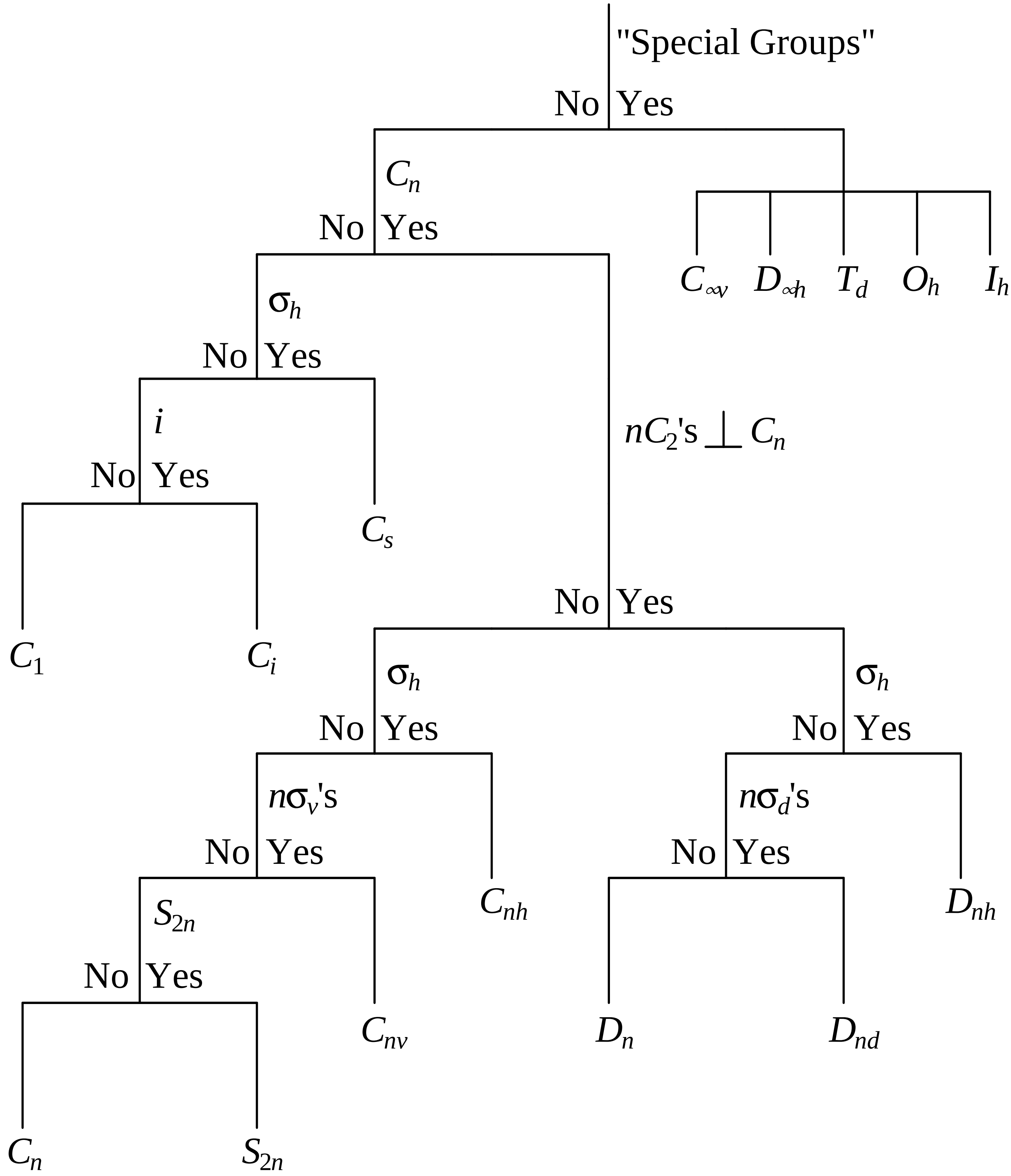
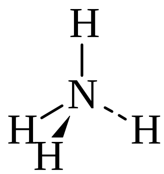
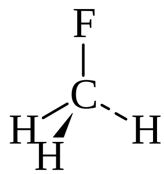
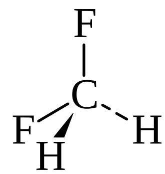


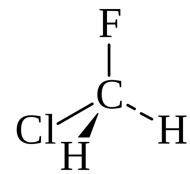
Fig. 1.17 Flow chart for systematically determining the point group of a molecule.

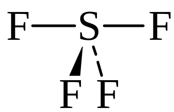
Examples for Point Group Classification

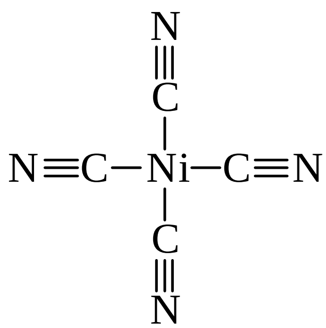


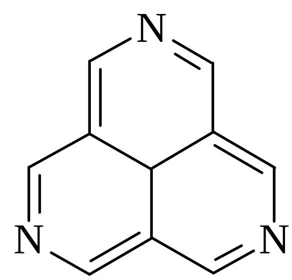


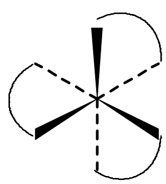


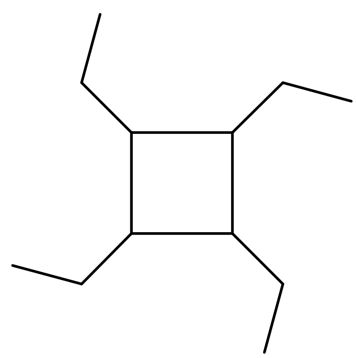












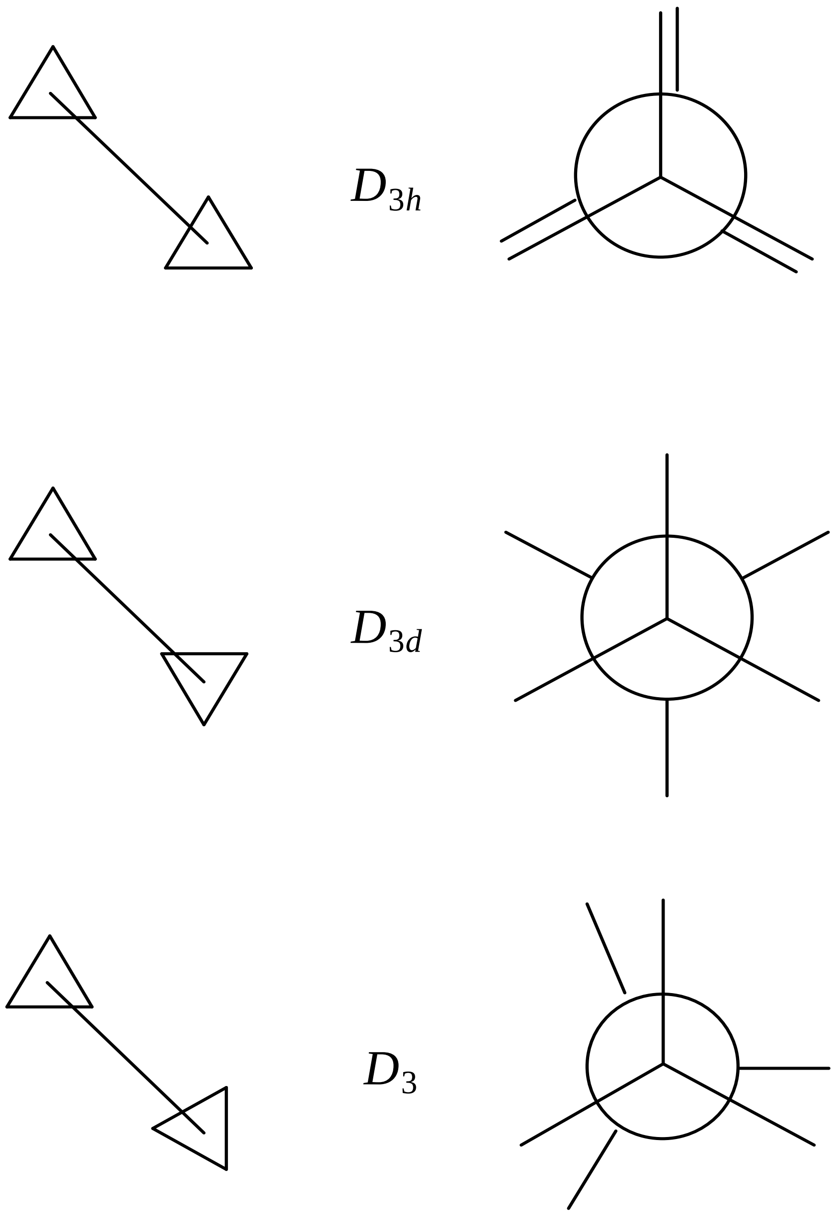


Fig. 1.19 Representations of the three conformations of ethane as two triangles separated along the C_3 axis. The corresponding Newman projections are shown on the right.

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 proper rotations (C_n), but they cannot have any other symmetry.

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

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

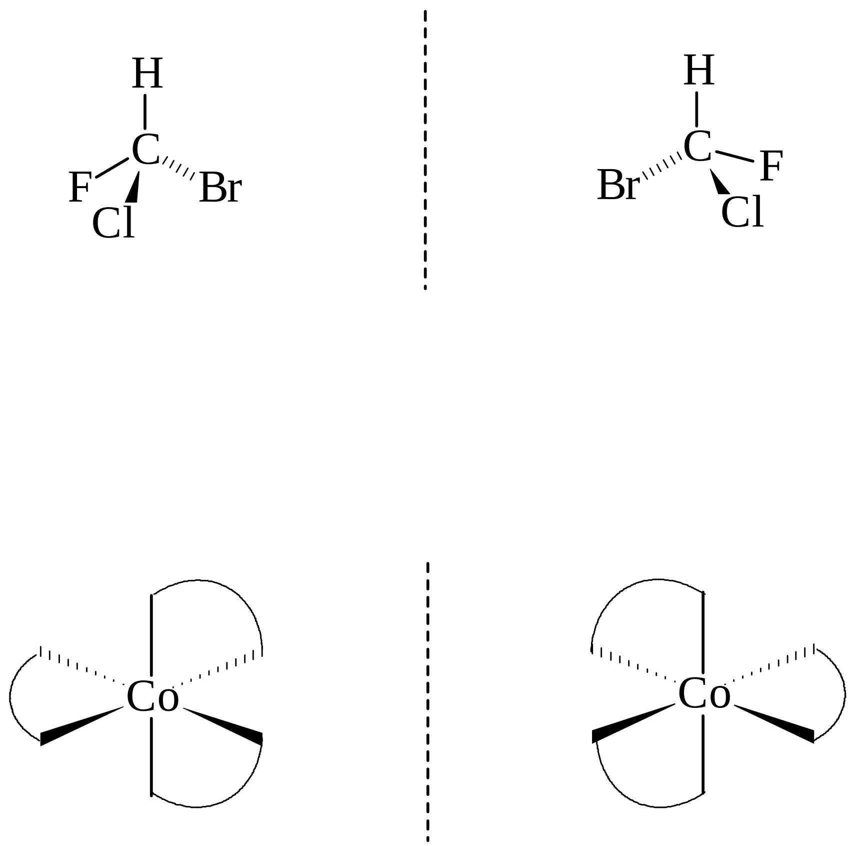


Fig. 1.20 Enantiomers of dissymetric species. CHFClBr (point group C_1) is asymmetric, but $[Co(en)_3]^{3+}$ (point group D_3) is not.

Non-Chiral Dissymetric Molecules

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

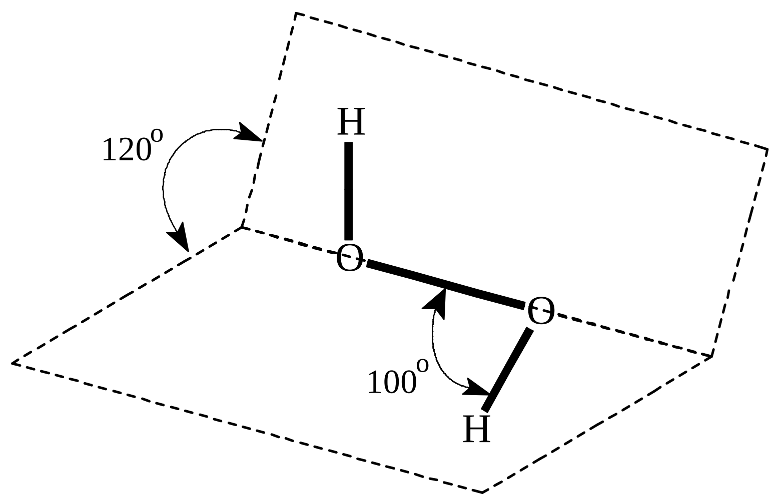


Fig. 1.21 The structure of hydrogen peroxide (point group C_2).