

## 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)	
$C_s$	$E, \sigma_h$	
$C_i$	$E, i$	
Single-axis Groups		
Symbol	Operations	$(n = 2, 3, \dots, \infty)$
$C_n$	$E, C_n, \dots, C_n^{n-1}$	
$C_{nv}$	$E, C_n, \dots, C_n^{n-1}, n\sigma_v$ ( $n/2 \sigma_v$ and $n/2 \sigma_d$ if $n$ even)	
$C_{nh}$	$E, C_n, \dots, C_n^{n-1}, \sigma_h$	
$S_{2n}$	$E, S_{2n}, \dots, S_{2n}^{2n-1}$	
$C_{\infty v}$	$E, C_{\infty}, \infty\sigma_v$ (noncentrosymmetric linear)	
Dihedral Groups		
Symbol	Operations	$(n = 2, 3, \dots, \infty)$
$D_n$	$E, C_n, \dots, C_n^{n-1}, nC_2(\perp C_n)$	
$D_{nd}$	$E, C_n, \dots, C_n^{n-1}, S_{2n}, \dots, S_{2n}^{2n-1}, nC_2(\perp C_n), n\sigma_d$	
$D_{nh}$	$E, C_n, \dots, C_n^{n-1}, nC_2(\perp C_n), \sigma_h, n\sigma_v$	
$D_{\infty h}$	$E, C_{\infty}, S_{\infty}, \infty C_2(\perp C_{\infty}), \infty\sigma_v, i$ (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)
$I_h$	$E, 6C_5, 6C_5^2, 6C_5^3, 6C_5^4, 10C_3, 10C_3^2, 15C_2, i, 6S_{10}, 6S_{10}^3, 6S_{10}^7, 6S_{10}^9, 10S_6, 10S_6^5, 15\sigma$ (icosahedron, dodecahedron)

## Cyclic Groups

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

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

✓ 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.,

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

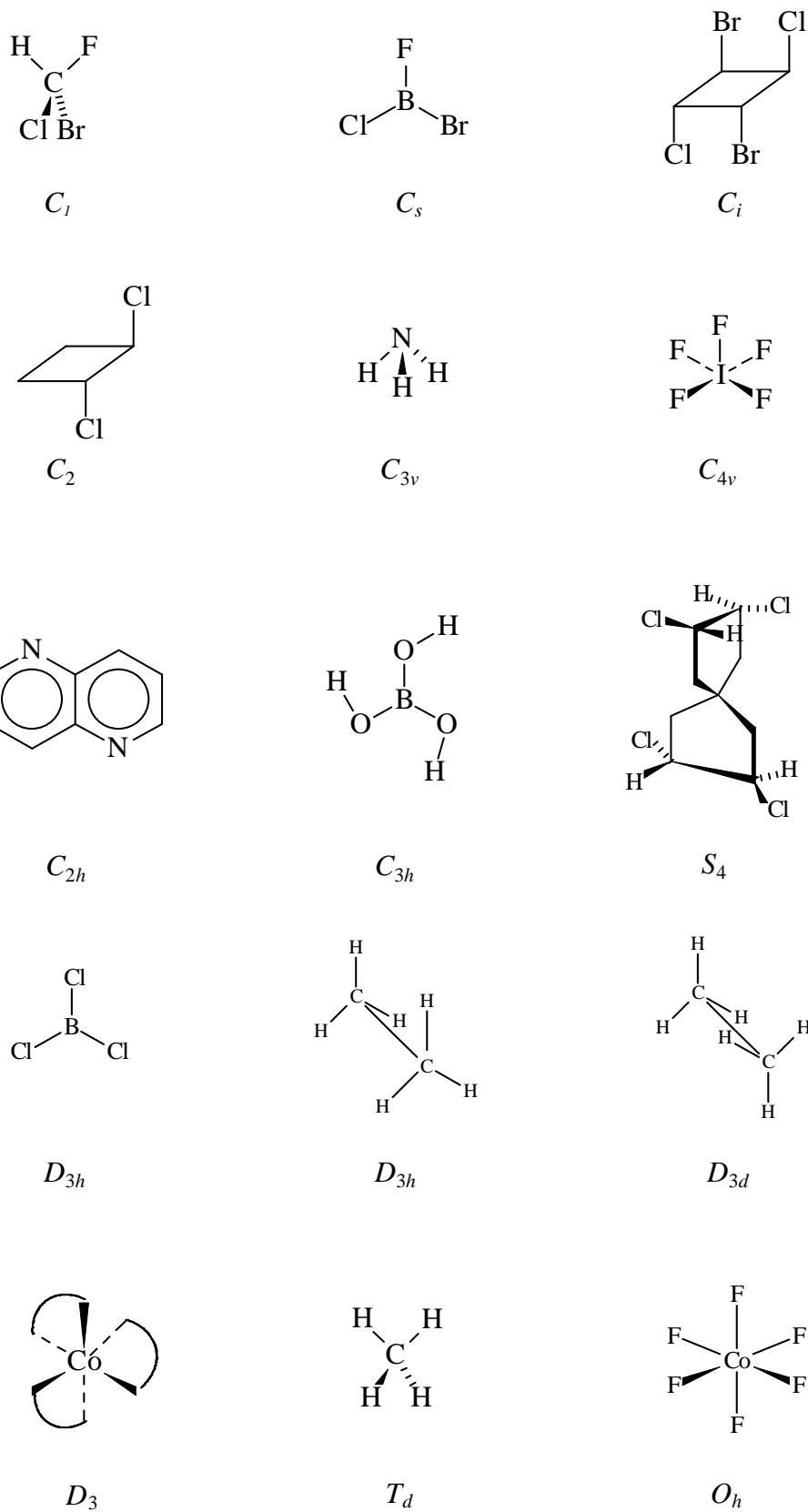


Fig. 1.14 Examples of molecules with various point group symmetries.

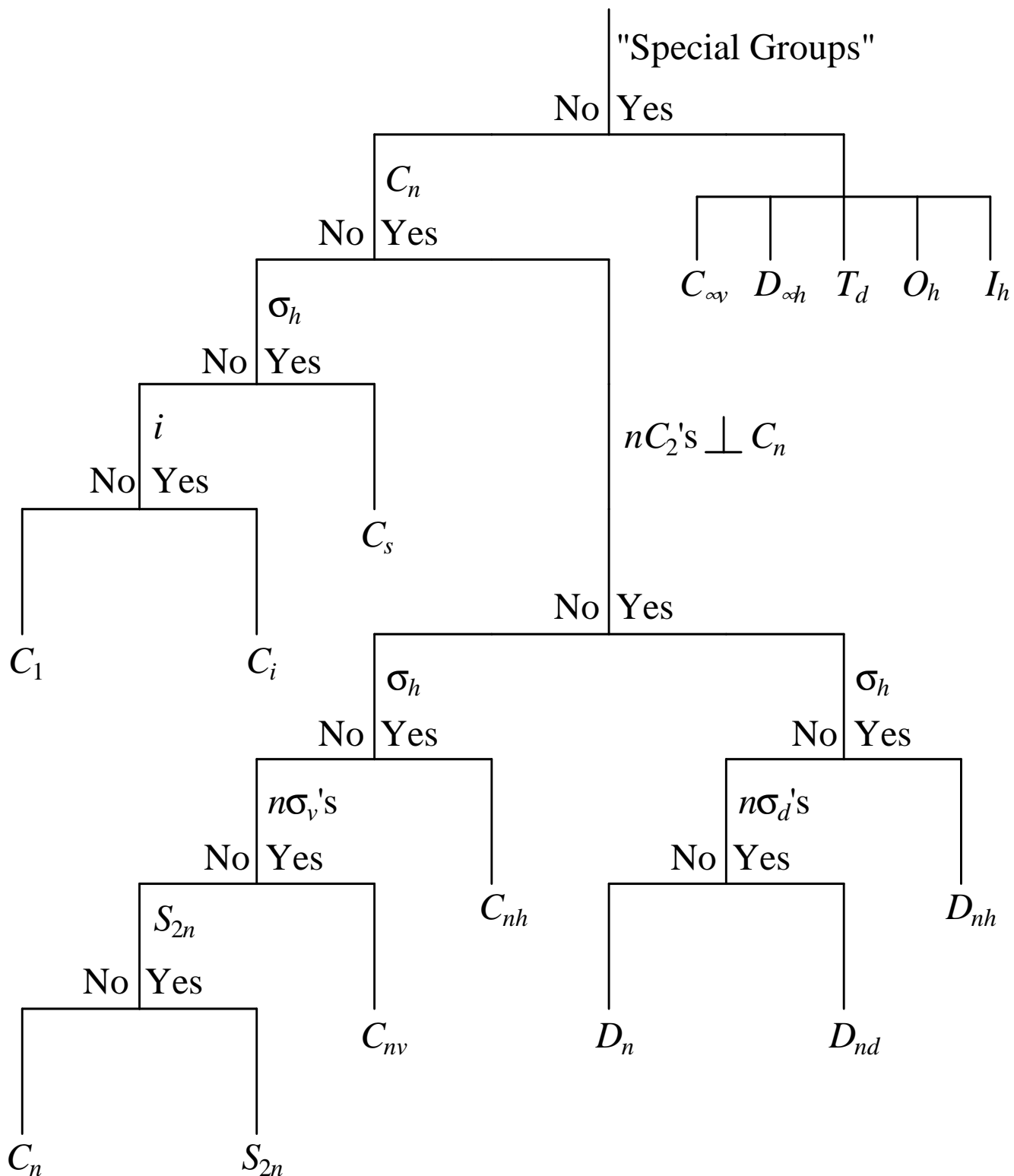
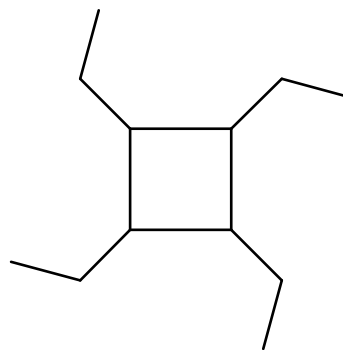
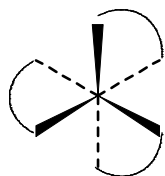
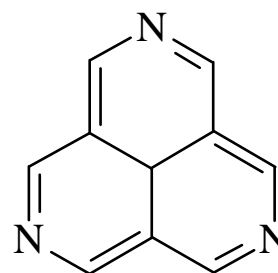
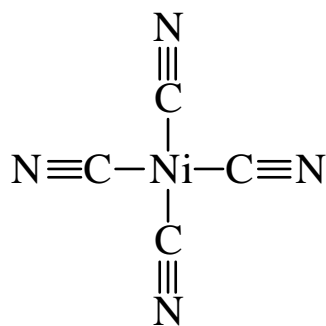
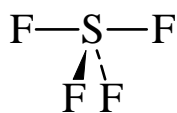
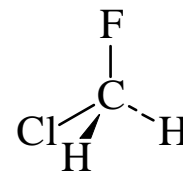
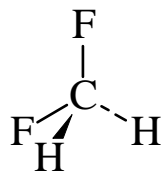
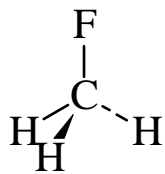
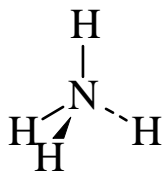


Fig. 1.17 Flow chart for systematically determining the point group of a molecule.

## Examples for Point Group Classification



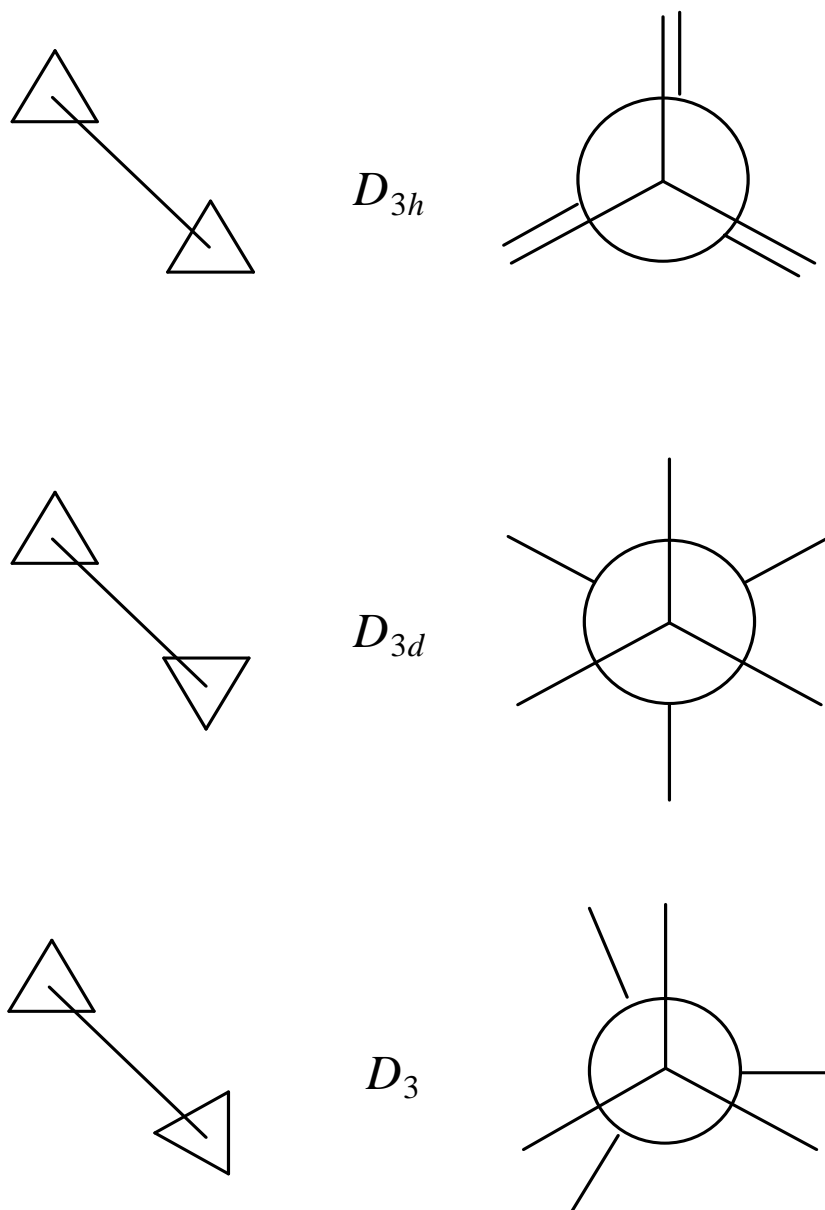


Fig. 1.19 Representations of the three conformations of ethane as two triangles separated along the  $C_3$  axis. The corresponding Newman projections are shown on the right.

## 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 dissymmetric molecules.
- ☞ Dissymmetric molecules can have no other symmetric but proper rotations ( $C_n$ ).
- ☞ Chiral molecules belong to one of the following point groups:

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

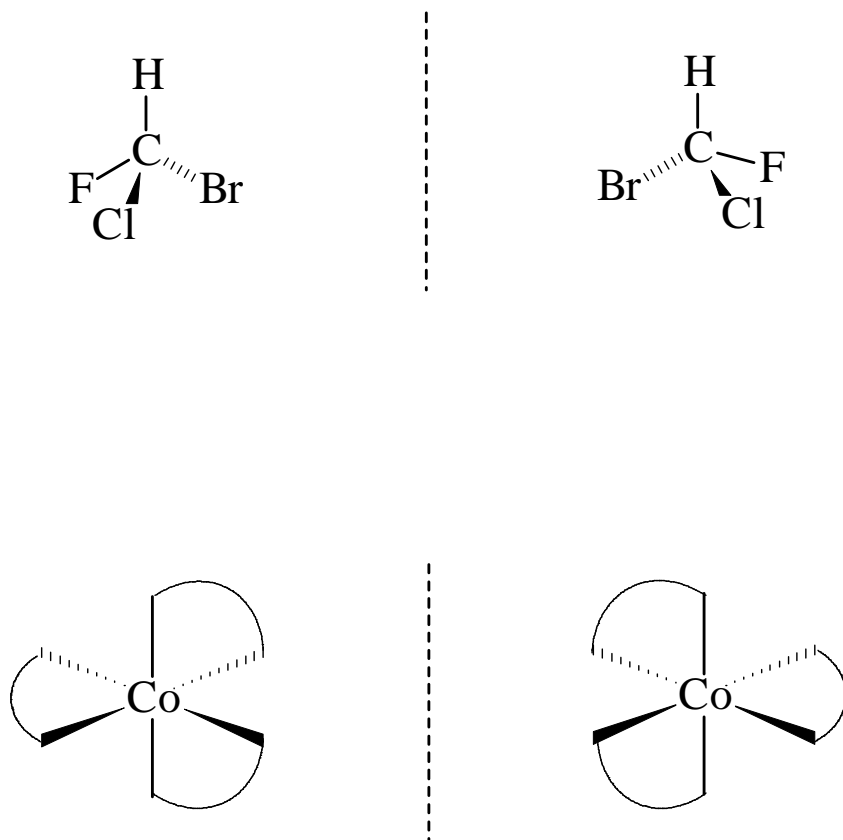


Fig. 1.20 Enantiomers of dissymmetric species.  $\text{CHClBr}$  (point group  $C_1$ ) is asymmetric, but  $[\text{Co}(\text{en})_3]^{3+}$  (point group  $D_3$ ) is not.

## Non-Chiral Dissymmetric Molecules

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

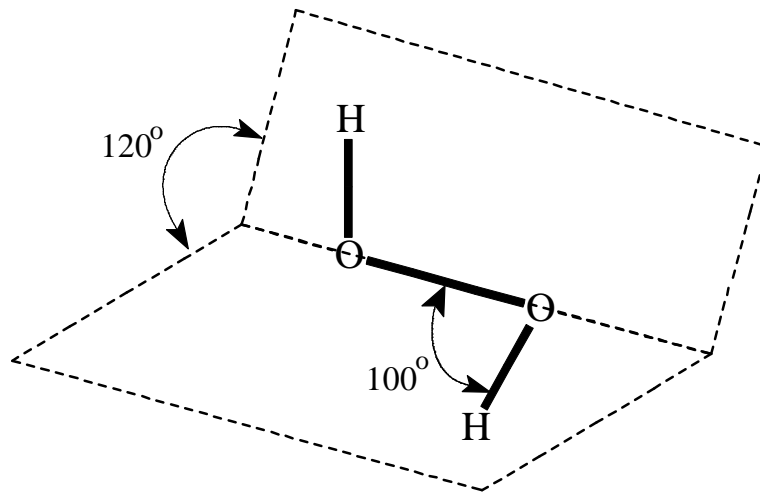


Fig. 1.21 The structure of hydrogen peroxide (point group  $C_2$ ).