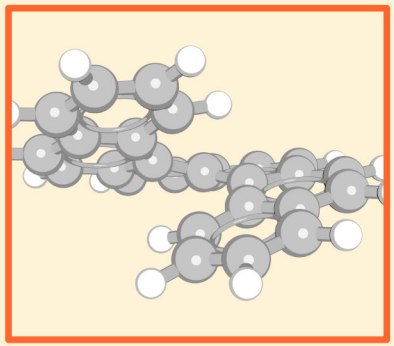
HIGHLIGHTS

- Priority rules (CIP rules)
- Defining configuration of inherently helical molecules (*P* or *M*)
- Defining configuration of conformers (*P* or *M*)
- Defining configuration of axially chiral molecules using both *R*/*S* and *P*/*M* systems



Determining the stereochemical descriptor of a stereogenic centre or molecule with point chirality is a staple of undergraduate organic chemistry. Applying the same process to other forms of chirality, molecules with a stereogenic axis, plane or helix is often ignored. Yet, in asymmetric catalysis many important ligands are either axial (BINAP) or planar chiral (Josiphos), so it is useful to see how the configuration of such molecules is defined.

A problem frequently encountered is that there is more than one descriptor (in other words, practicing chemists ignore recommendations & stick to what they know). This summary looks at helical chirality and axial. The next will tackle planar chirality.

CHEMISTRY CLASSICS

STEREOCHEMICAL DESCRIPTORS

AXIAL AND HELICAL CHIRALITY

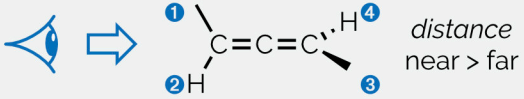
Descriptors for Helical & Axial Chirality

1. Priority rules

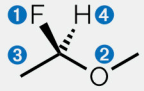
Groups on a stereogenic element must be ranked according to CIP rules.

Highest priority = **1** to **lowest** = **4**.

Rule 0: Proximity - groups closer to the viewer have higher priority.

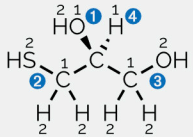


Rule 1: Atomic number - higher atomic number higher priority.



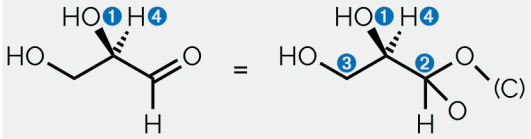
higher atomic number
F > O > C > H

Rule 2: Move along chain - rank atoms in same position until difference found.

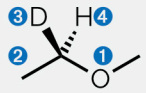


groups	HO	H	CH_2OH	CH_2SH
1st atom	**O**	**H**	C	C
2nd atom			O,H,H	**S**,H,H
priority	1	4	3	2

Rule 3: Multiple bonds - count as multiple single bonds to same atom.

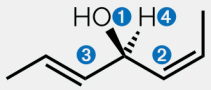


Rule 4: Atomic mass - higher mass of an isotope takes priority.



atomic mass
D > H

Rule 5: Configuration - *Z*, *R* & *M* have higher priority than *E*, *S* & *P*.



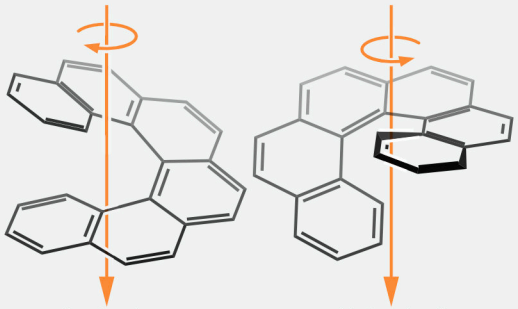
configuration
Z (cis) > *E (trans)*

2. Helical chirality

Helical chirality - some inherently chiral molecules possess helical chirality. To determine stereochemical descriptor:

(i) Identify axis - the stereogenic axis.

(ii) View along axis - rotation clockwise as move from front to back = *P* or *plus* while anticlockwise = *M* or *minus*



clockwise
P plus

anticlockwise
M minus

3. Helicity & conformers

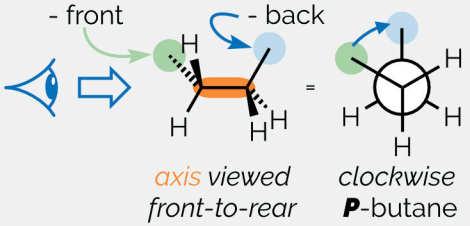
Chiral conformers can be defined as a helix:

(i) Identify axis - the bond being rotated

(ii) Identify highest ranked groups - at front & rear of axis

(iii) Draw arrow connecting groups - start with front group & move to rear by smallest angle

(iv) Assign descriptor - clockwise arrow = P & anticlockwise arrow = M

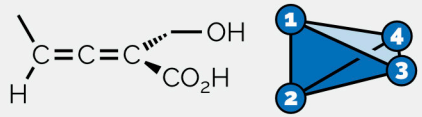


axis viewed front-to-rear

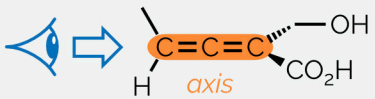
clockwise
P-butane

4. Axial chirality *R*/*S*

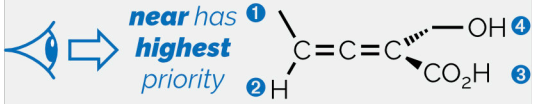
Axially chiral compounds can be treated as an ***elongated tetrahedron*** and defined as R_a *or* a*R* or S_a *or* a*S*:



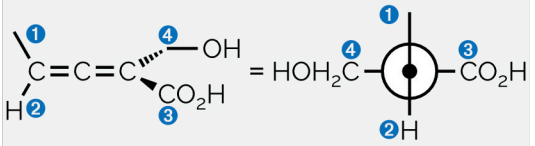
(i) Identify axis & view along axis - often cumulated double bonds or the bond with restricted rotation in atropisomers. Can be viewed from either end.



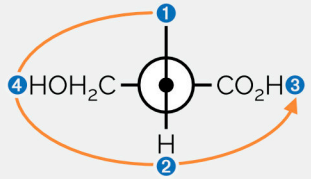
(ii) Rank groups - two groups closest to viewer have the highest ranks (rule 0).



(iii) Draw Newman projection - along axis from same point of view as ranking.



(iv) Assign configuration - draw arrow connecting priority 1→2→3. Clockwise = ***R_a*** or anticlockwise = ***S_a***.

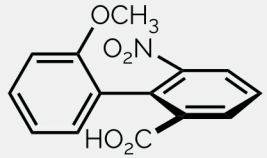


anticlockwise
S_a

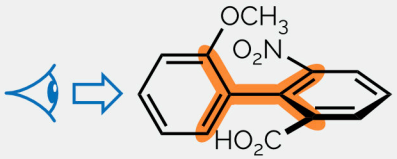
Biaryl atropisomers - are treated in exactly the same manner (see website)

5. Axial chirality *P*/*M*

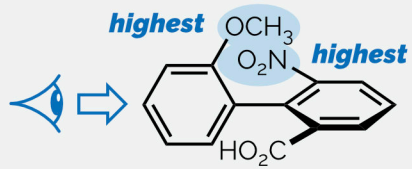
A stereogenic axis can be viewed as a ***helix*** and defined as either *P* or *M*:



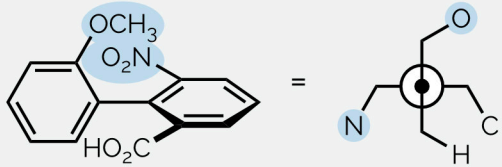
(i) Identify axis & view along axis - often cumulated double bonds or the bond with restricted rotation in atropisomers.



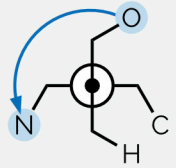
(ii) Rank highest group - at the front of the axis and the highest at rear of axis. .



(iii) Draw Newman projection - along axis (doesn't matter which end).



(iv) Assign configuration - draw arrow connecting **front** group to **back** group. Clockwise = ***P*** or anticlockwise = ***M***.



anticlockwise
M

For axial chirality only - S_a = *P* & R_a = *M*