

Chemistry I (Organic): Stereochemistry

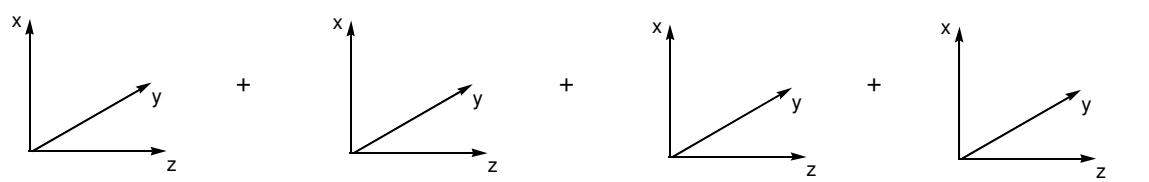
Hybridisation and Molecular Shape: Enantiomers

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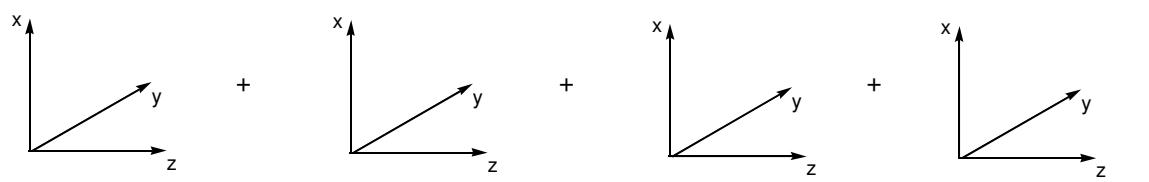
A Qualitative Guide to Hybridisation of Carbon:

Carbon (group 4 of periodic table) – 4 valence electrons

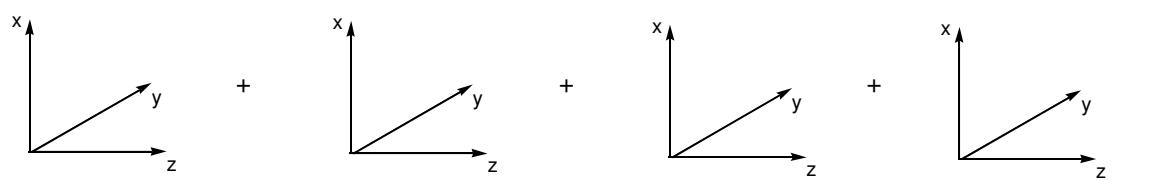
atomic structure: $1s^2 2s^2 2p^2$ (4 \times atomic orbitals)



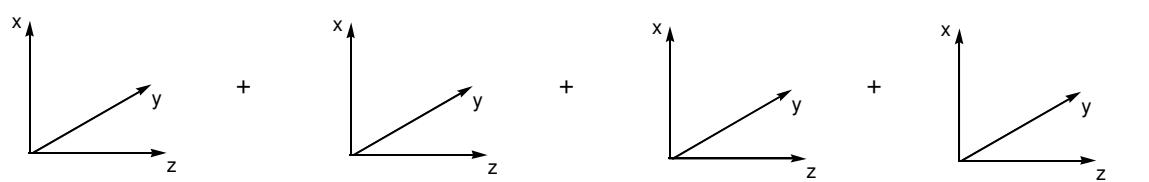
Sp^3 hybridised: tetrahedral (4 \times hybrid orbitals)



Sp^2 hybridised: trigonal planar (3 \times hybrid orbitals and 1 \times atomic orbital)



Sp hybridised: linear (2 \times hybrid orbitals and 2 \times atomic orbitals)



Nomenclature of Stereochemistry:

Stereochemistry deals with the way that chemistry is affected by differing orientations of the same groups in space. **Stereoisomers** are isomers whose atoms are connected in the same order (contrast *structural isomers*), but their *spatial arrangement* differs.

Stereoisomers are of two kinds – **enantiomers** (this lecture) and **diastereomers** (lecture 3).

Enantiomers:

Definitions:

- 1) **Enantiomers** are stereoisomers that are non-superimposable mirror images.
- 2) **Enantiomers** are stereoisomers lacking any **improper rotation axes** (see ‘symmetry workshop’).

Molecules related as non-superimposable mirror images (*i.e.* **enantiomers**) are said to be **chiral**. A common, but not obligatory, feature of enantiomers is that they contain a **chiral/stereogenic centre**.

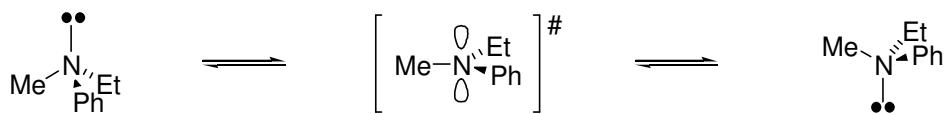
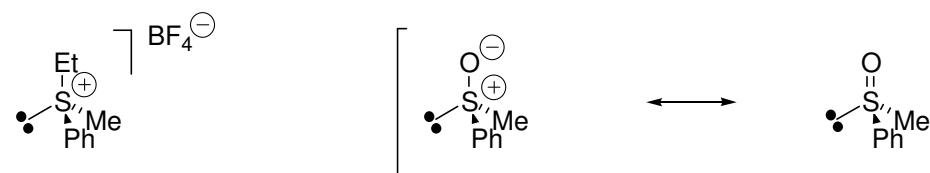
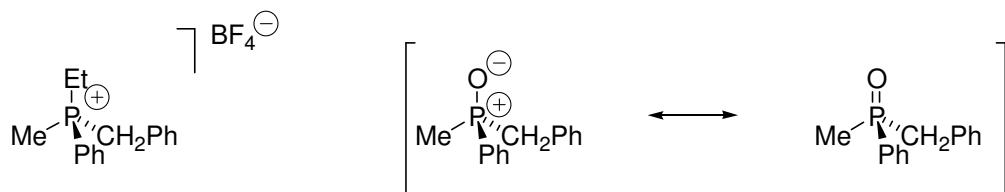
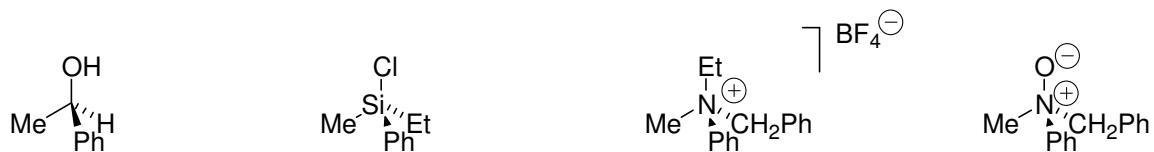
e.g. a carbon atom with four different groups attached.

Such molecules are **asymmetric** and have only a C_n ($n = 1$, *i.e.* C_1) **proper rotation axis**.

Dissymmetric molecules, which have C_1 and C_n ($n = \text{integer} > 1$) **proper rotation axes** only, are also **chiral**.

Some chiral molecules with a single chiral/stereogenic centre

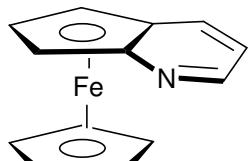
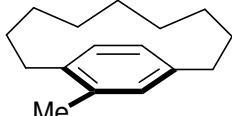
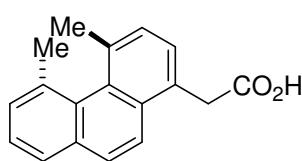
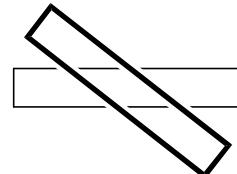
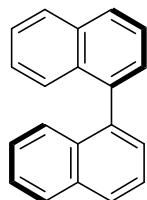
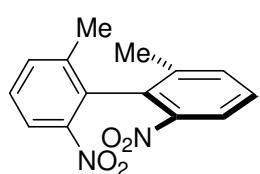
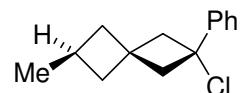
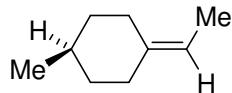
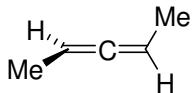
asymmetric molecules (C_1)



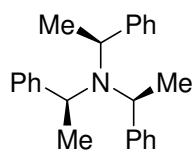
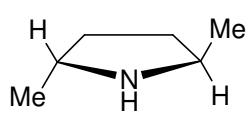
N.B. Structures boxed in red are configurationally labile at an appropriate temperature. They all have a lone pair of electrons as one 'substituent' off the tetrahedral centre. Lone pairs are able to 'tunnel' through the central atom; this results in an inversion of configuration of the molecule (*i.e.* the enantiomers can interconvert, as shown explicitly for the *tert*-amine case above). The temperature/rate at which this happens depends on the central atom and the other substituents present. For example, most *tert*-amines rapidly interconvert their configuration at room temperature but the aziridine shown bottom left can be separated into its enantiomers at this temperature.

Some chiral molecules without a chiral/stereogenic centre

asymmetric molecules (C_1)



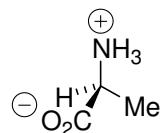
dissymmetric molecules (C_n)



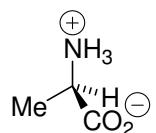
N.B. As on the previous page, structures boxed in red are configurationally labile at an appropriate temperature. In these cases, interconversion between enantiomers results when the steric barriers to rotation about certain single bonds becomes energetically possible.

In all other cases interconversion between enantiomers requires breaking and reformation of either σ (sigma) bonds or π (pi) bonds. The high energy required to do this is not generally available thermally.

Enantiomers have identical chemical and physical properties, except insofar as they rotate the plane of polarised light equally, but in the opposite directions, e.g.

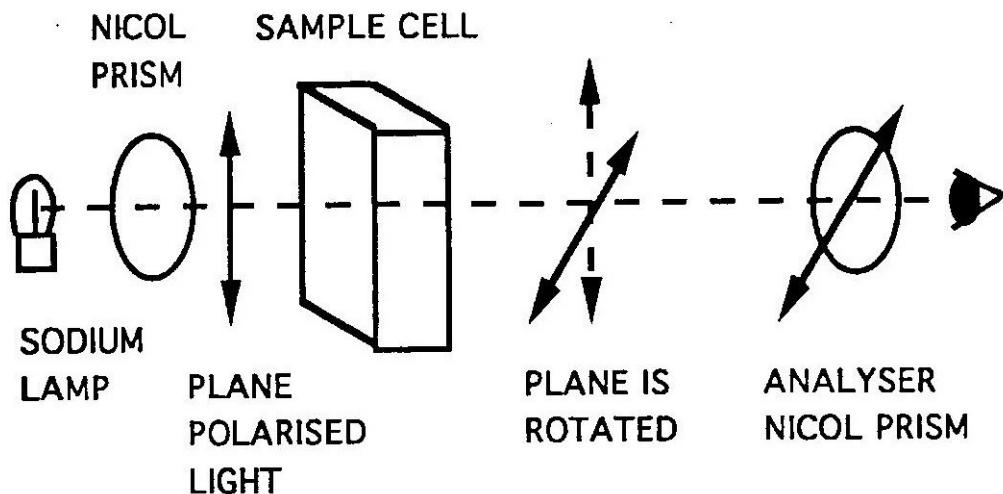


(+)-alanine $[\alpha]_D = +8.5^\circ$



(-)-alanine $[\alpha]_D = -8.5^\circ$

The rotation of the plane of polarised light is measured using a **polarimeter**:



Compounds which rotate the plane of polarised light clockwise are called **(+)-isomers**, or **dextrotatory (d)**. Conversely, those that rotate the plane anticlockwise are called **(-)-isomers** or **laevorotatory (l)**.

The separation of mirror image molecules is called **resolution**. Because enantiomers have the same chemical properties, *resolution of enantiomers can be difficult*. The first recorded resolution carried out by humans is that of **Louis Pasteur** in 1848.
