USACH. Santiago, Chile 5 - 9 de Junio, 2023

Shape & symmetry in structural chemistry

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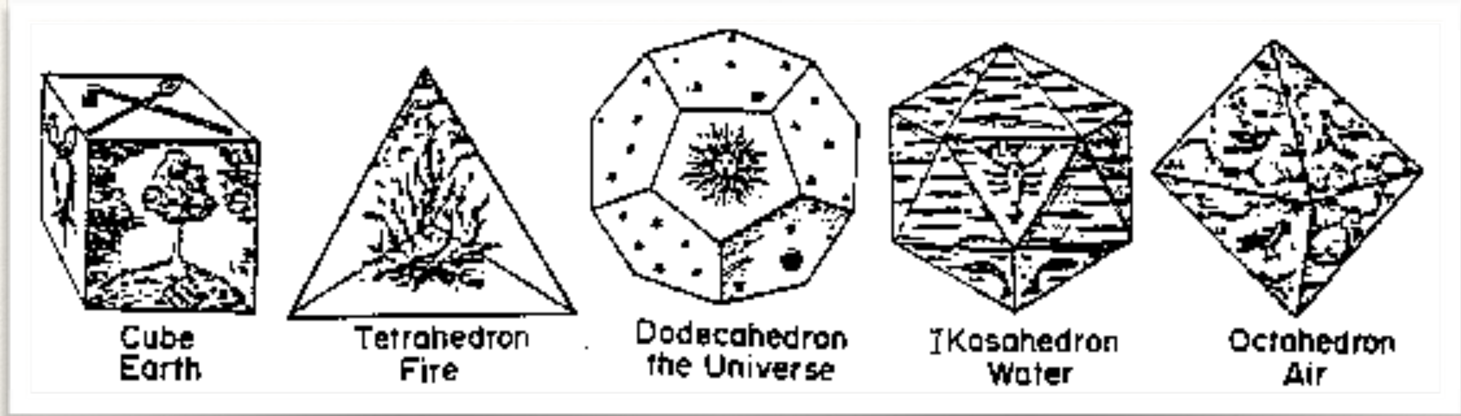
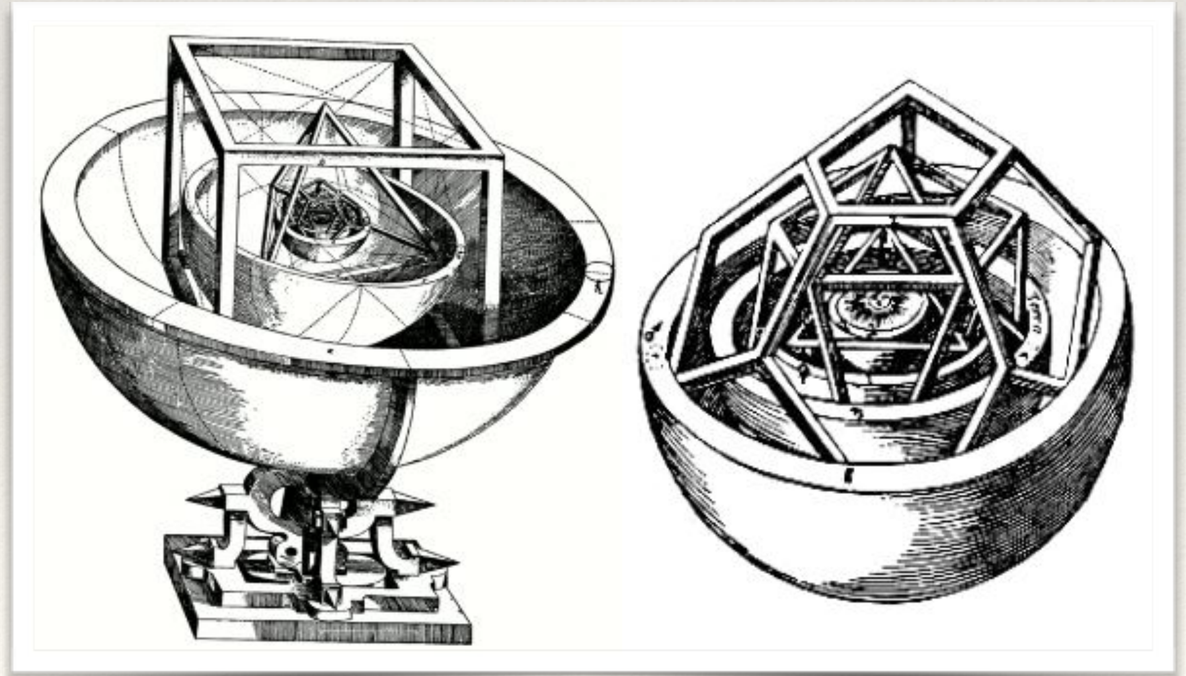
Universitat de Barcelona

Describing the world through shape and symmetry

Association between elements and platonic polyhedra

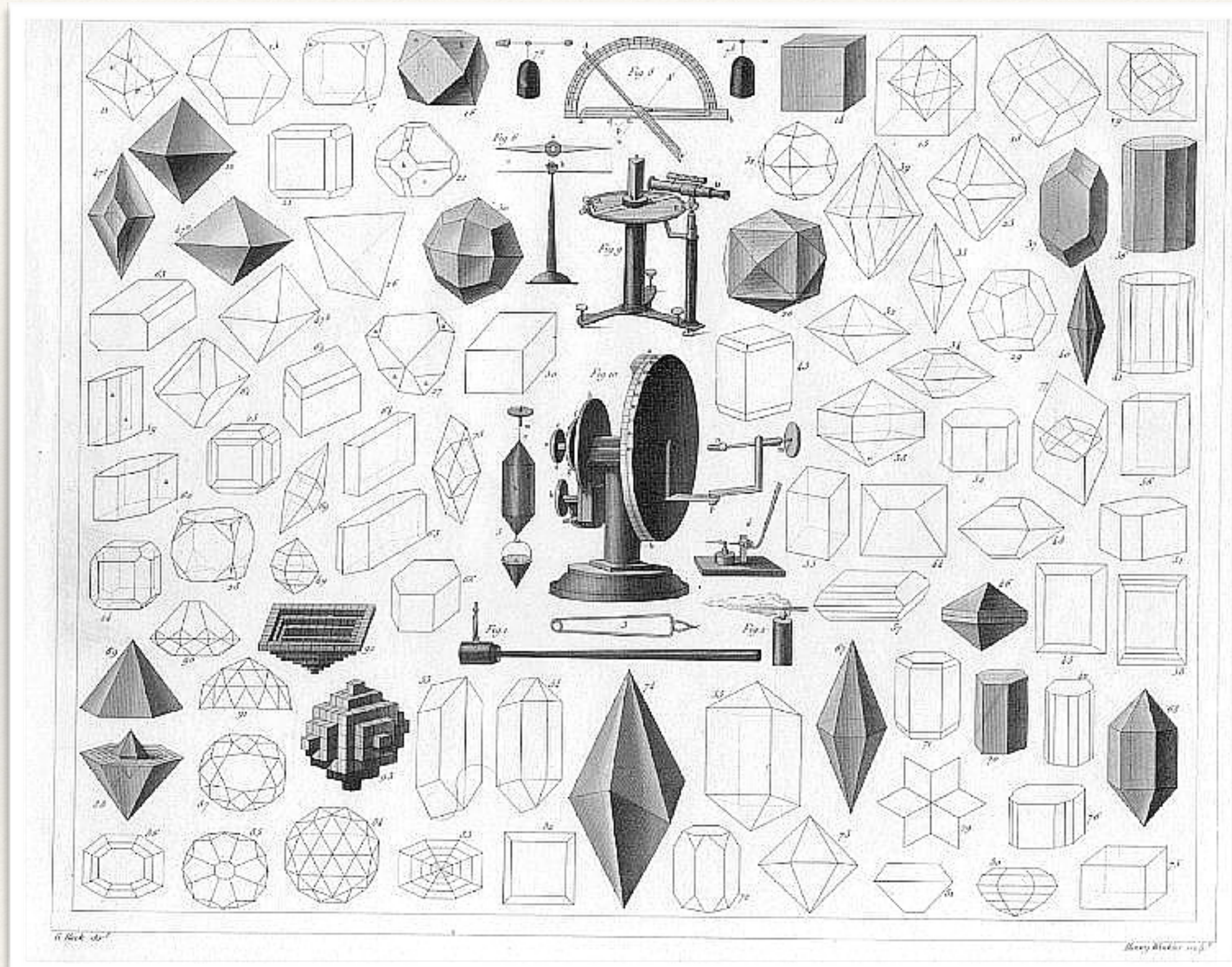




Kepler's early model for the universe

J. Kepler *Mysterium Cosmographicum* (1596)

Shape & symmetry of crystals



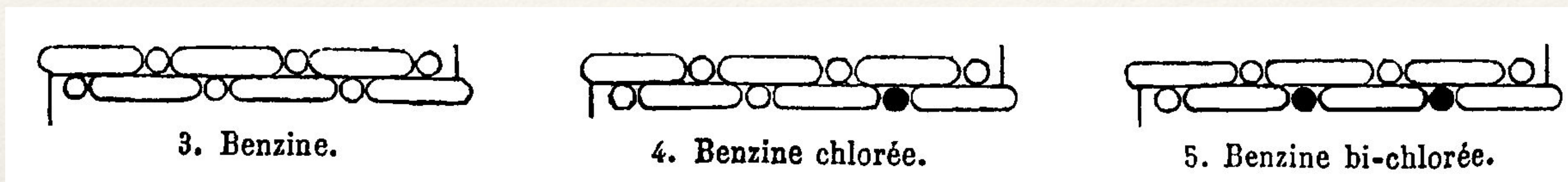
Crystallographic illustrations ~1850

Symmetry as an Organising Principle in Nature

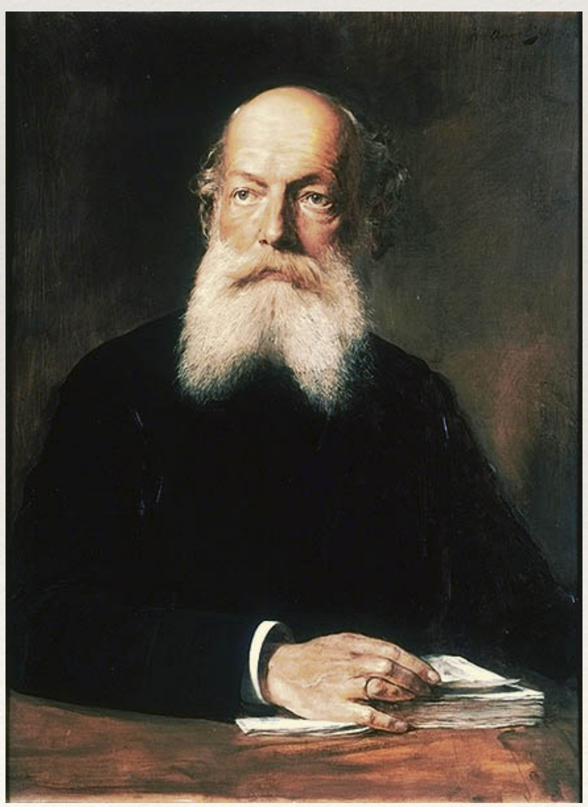
Ernst Haeckel *Kunstformen der Natur* (1899-1904)

Symmetry explains chemical behaviour

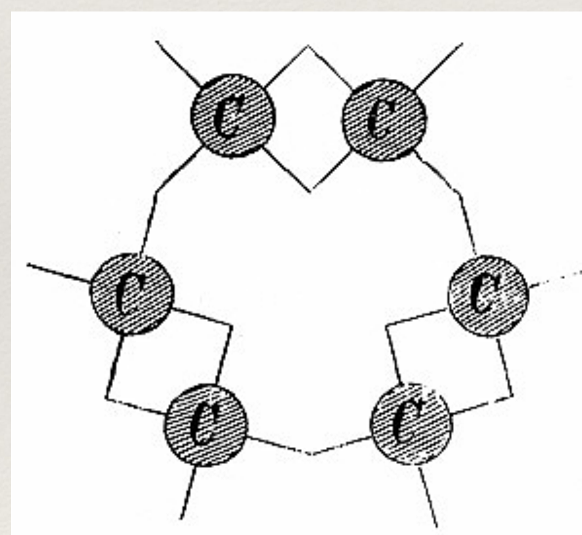
Symmetry was introduced in chemistry already before the establishment of the atomic structure of nature:

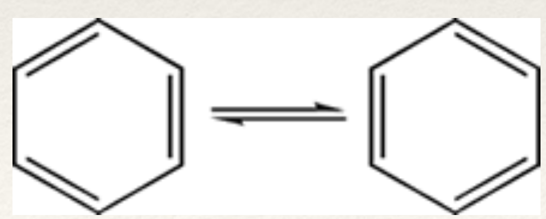


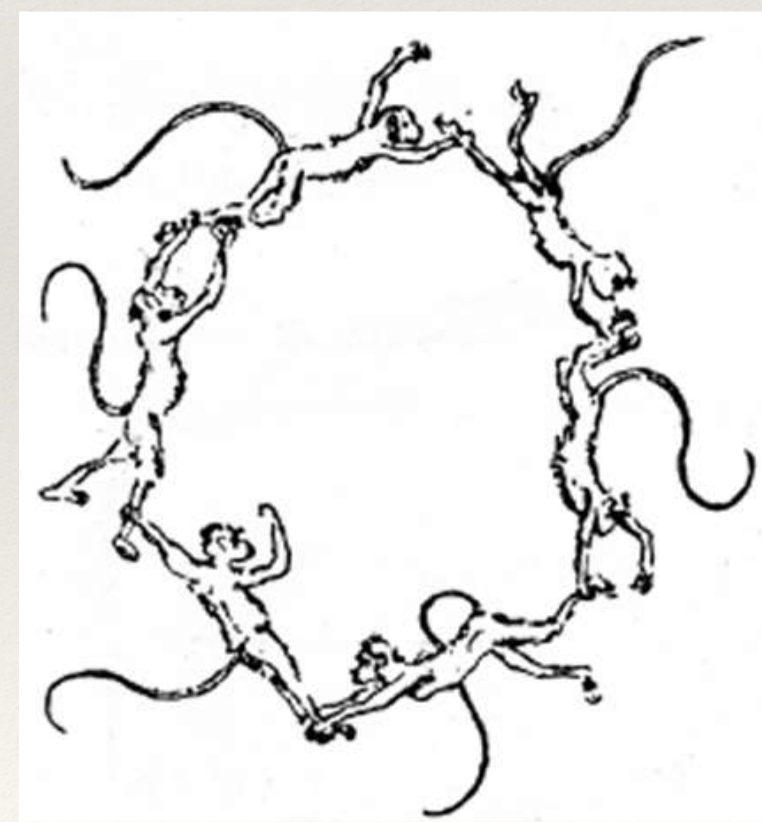
C_6H_6 gives only one monosubstituted product C_6H_5Cl
and three different disubstituted $C_6H_4Cl_2$ products



August Kekulé (1829 – 1896)



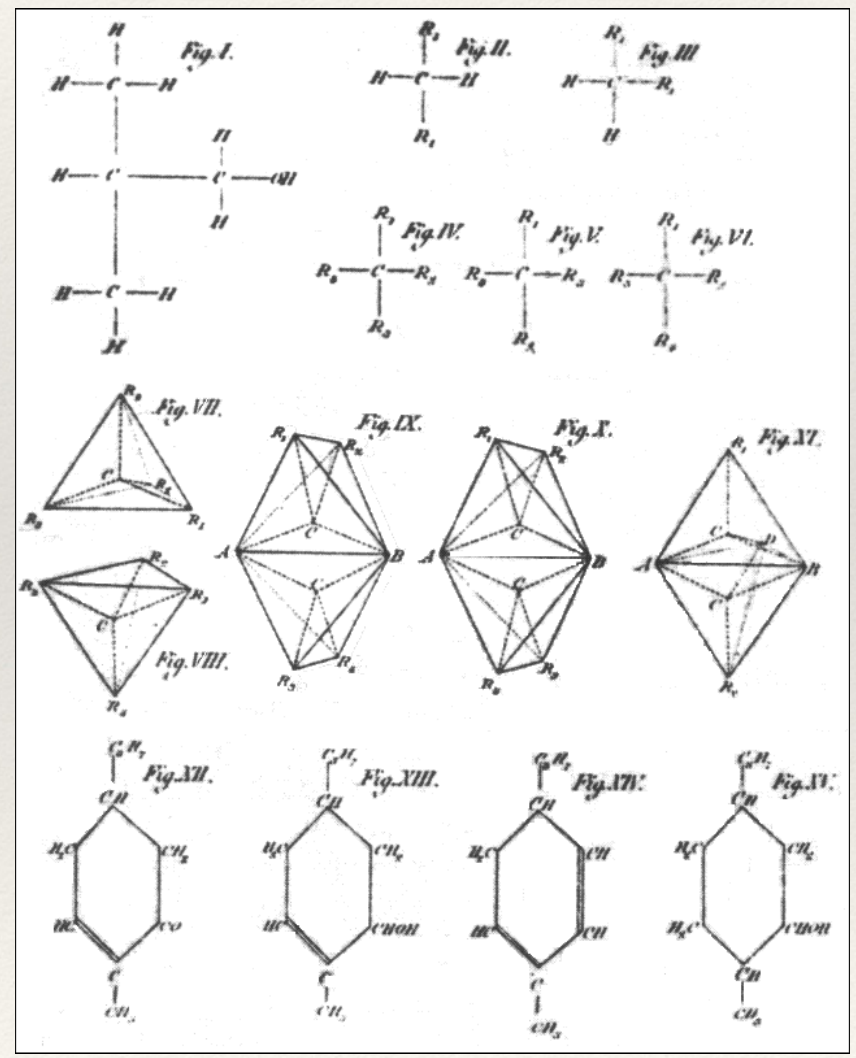




Organic chemistry is tetrahedral

Physical properties of molecules (optical rotation) depend on the spatial distribution of atoms (and on the symmetry of this distribution)

Jacob H. van’t Hoff (1852 – 1911)

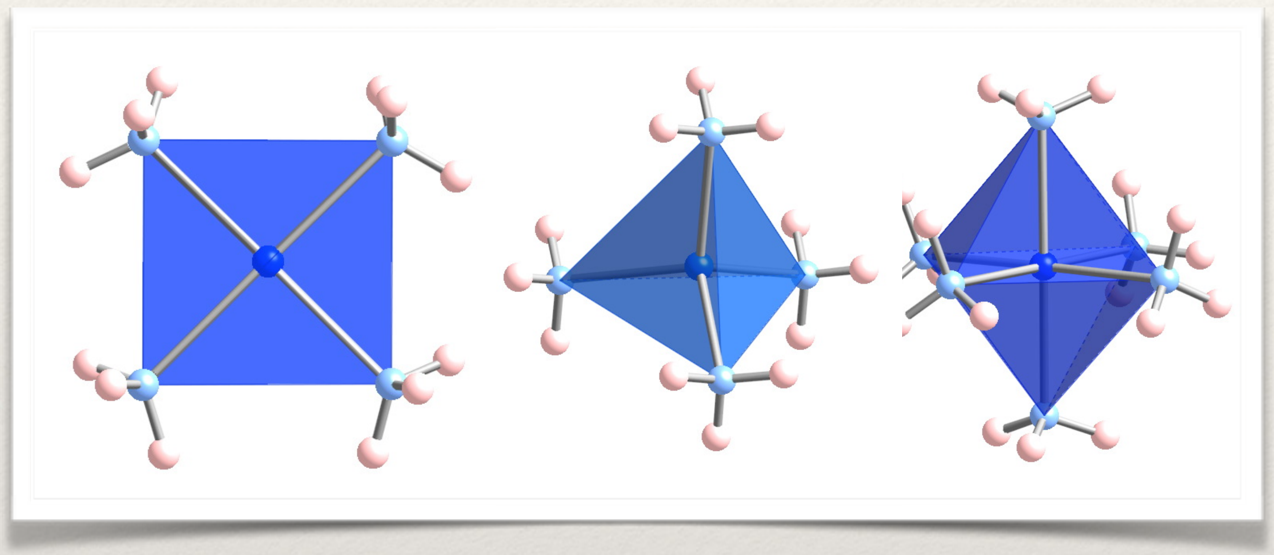


J. H. van’t Hoff: La chimie dans l'espace (1874)

Joseph le Bel (1847 – 1930)

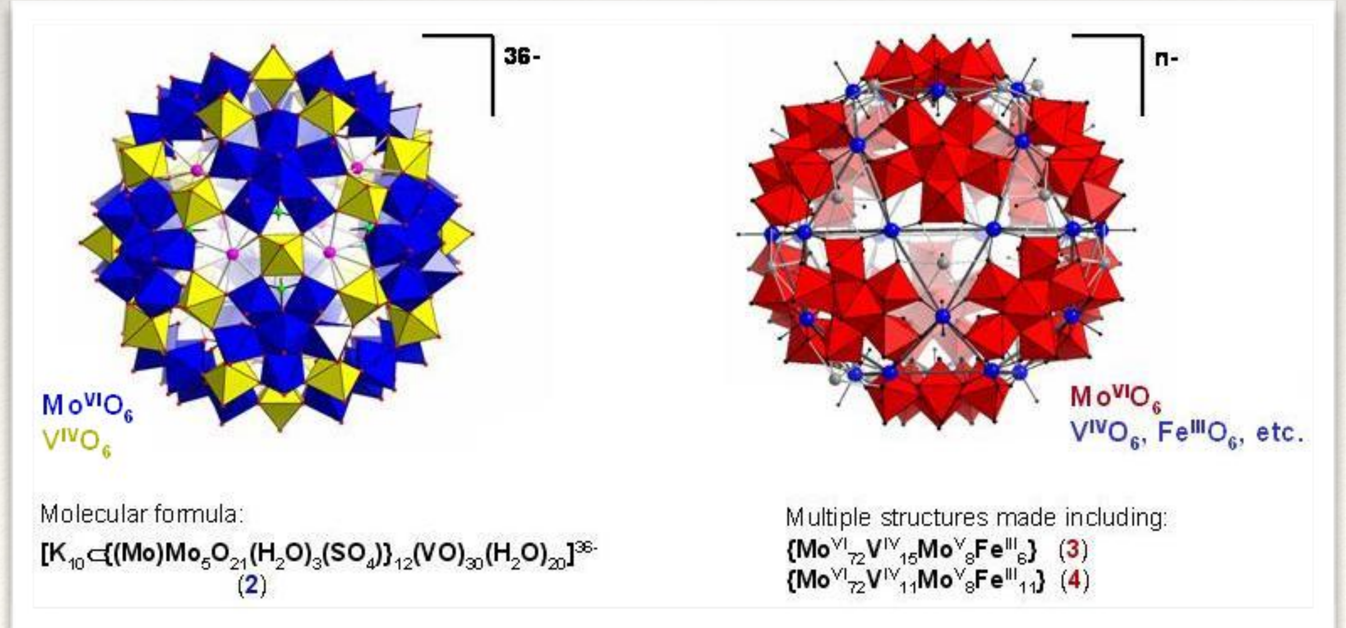
Polyhedral models in structural chemistry

1n 1893 Werner suggests to describe the coordination environment of transition metal atoms in coordination compounds by ideal polyhedra (tetrahedra, octahedra, …)



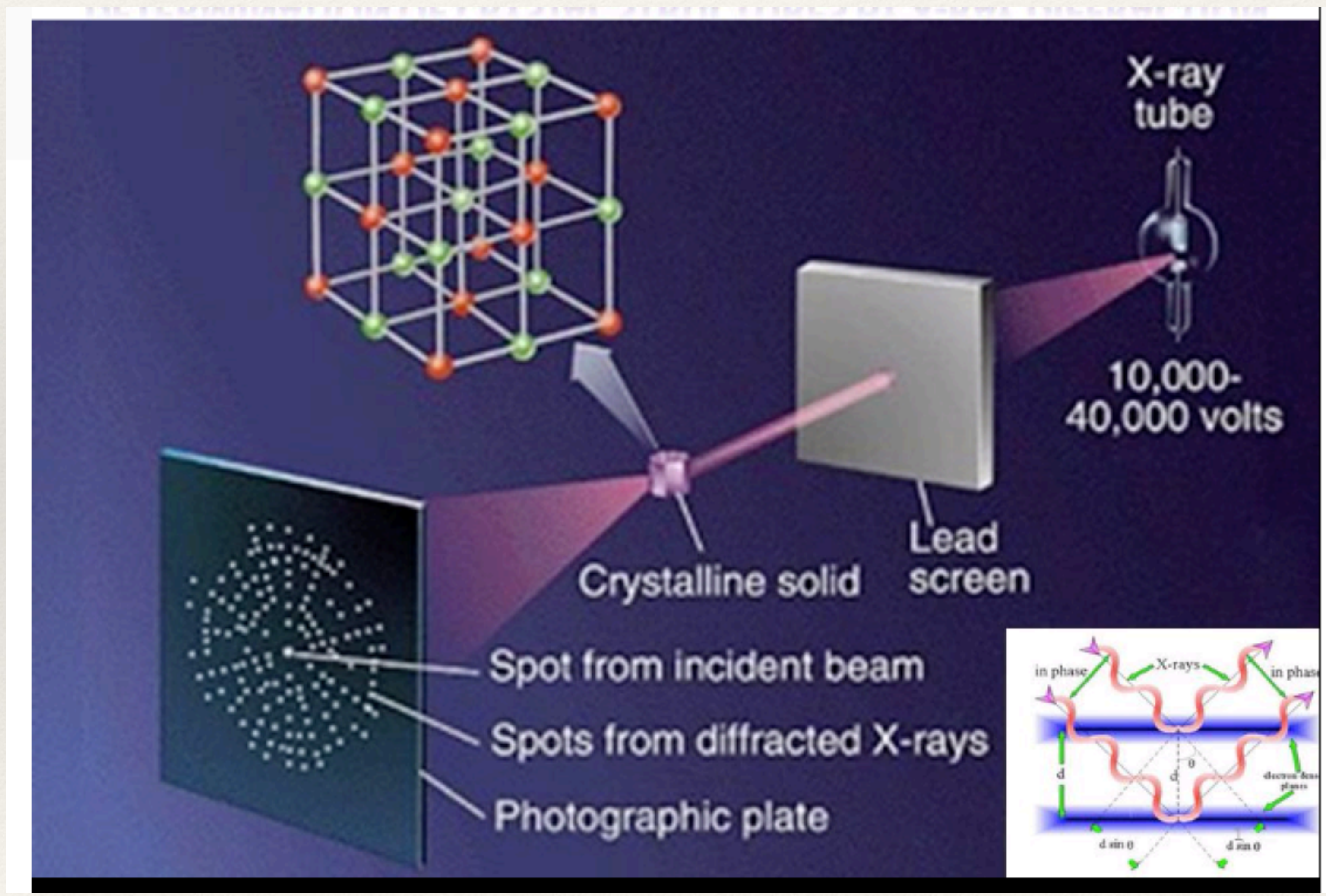
Alfred Werner (1866 – 1919)

The shape and symmetry of complex molecules (solids) is often discussed as that of an ordered ensemble of connected polyhedra



Modern crystallography & X-ray diffraction

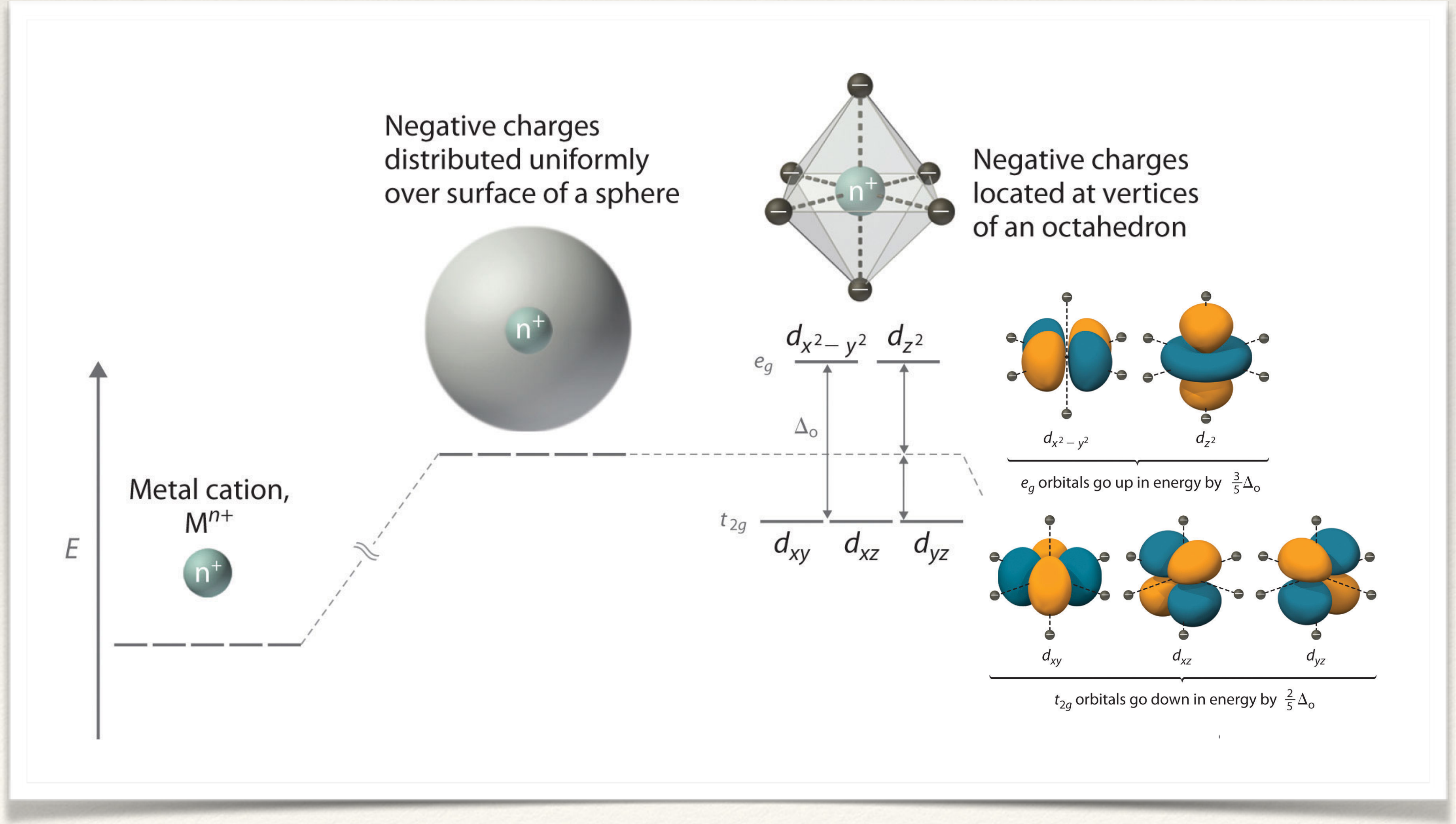
Crystals are regular (symmetric) arrays of atoms which scatter X-ray waves producing a pattern of spots from which we may deduce the details of the arrangement of atoms in space.



There are only 230 possible symmetries for the arrangement of atoms in crystal structures.

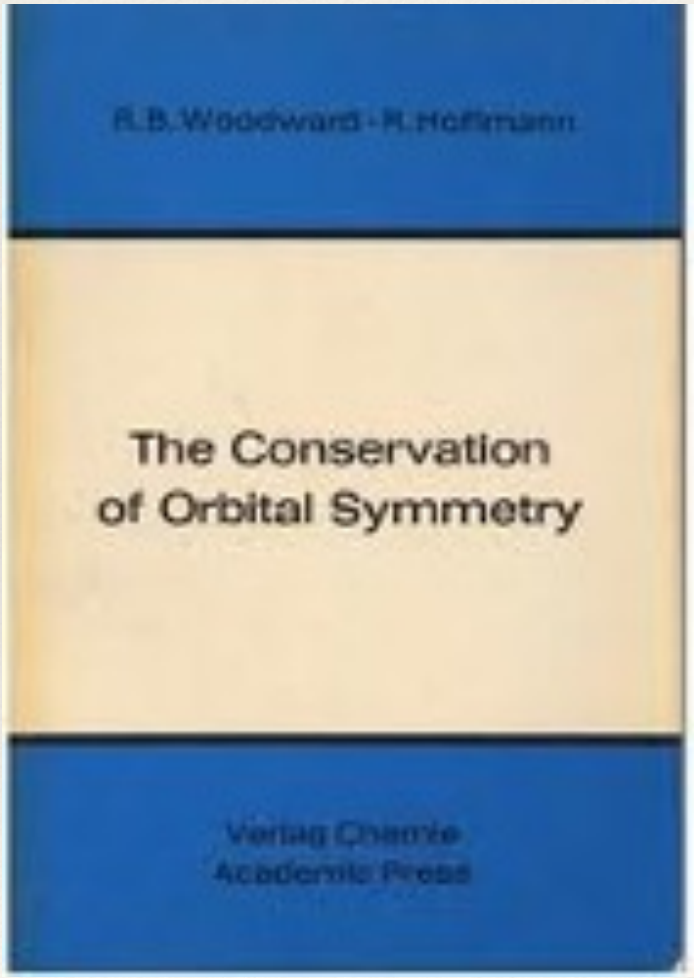
Symmetry & quantum mechanics

Chemistry depends on the **behavior of electrons** which are properly described by **quantum mechanics**. Electron wave-functions must have the same symmetry as the potential energy arising from the arrangement of nuclei. Symmetry dictates the degeneracy of energy levels.



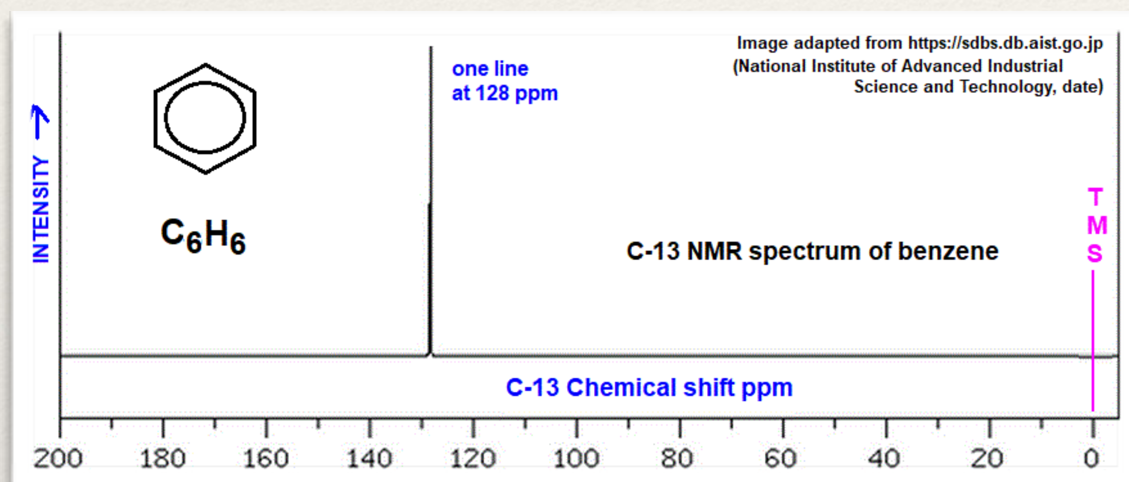
Symmetry & chemical reactions

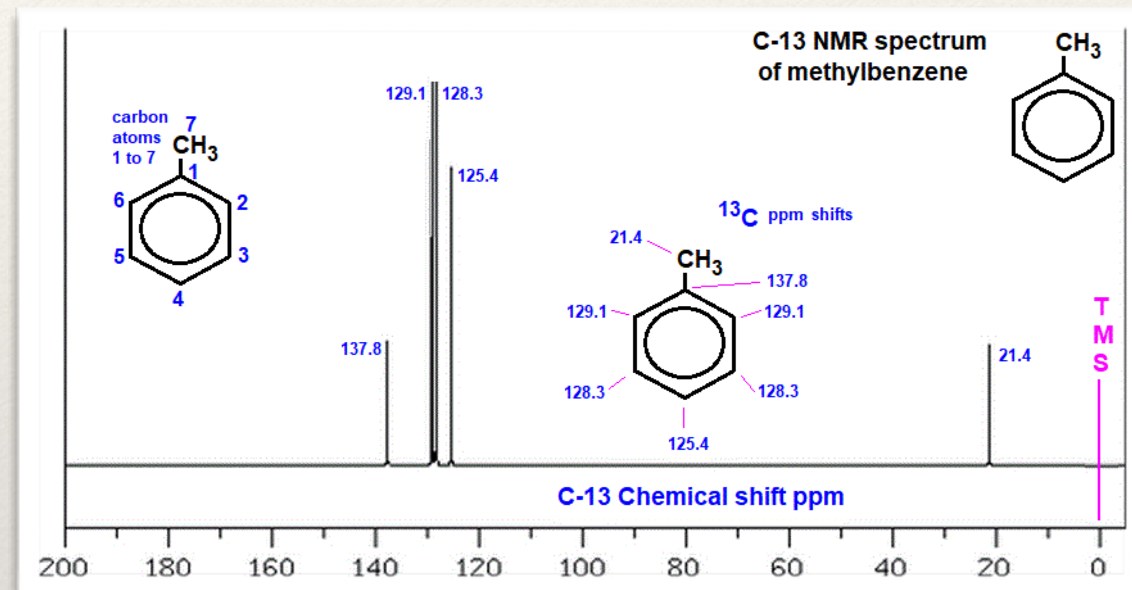
The changes in symmetry of molecular orbitals are fundamental in determining whether a reaction will happen or not.

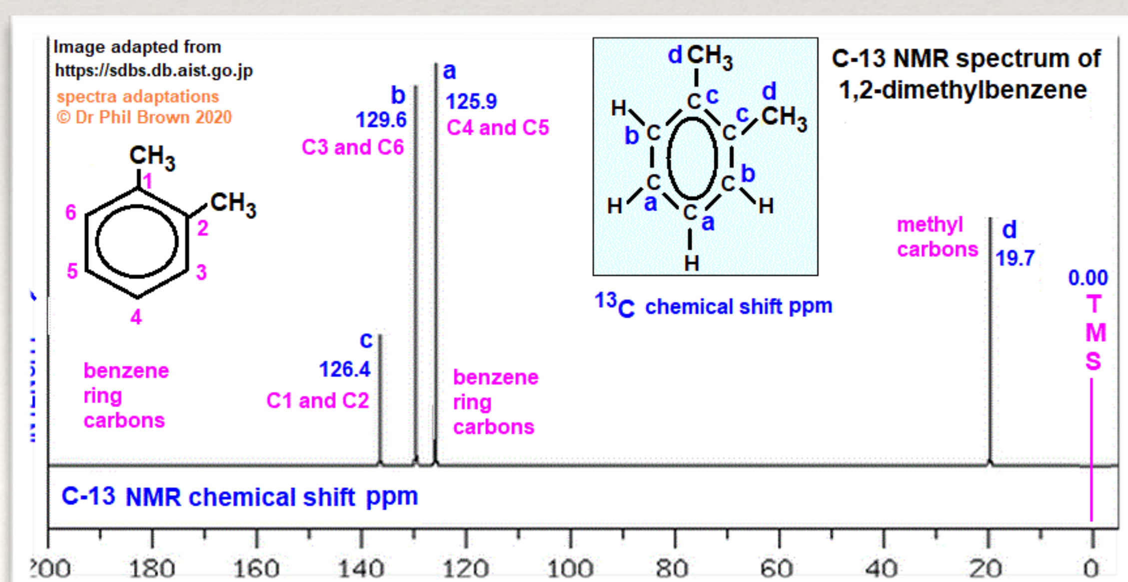


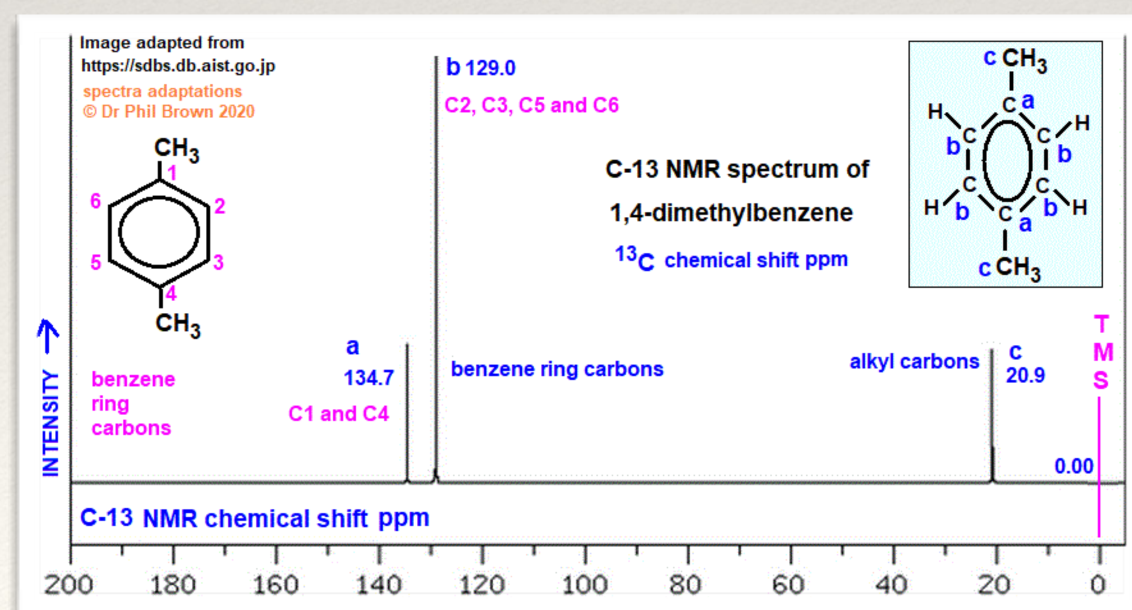
Symmetry & spectroscopy

Spectroscopy provides useful structural information, with molecular symmetry having a key role in the resulting spectrum. General trend: the more symmetric the structure, the simpler the spectrum.



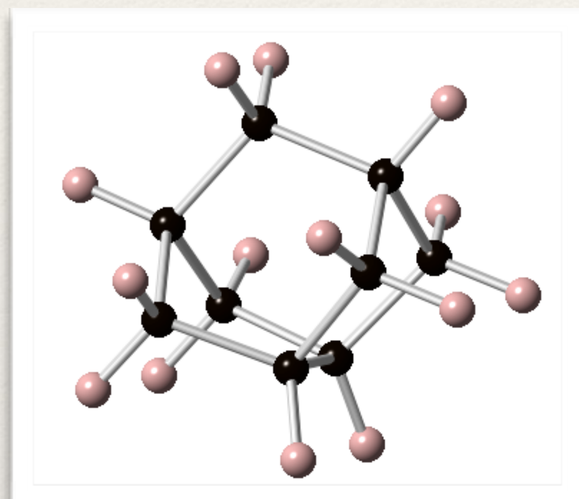






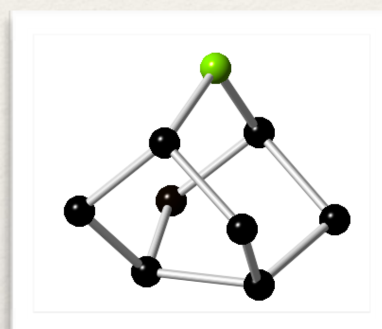
Symmetry & enumeration problems

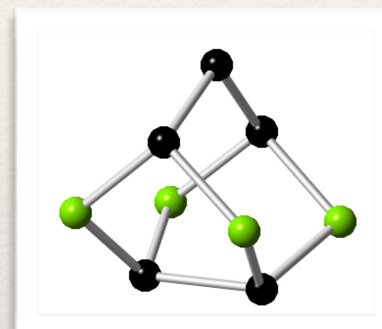
Symmetry plays also a fundamental role in enumeration problems.



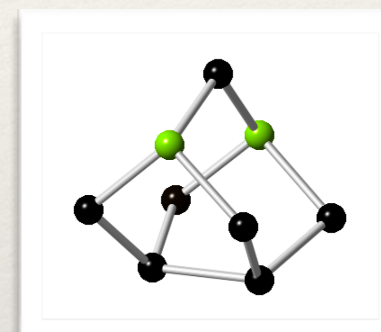
Adamantane

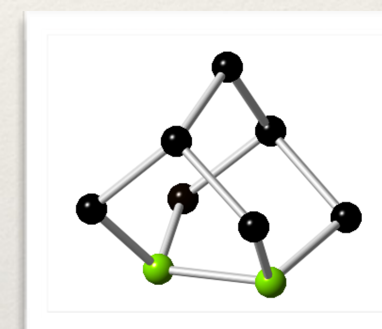
4 different sets of equivalent C atoms





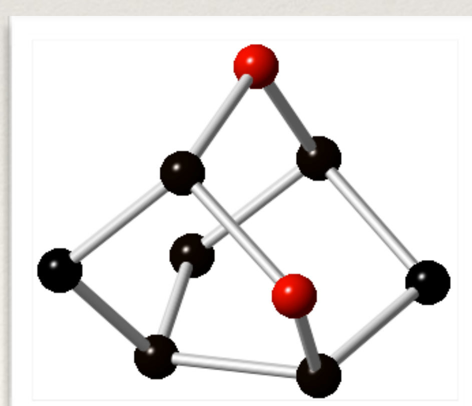
Local C_2 symmetry

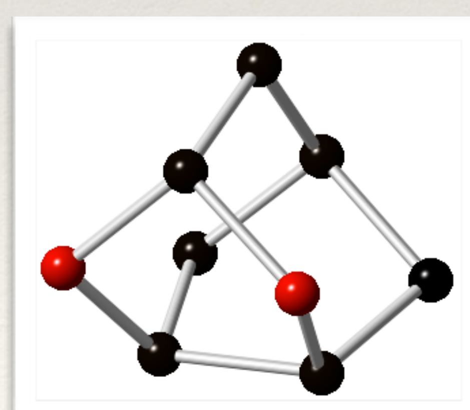


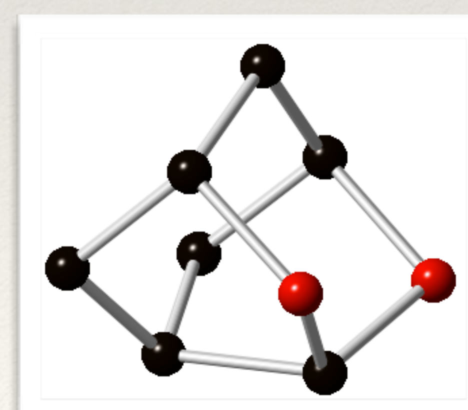


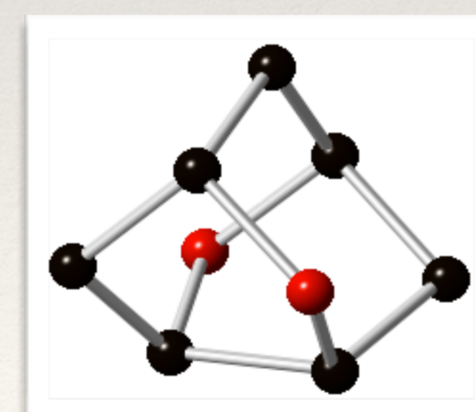
Local C_3 symmetry

Possible C_7O_2 isomers



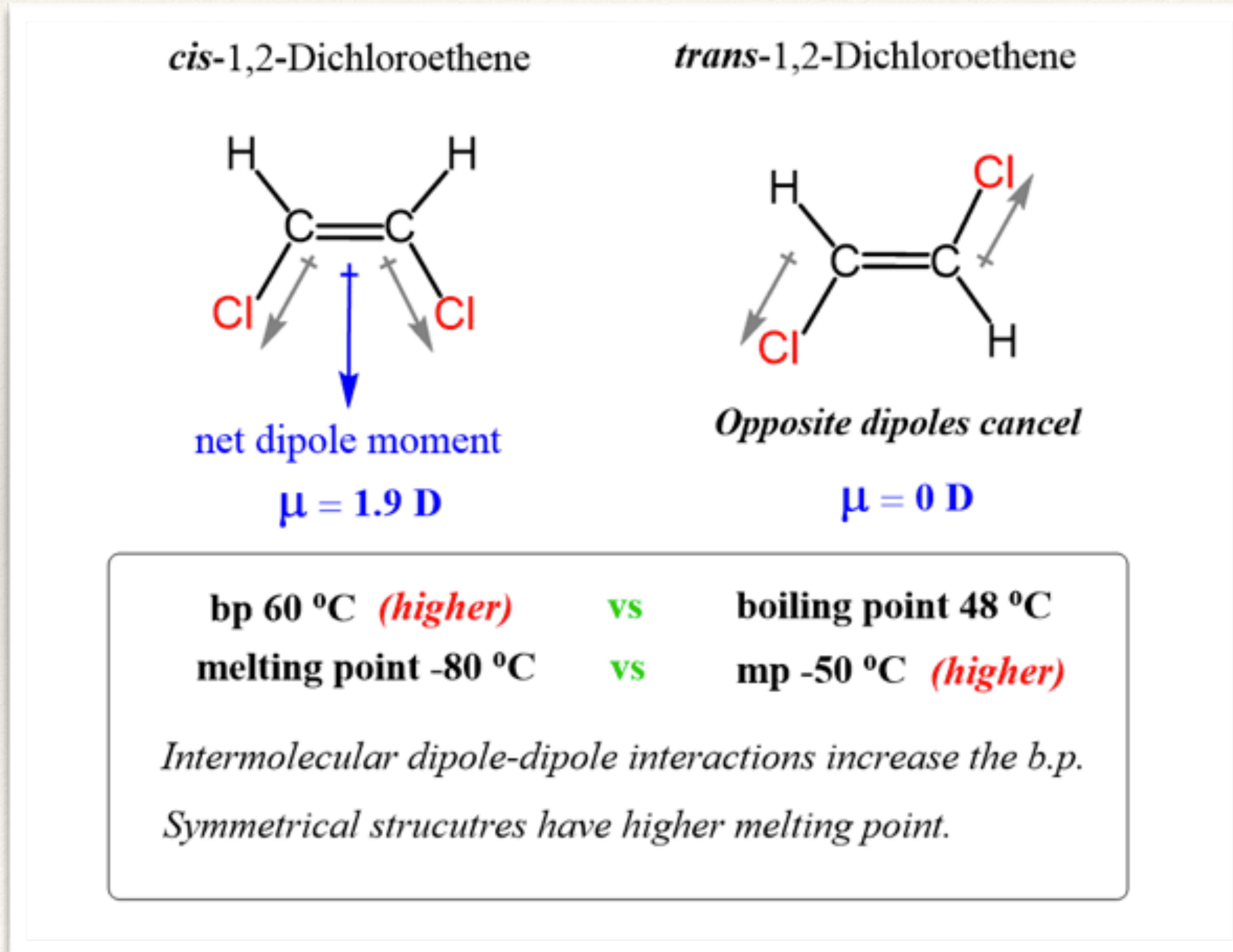






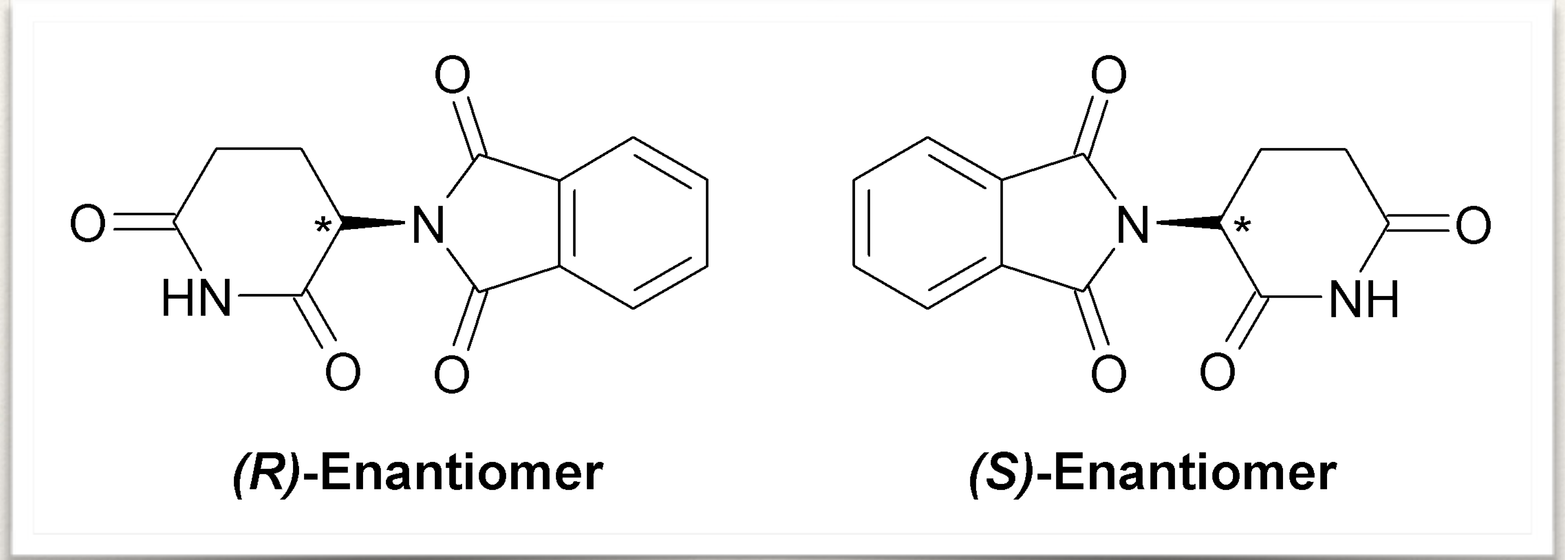
Symmetry & physical properties

Many physical properties are affected by symmetry



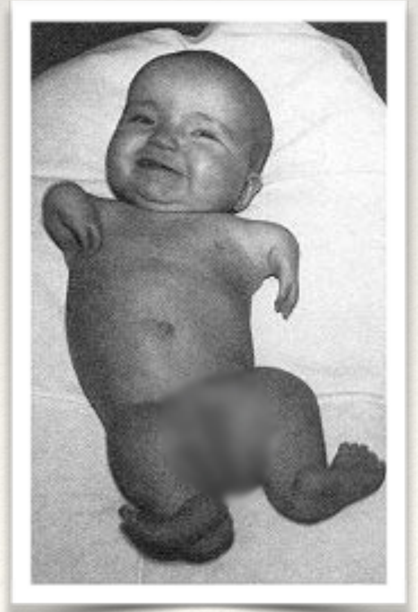
Symmetry & chemical properties

Subtle differences in symmetry may lead to different chemical behavior.



Enantiomers (specular images) of thalidomide:

(R)-Enantiomer: sedative effects
(S)-Enantiomer: embryo-toxic and teratogenic effects



Nature Escapes the Rigid Laws of Symmetry

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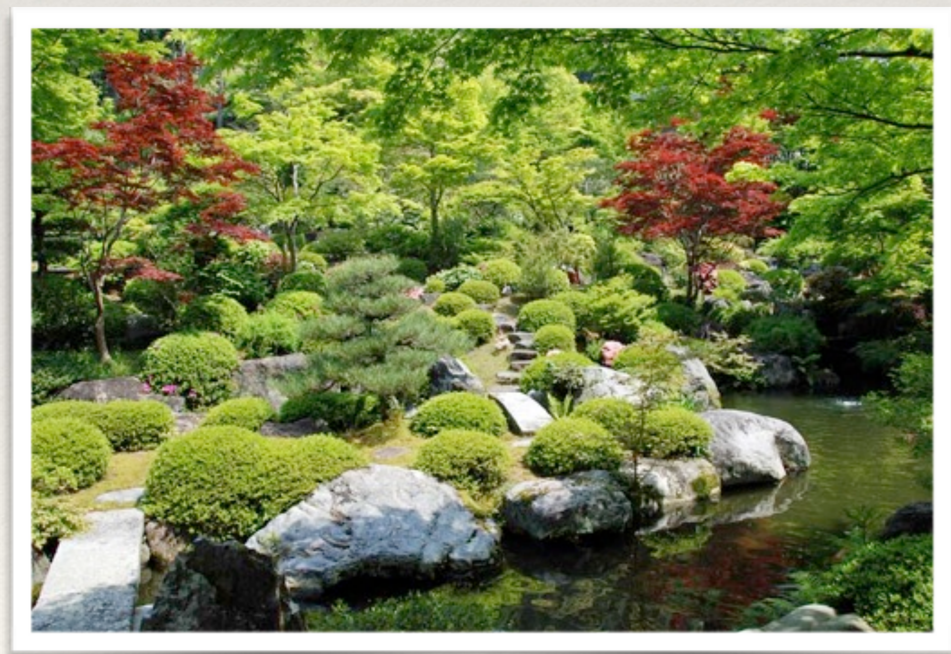

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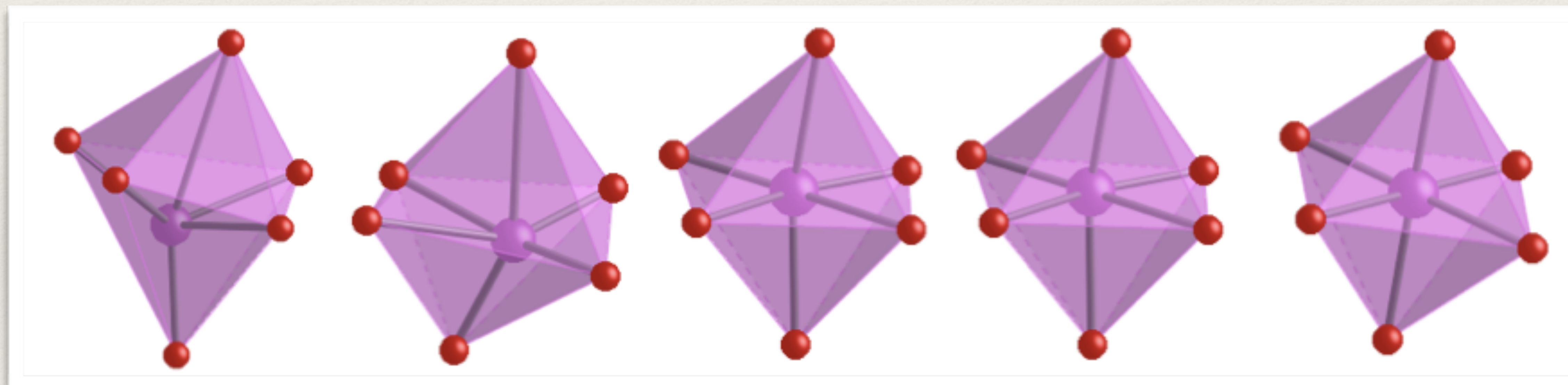
Describing shape & symmetry

Strongly distorted | Moderately distorted | Slightly distorted | Octahedron

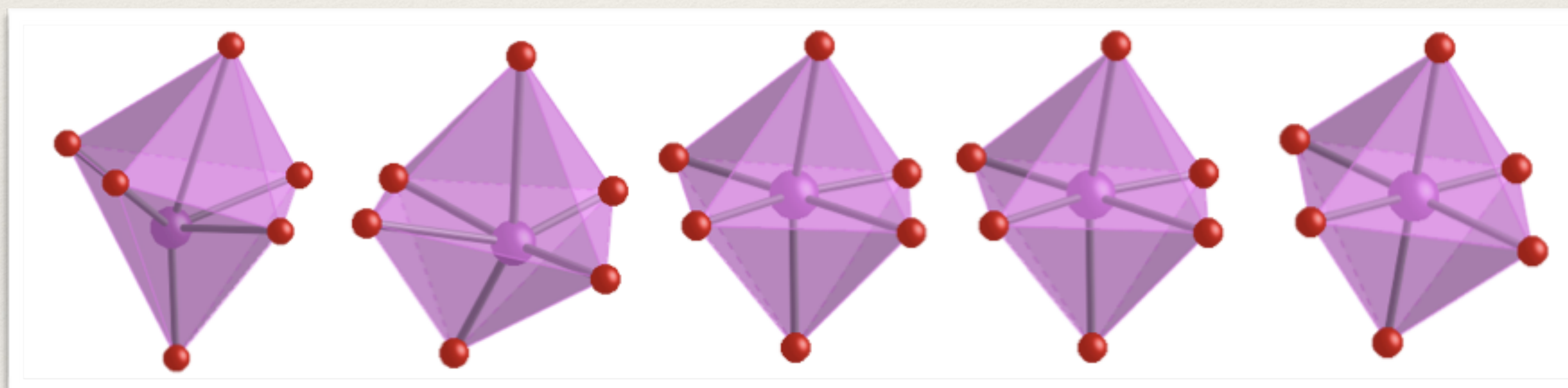


Non-octahedral | Octahedral

Measuring (A)symmetry

Strongly distorted	Moderately distorted	Slightly distorted	Octahedron

5.65	1.70	0.68	0.12	0.00



Non-octahedral

Octahedral