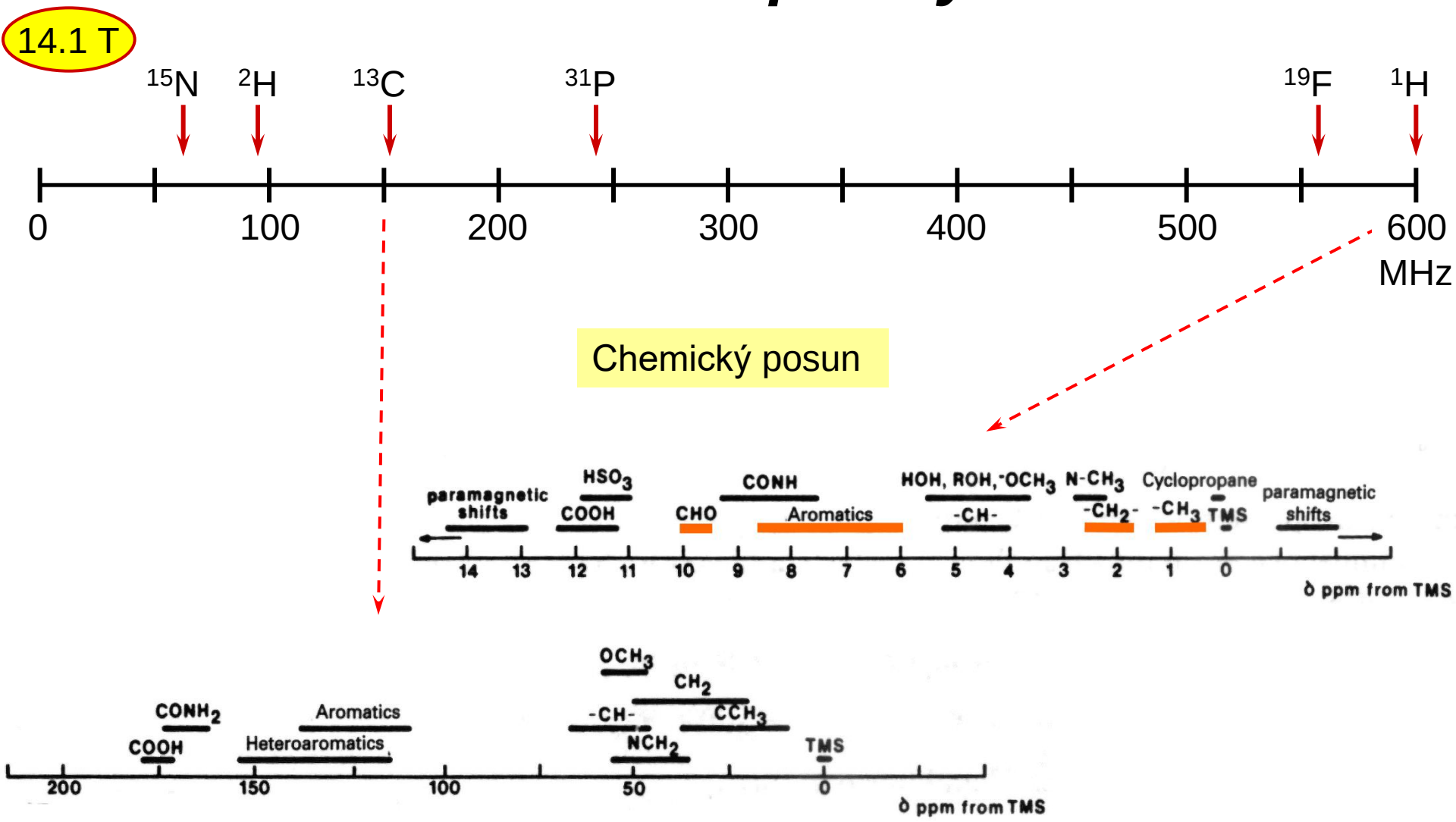
NMR spectroscopy

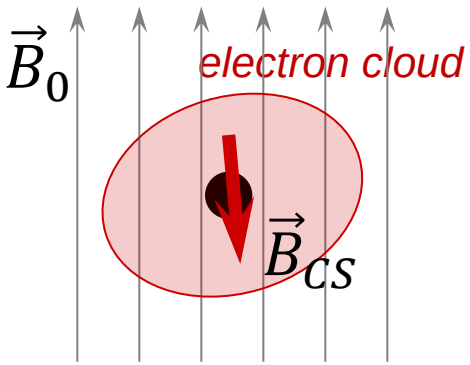
- Chemical shielding and chemical shift
- Symmetry and equivalence
- Intensity of signals

NMR Frequency



The resonance frequency varies depending on the chemical surroundings of the nuclei

Chemical shielding



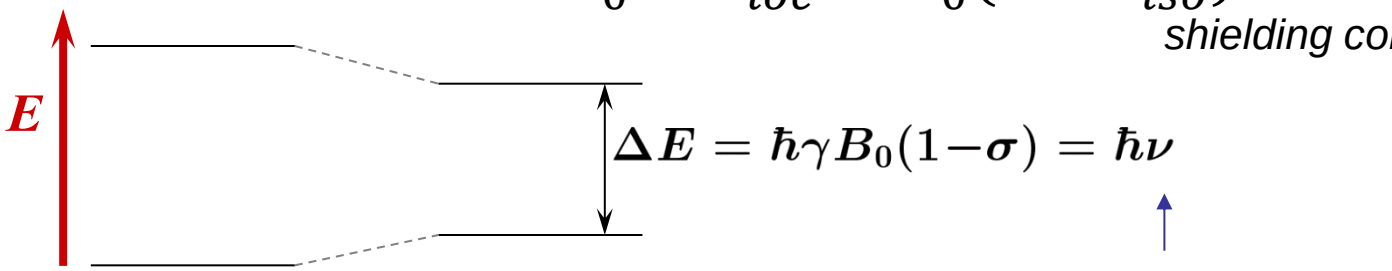
$$\vec{B}_{CS} = -\overleftrightarrow{\sigma}\,\vec{B}_0$$

Tensor of chemical shielding

- Electrons surrounding the nucleus respond to an external magnetic field
- They create an additional magnetic field $\vec{B}_{CS}$
- The nuclei sense a diminished local magnetic field $\vec{B}_{loc}$ and thus their Larmor frequency is altered
- The distribution of electrons is not always symmetrical ⇒ shielding depends on the orientation of the molecule with respect to the magnetic field
- Fast random rotation of molecules in solution averages the anisotropy of the chemical shielding

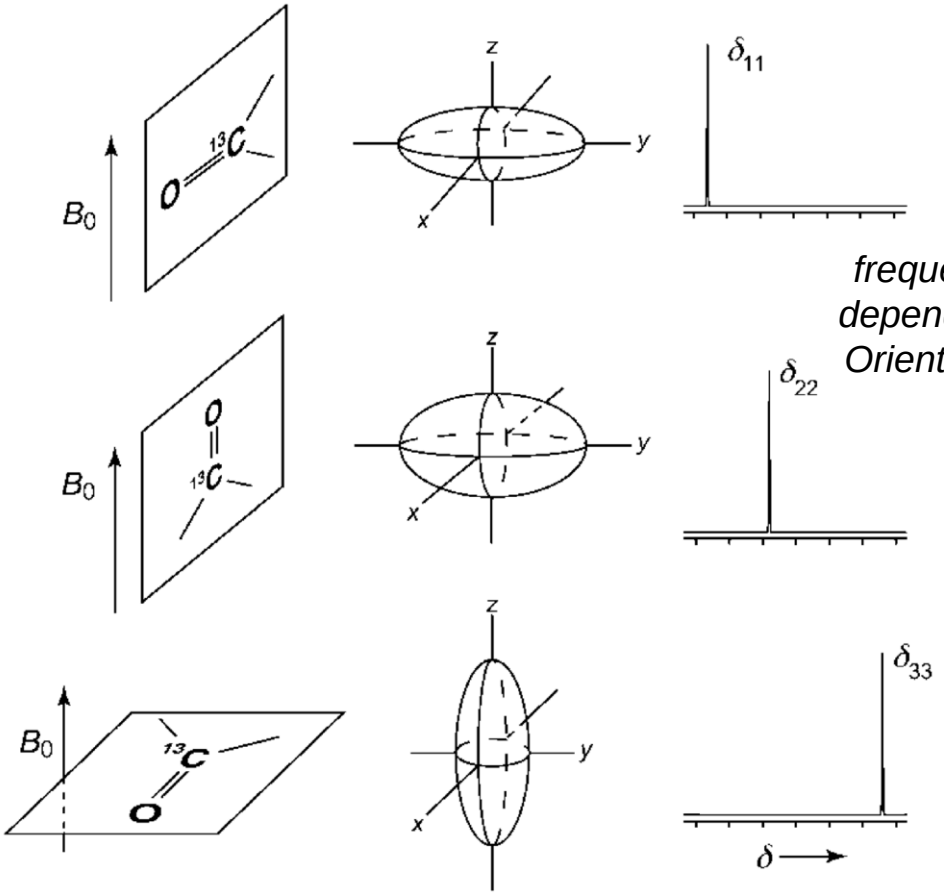
$$B = B_0 + B_{loc} = B_0(1 - \sigma_{iso})$$

shielding constantsa



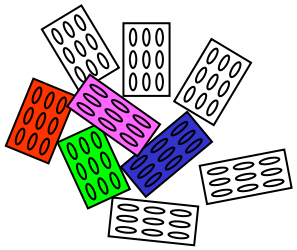
Chemical shielding

Anisotropy of chemical shielding

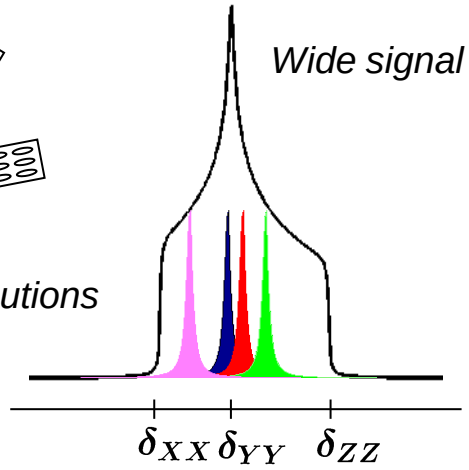


frequency depends on Orientation

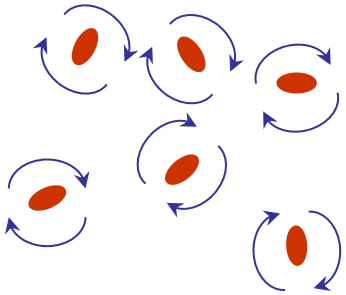
Powder sample



sum of contributions



Solution



Averaged by fast motion / tumbling

Chemical shift

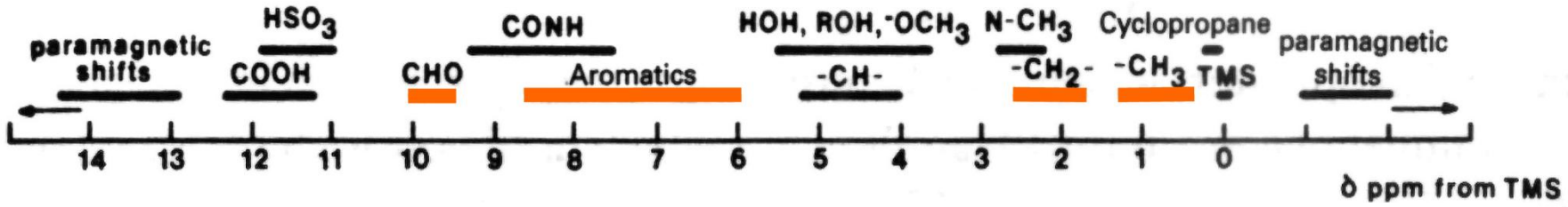
- The differences in frequencies are small
- The actual frequency is related to a standard molecule (TMS – tetrametylsilan)
- Chemical shielding σ is proportional to the external magnetic field
- Chemical shift δ is independent of the magnetic field
- The chemical shift is the same on all NMR spectrometers

$$\delta = 10^6 \frac{\nu - \nu_{ref}}{\nu_{ref}}$$

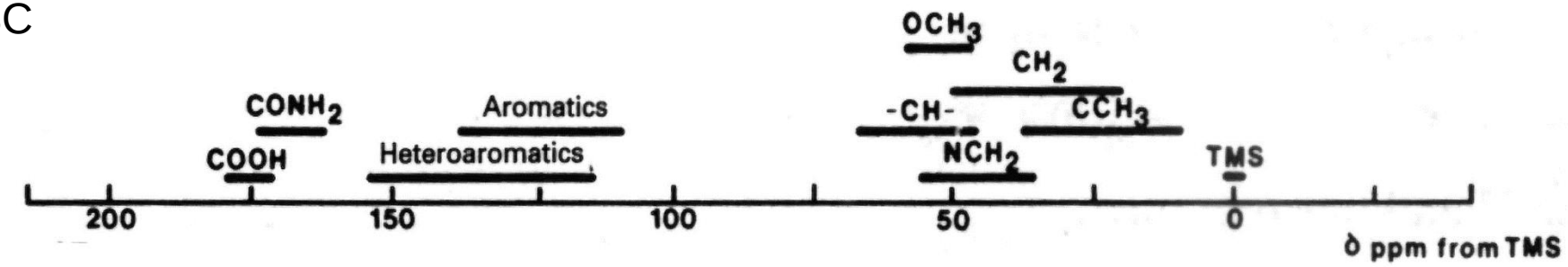
ppm

parts per milion

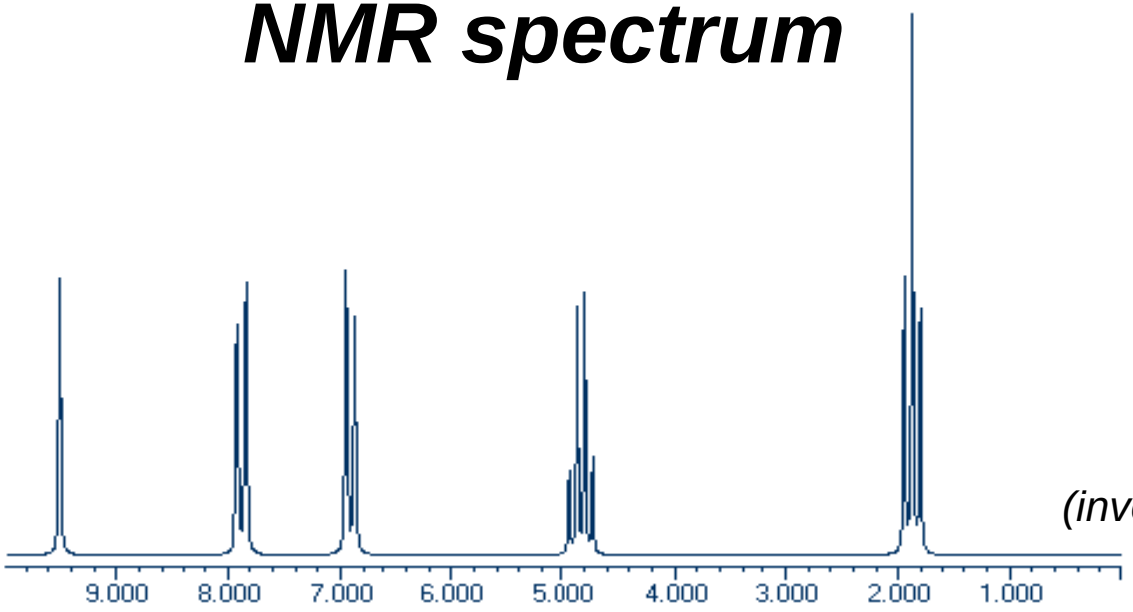
1H



13C



NMR spectrum



(inverted axis)

ppm, frequency

Chemical shielding

high δ	low δ
low field	high field
downfield	upfield
paramagnetic shift	diamagnetic shift
deshielding	shielding

Chemical shielding

$$\sigma = \sigma^{dia} + \sigma^{para} + \sigma^{local}$$

Contributions

dia — electrons in s-orbitals, reduce the local magnetic field

para — π-electrons and electrons in p-orbitals, increase the local magnetic field

local — The influence of surrounding substituents, chemical groups, can be positive or negative

strongest

General principle

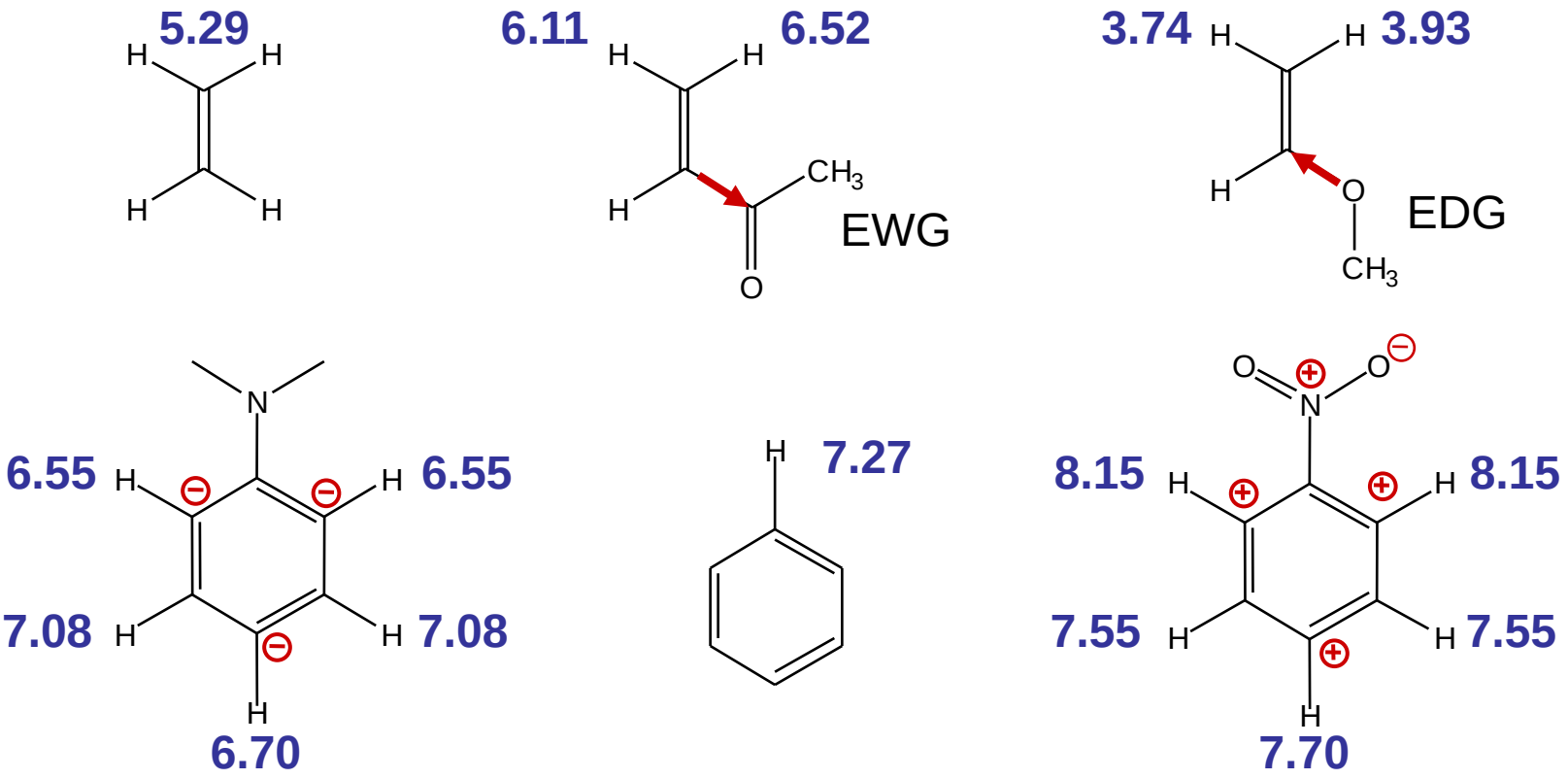
The more electrons around the nucleus
- the stronger the shading effect
- the lower the chemical shift values

Chemical shift of protons

	CH4	CH3I	CH3Br	CH3Cl	CH3F
Electronegativity	2.1	2.5	2.8	3.0	4.0
Shift [ppm]	0.23	1.98	2.45	2.84	4.13

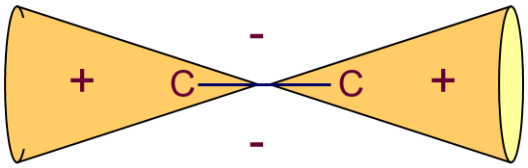
(shift increases with electronegativity)

Resonant (mesomeric) effect



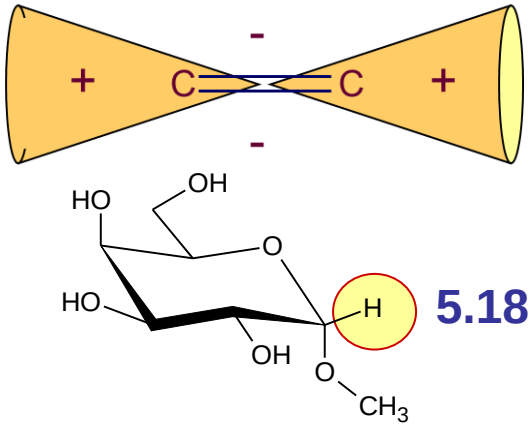
Chemical shift of protons

Anisotropic effect

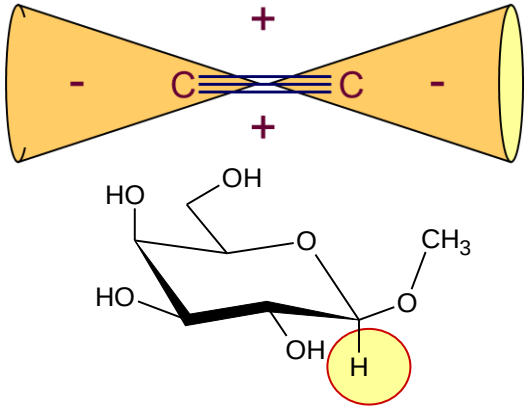


\+ larger δ

\- lower δ

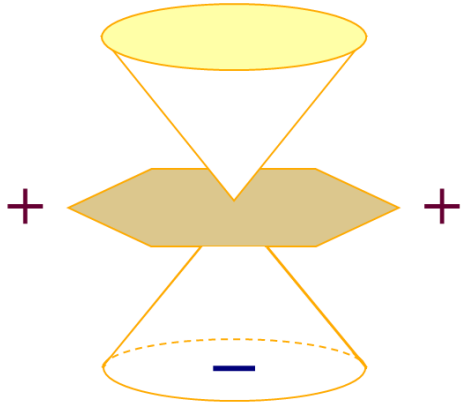


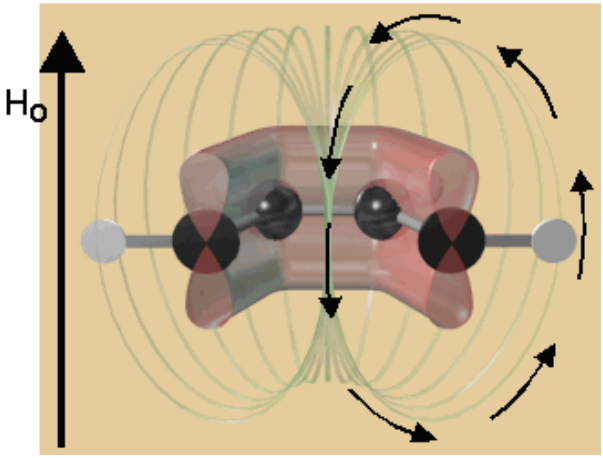
5.18

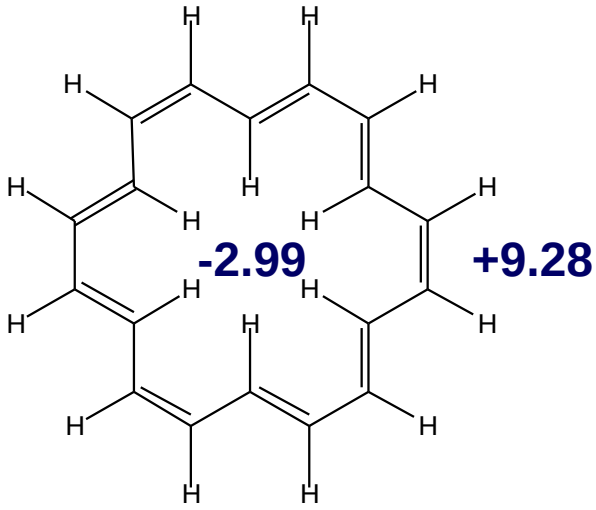


4.69

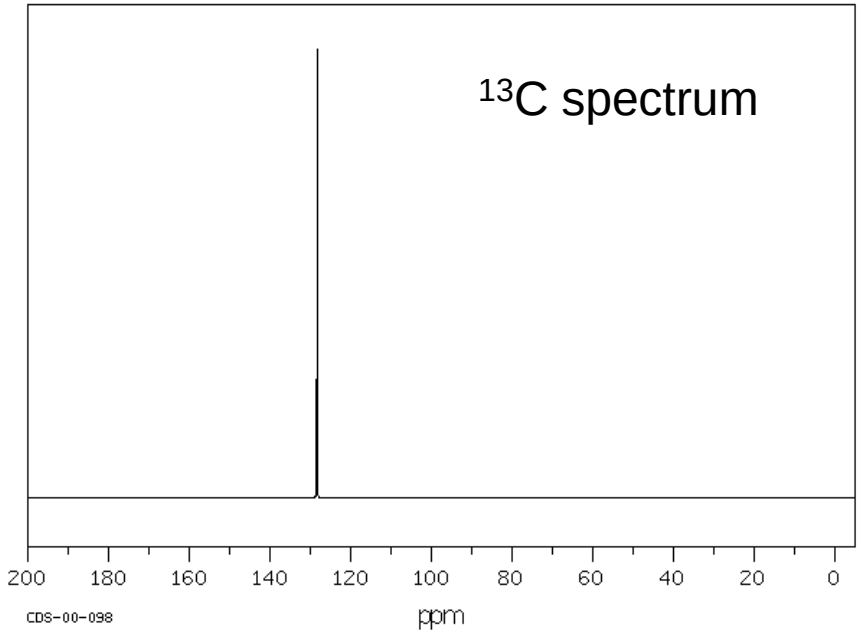
„Ring current" effect



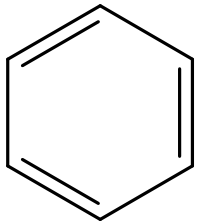




Symmetry and chemical shift

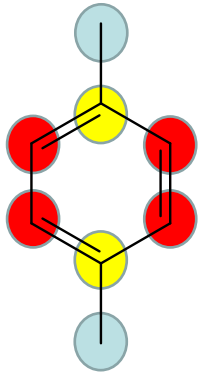


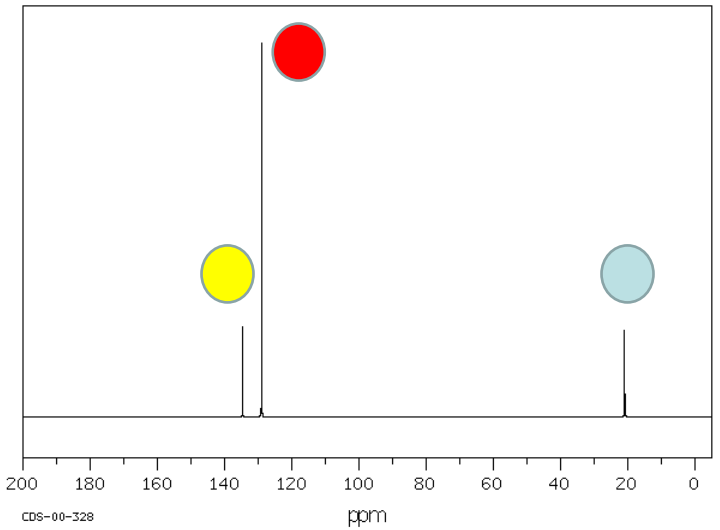
The same chemical environment
=
the same shielding



sixfold axis of symmetry

Number of signals
=
Number of non-equivalent nuclei



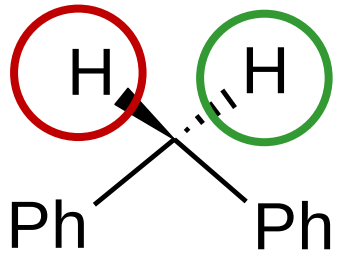


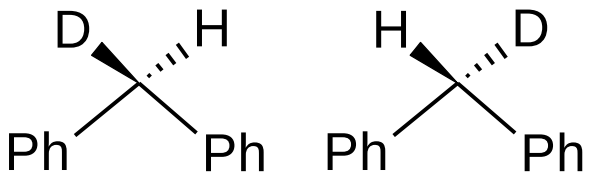
Chemical equivalence

- Nuclei are chemically equivalent if there is a symmetry operation, that transfers them to itself
- Protons in CH_3 groups are always equivalent due to the rapid rotation
- Chemically equivalent nuclei have the same chemical shift

Identification aid: Thought of replacing hydrogen with deuterium

Homotopic nuclei

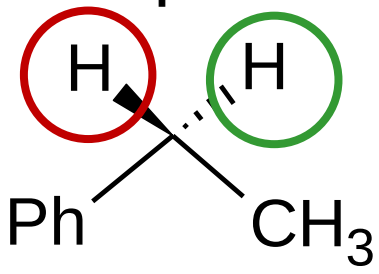


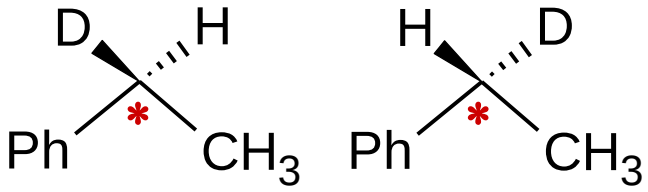


identical molecules

chemically equivalent

Enantiotopic nuclei





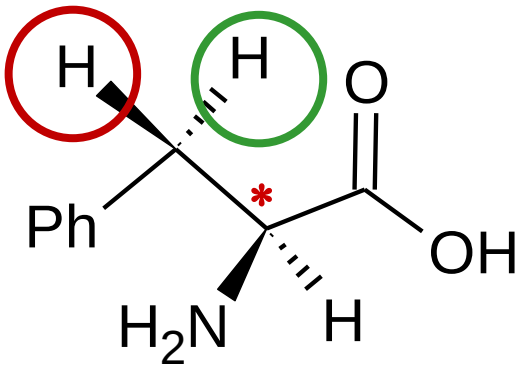
Enantiomers

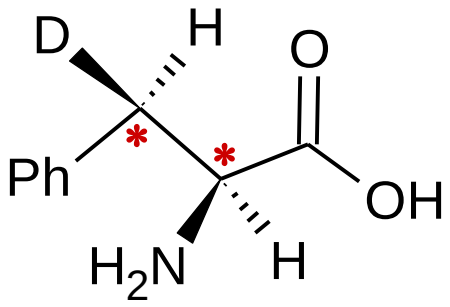
chemically equivalent

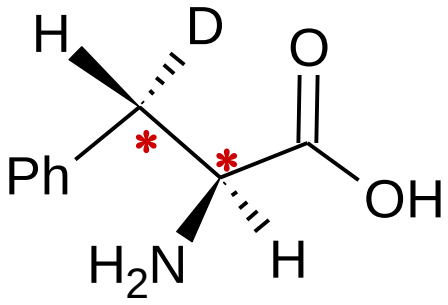
(mirror images)

Chemical equivalence

Diastereotopic



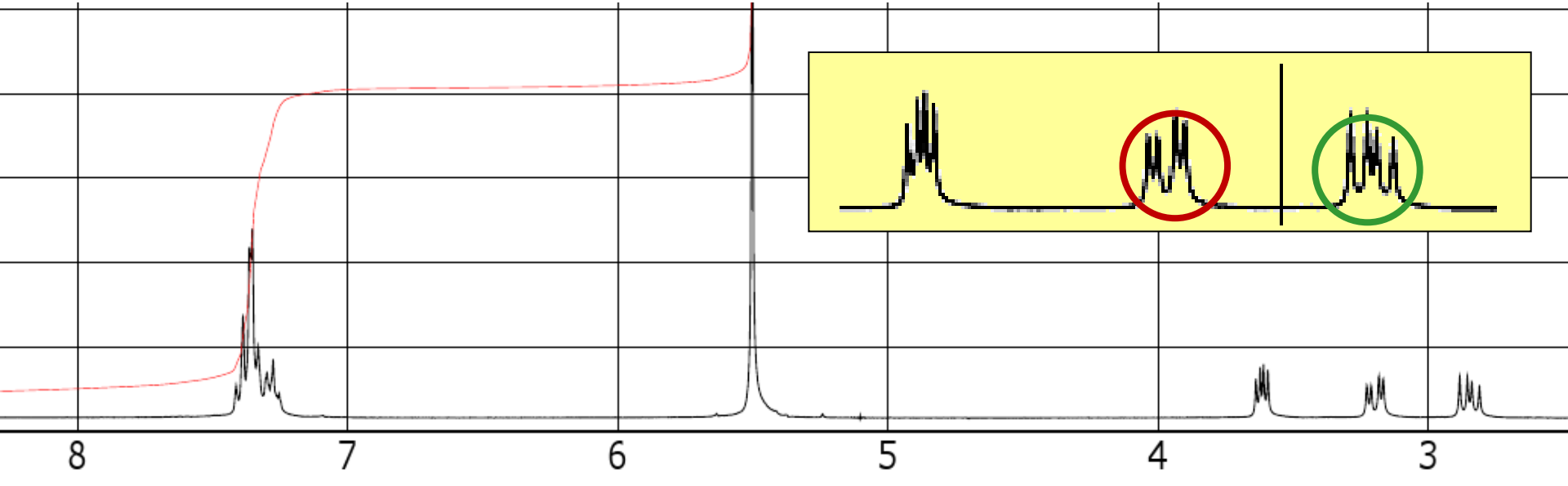




Two chiral centres - diastereomers

They are NOT chemically equivalent

Different chemical shifts!!



Intensity of signal

^{1}H spectrum

Intensity of signal
=
Number of equivalent nuclei

integration – area under the signal