Four Contributions to the Resonance Frequency of Nuclei in Matter

$$\omega = \gamma B$$

ALL TENSORS

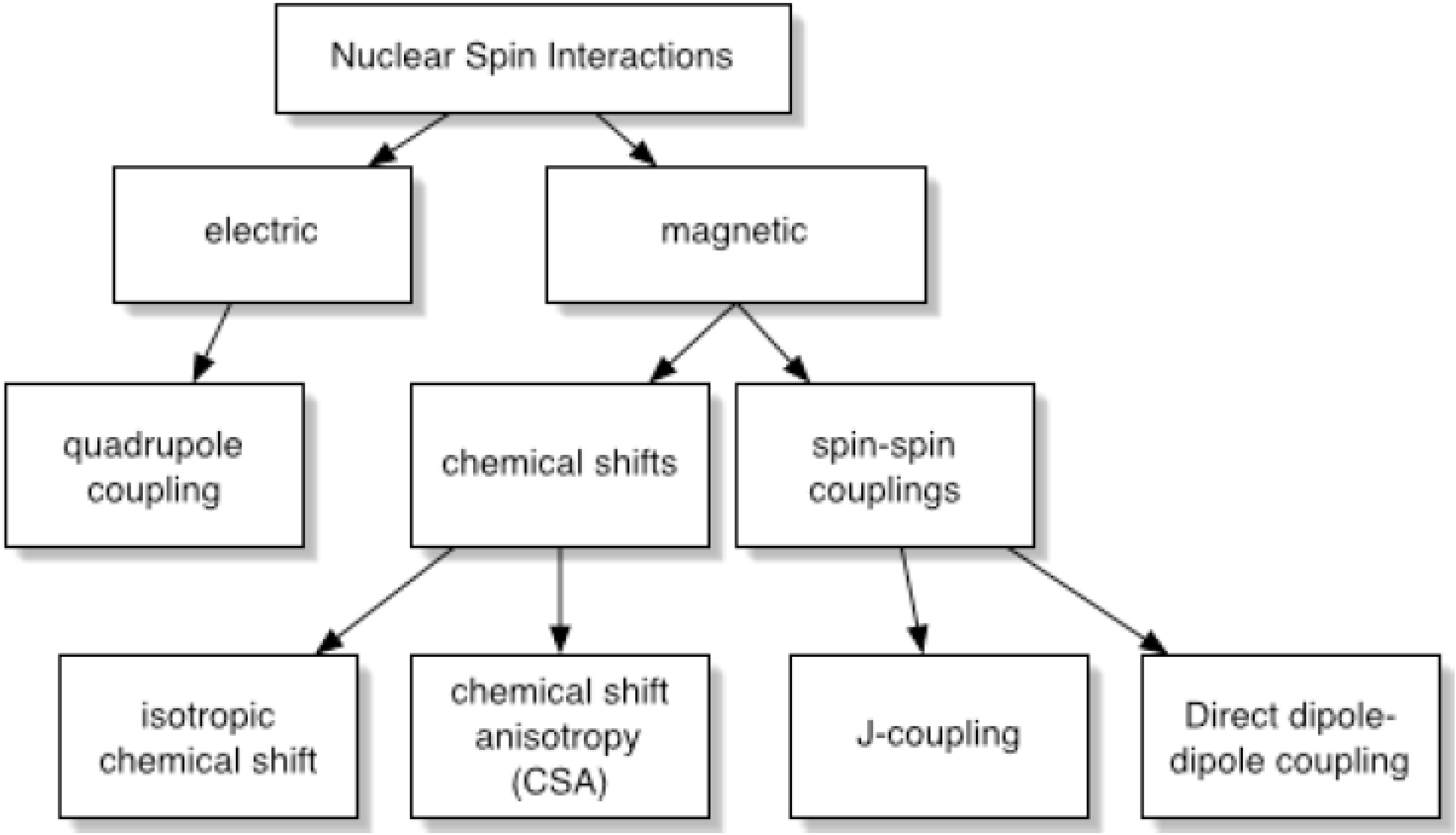
1) Shielding, chemical shift
electron distribution around nuclei, induced magnetic field

2) Dipolar interactions
magnetic nuclei distribution, through space interactions, in solids

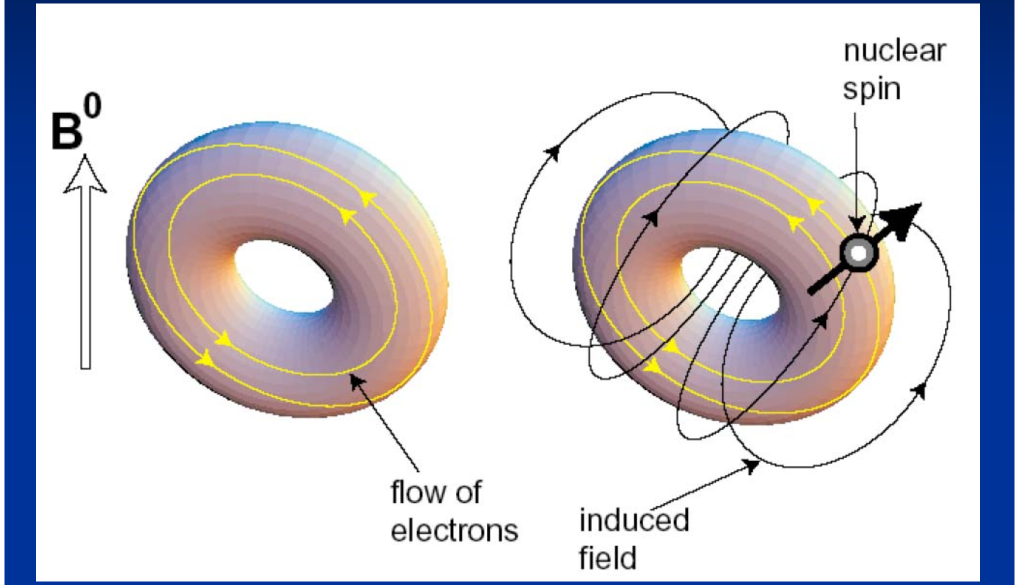
3) Electric field gradient
distribution of nuclei (positive charge) and electrons (negative charge)
quadrupolar nuclei

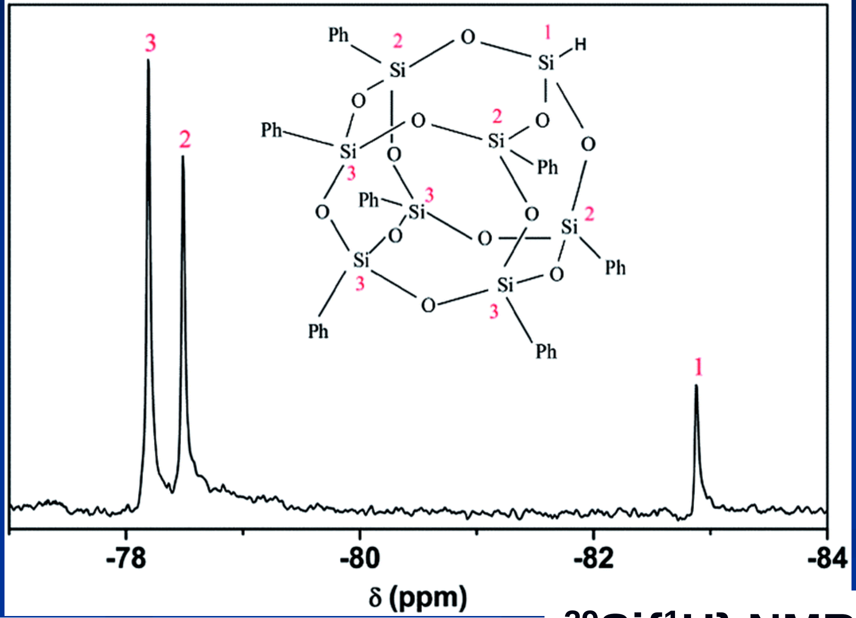
4) Scalar coupling
dipolar interactions through electrons in molecules, bonds

Nuclear Spin Interactions

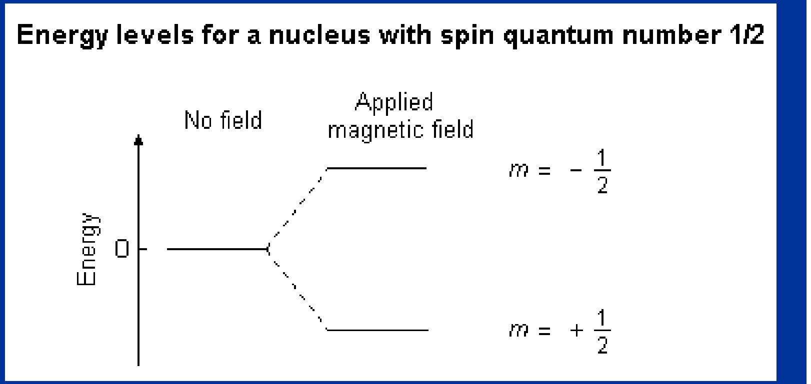


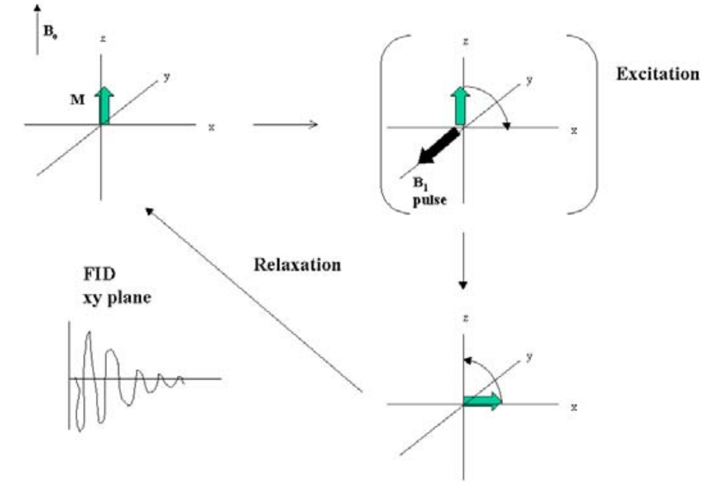
Shielding, Chemical shift





^{29}Si{^{1}H} NMR





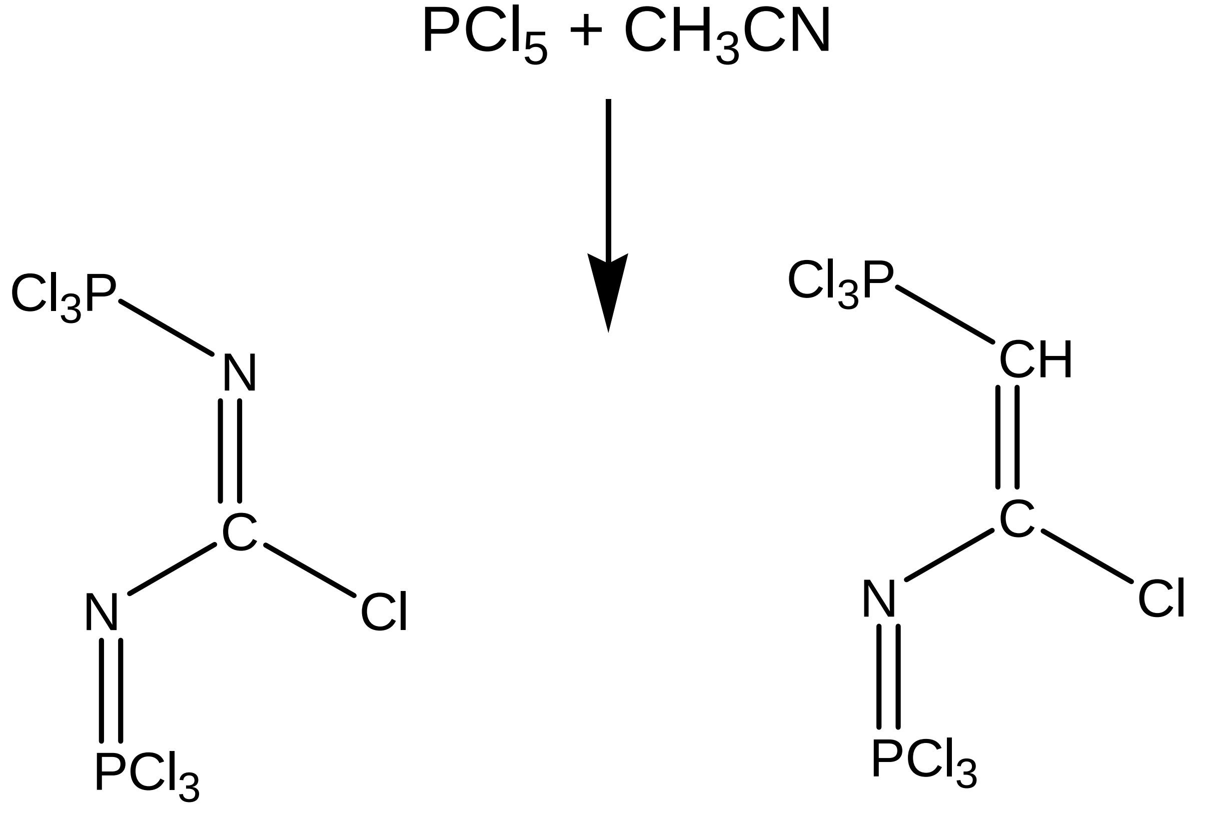
$$\nu = \gamma B / 2\pi$$

Chemical Shift Information

- (The presence of an element in the sample)
- **Number of signals** = number of chemically different atoms
  Symmetry of the molecule
- **Relative intensity** = ratio of atoms – integration
- **Position** = chemical shielding / shift – electronic
  environment, type of bonds, oxidation state,
  coordination number
- **Multiplicity** = connectivity of functional groups, J-coupling

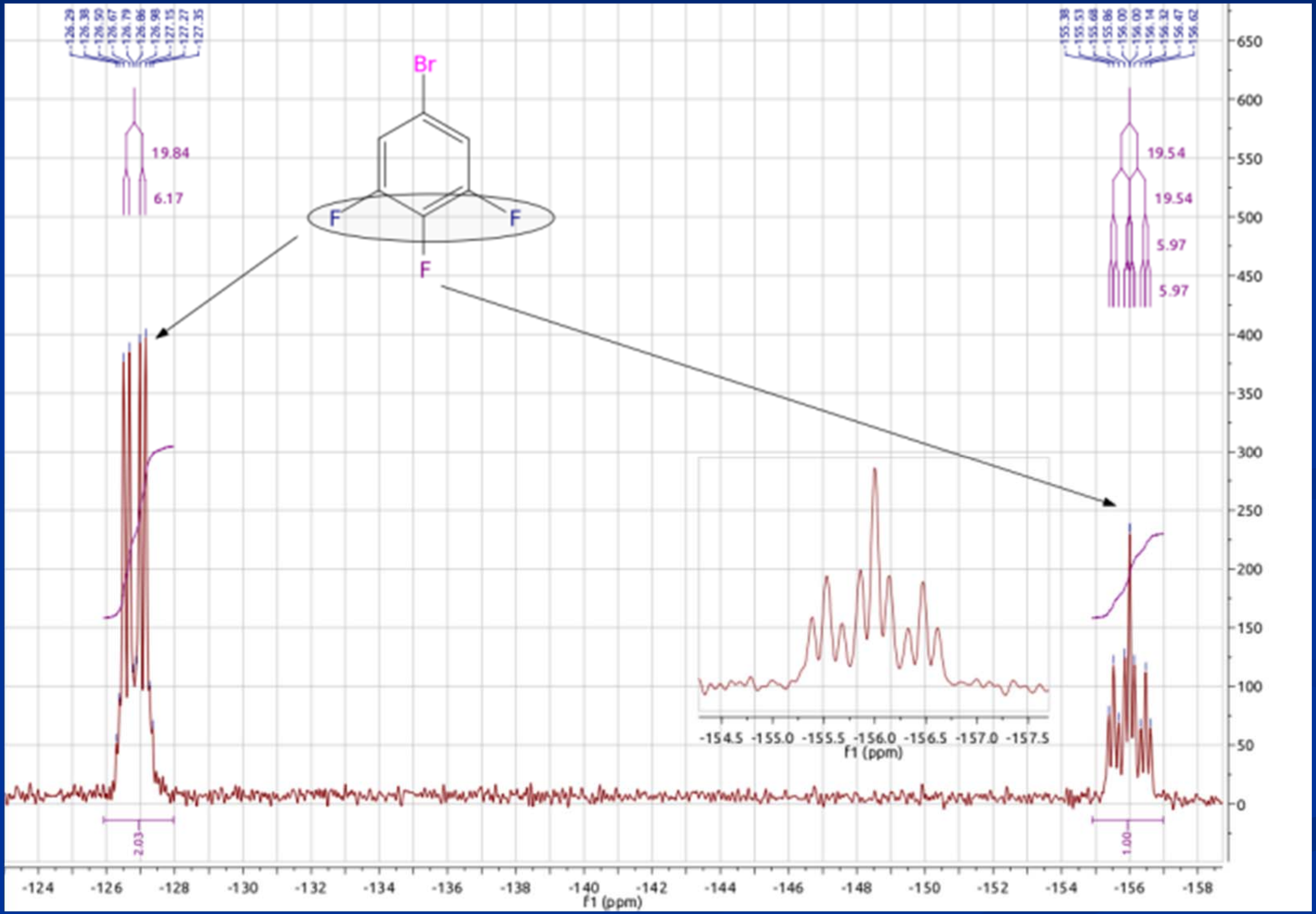
Chemical Shift Information

The presence of an element in the sample



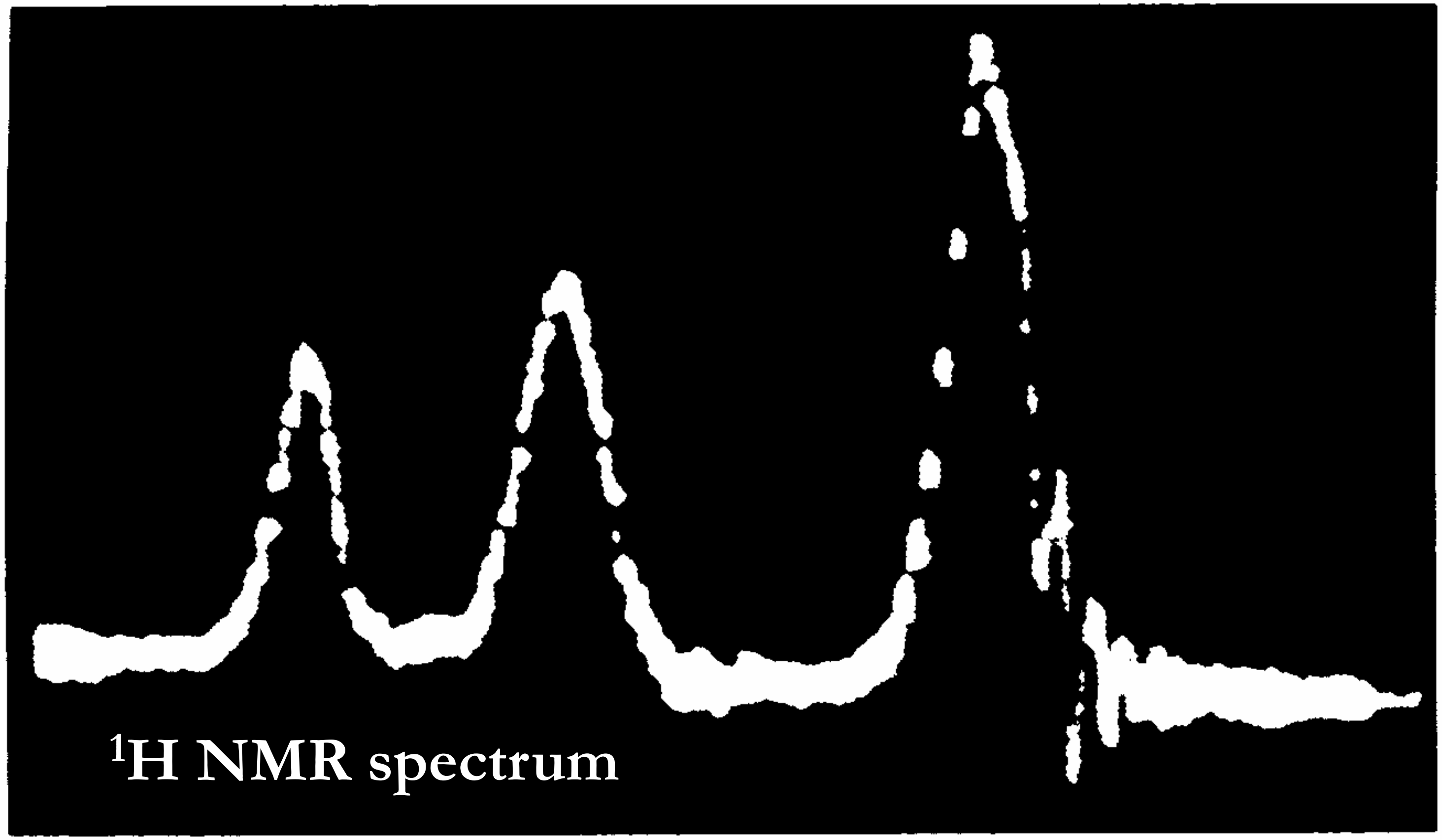
X-ray crystallography ^{1}H NMR (6.3 ppm, dd 43 and 13 Hz)

Chemical Shift Information



^{19}F NMR

Chemical Shift

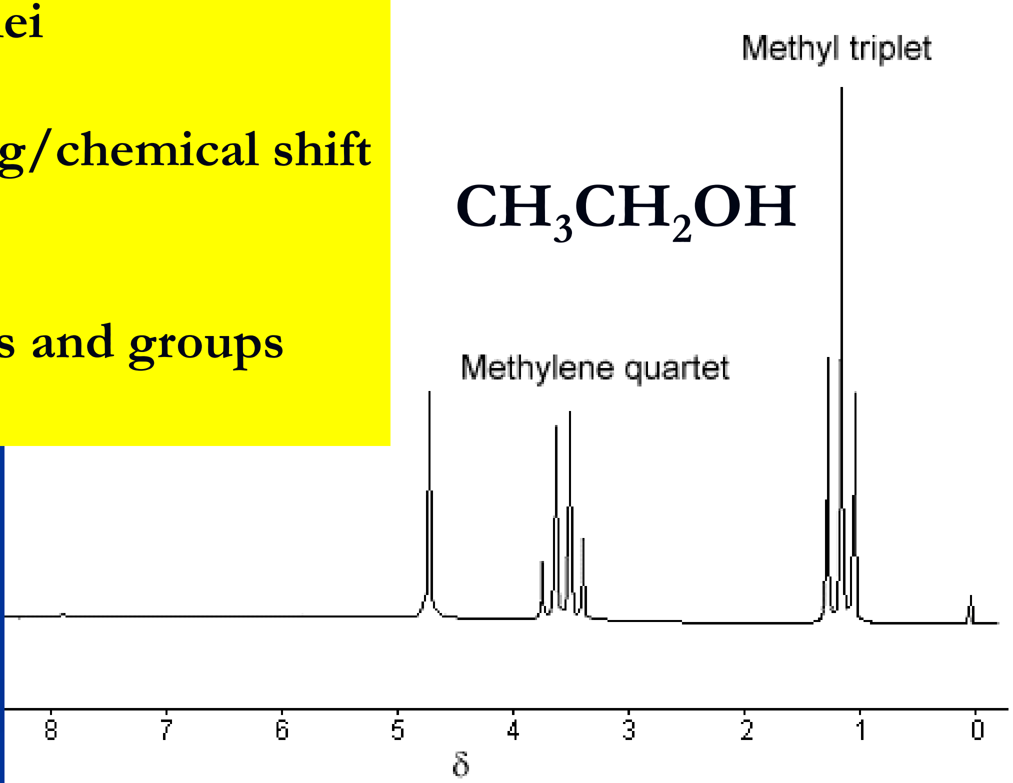


The three peaks of ethyl alcohol as first observed in 1951 at Stanford University.

Chemical Shift

Chemical shift for a given molecule:

- Number of signals = nonequivalent nuclei molecular symmetry
- Relative intensity = number of nuclei
- Position in the spectrum = shielding/chemical shift electronic structure
- Multiplicity = connectivity of atoms and groups

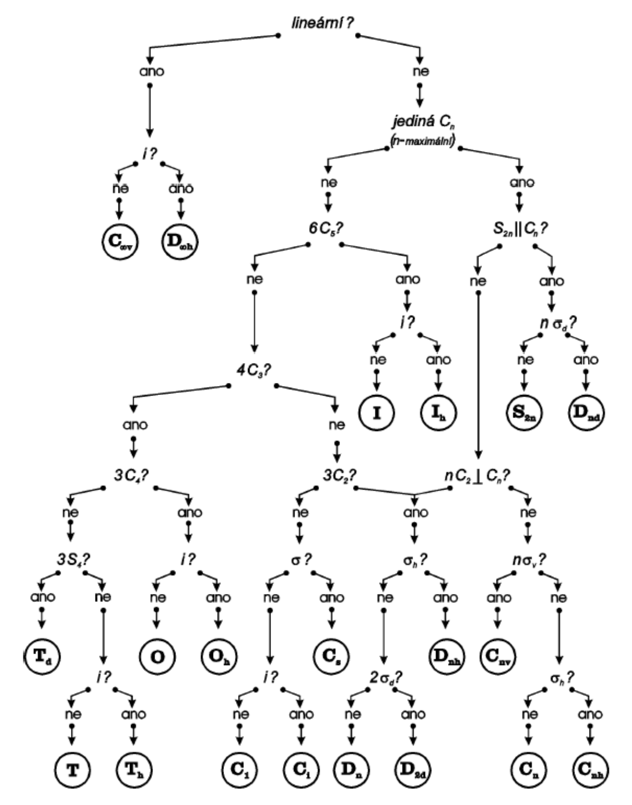


CH_3CH_2OH

Molecular Symmetry

Number of signals = nonequivalent nuclei, molecular symmetry

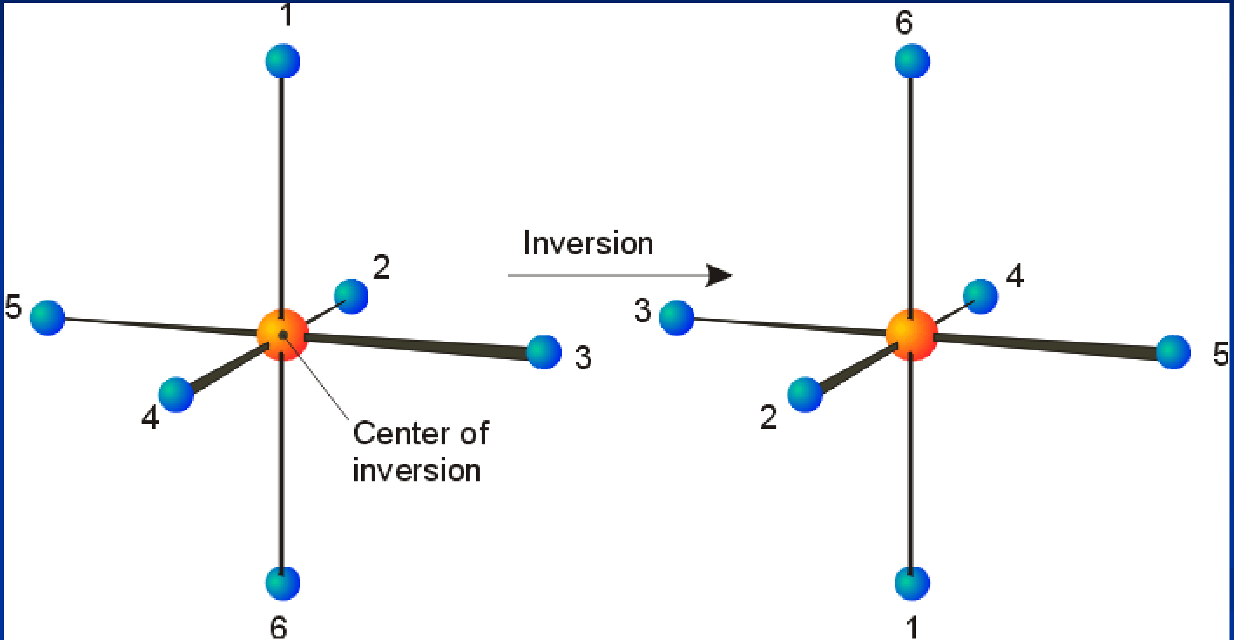
Flow chart for point group determination



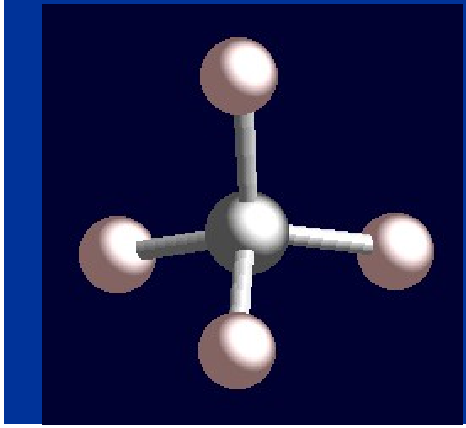
Symmetry Elements and Operations

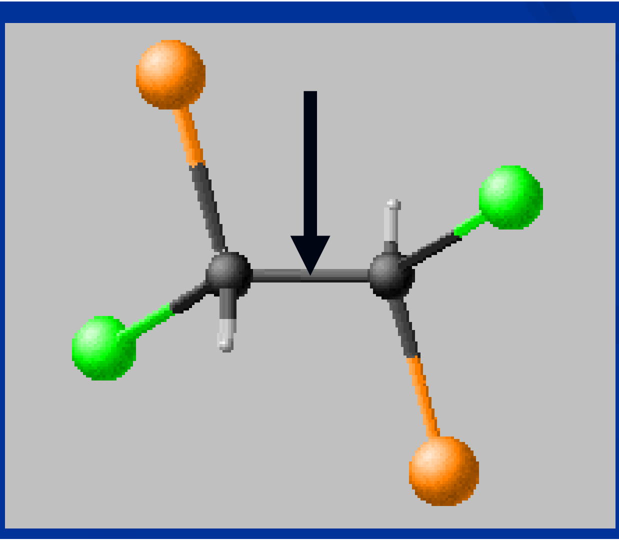
Symbol	Element	Operation	
E	Identity	Identity	No change, (= 1)
i	Center of symmetry (inversion center) POINT	Inversion	Inversion through the central point every point x,y,z translated to -x,-y,-z
C_n	Rotation axis LINE	True (proper) rotation	Rotation by an angle 360/n
σ	Plane of symmetry, mirror PLANE	Reflection	Reflection through a mirror plane
S_n	Improper axis Roto-reflection axis LINE	Improper rotation	Rotation by an angle 360/n followed by reflection through a mirror plane

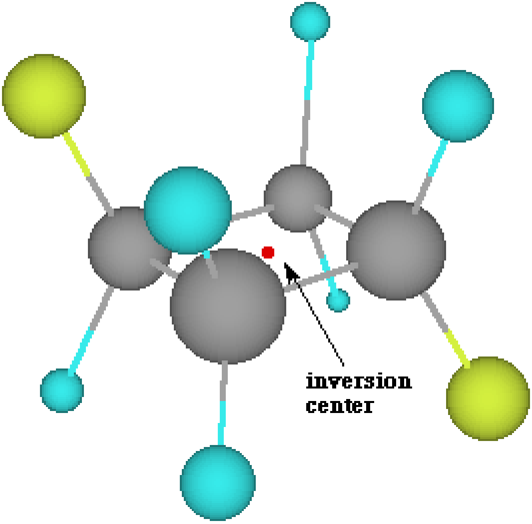
Inversion Center



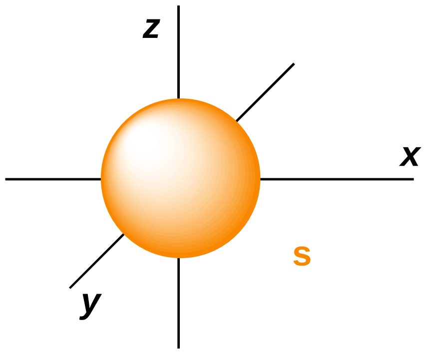
NO inversion center

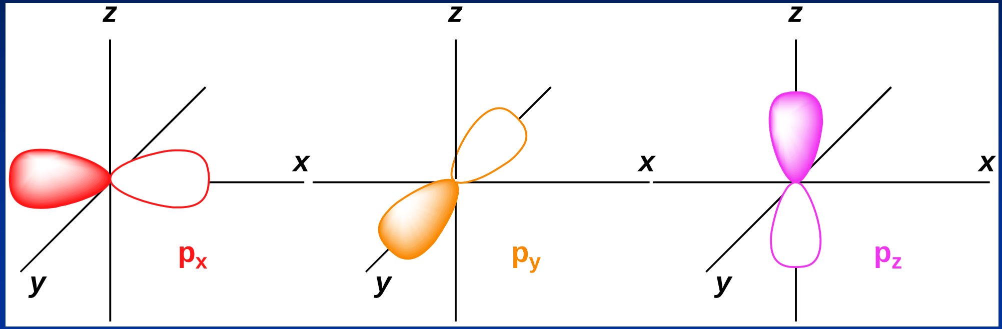


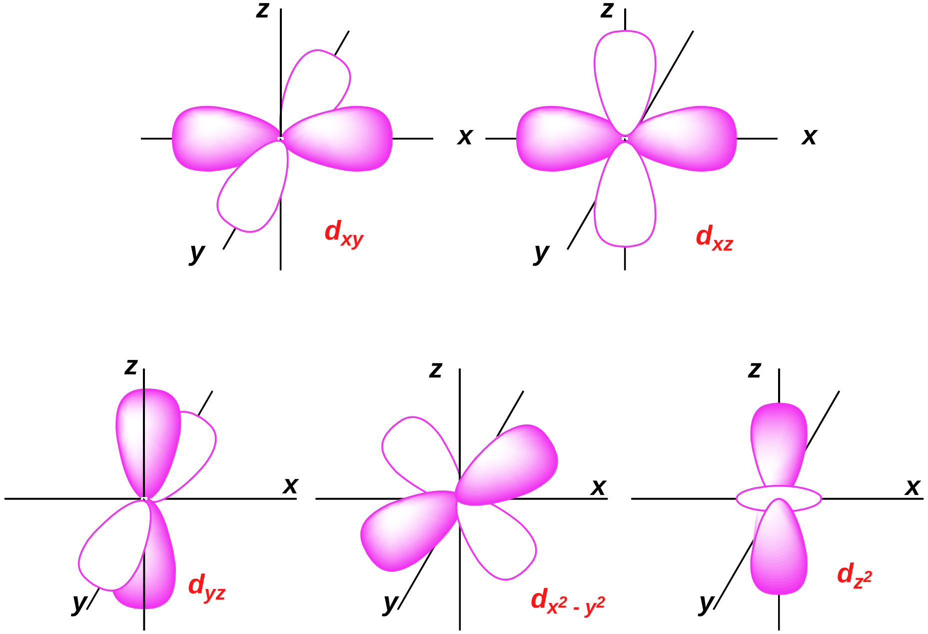


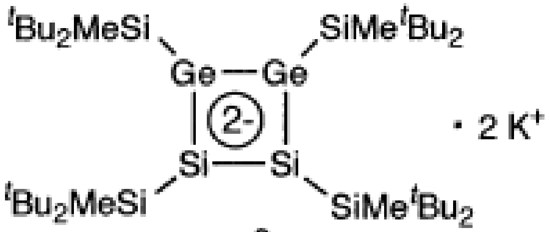


Inversion Center

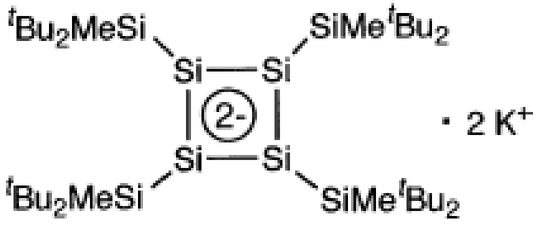








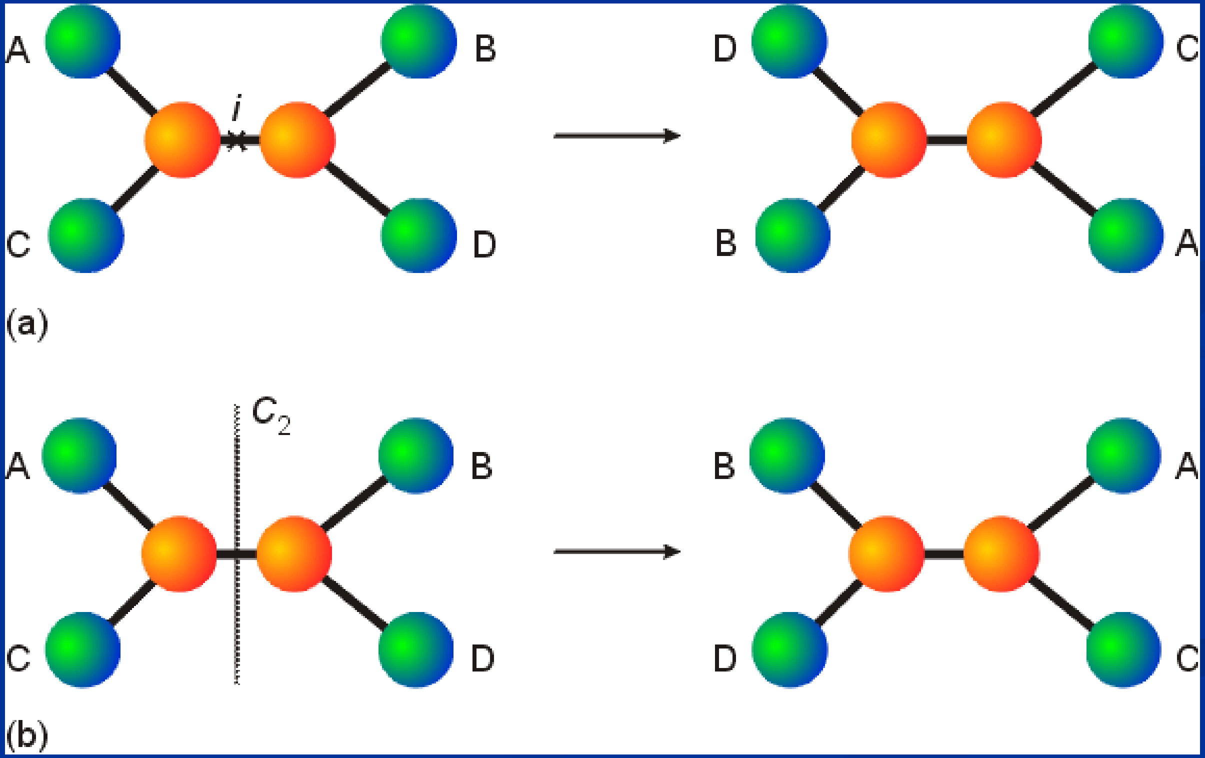
2^{2-}



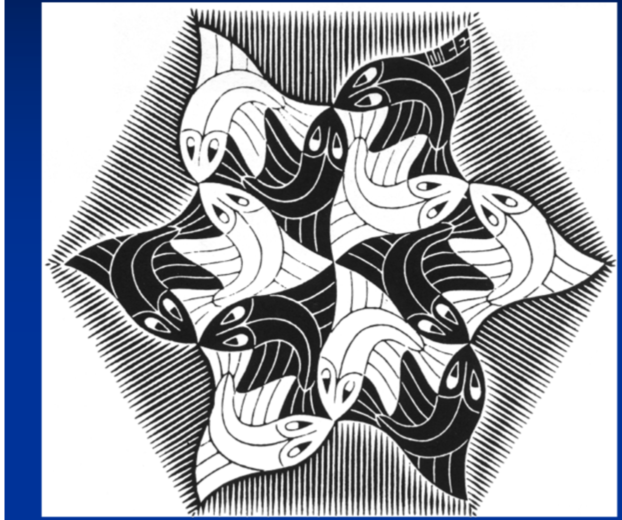
4^{2-}

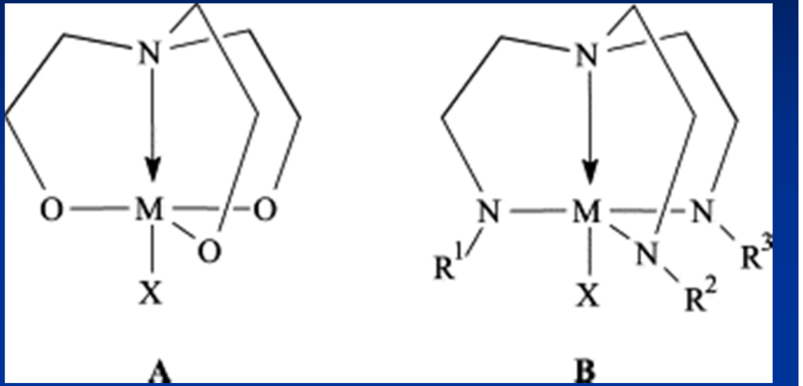
Rotation Axis C_2

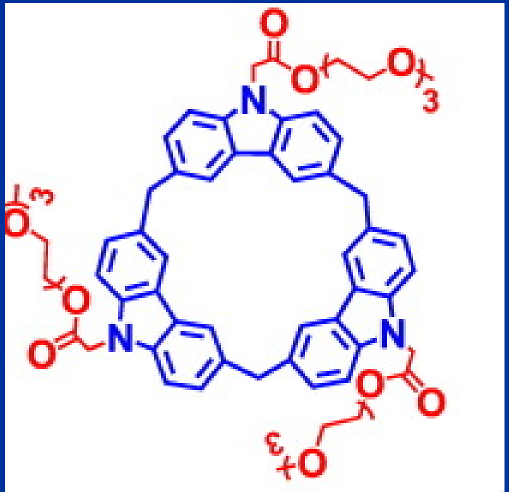
Rotation by 360/n about C_n brings the object to an indistinguishable position from the original



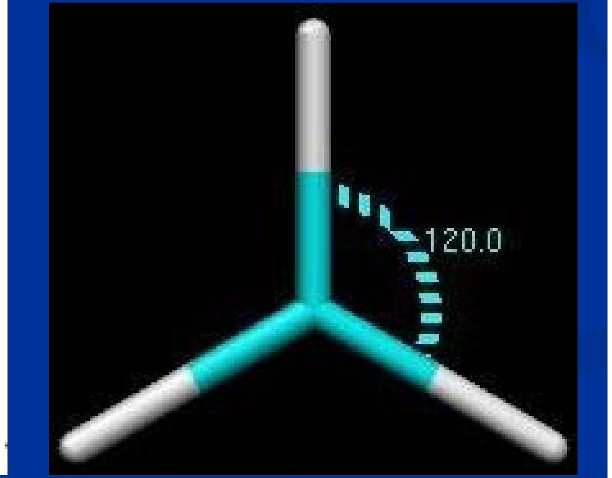
Rotation Axis C_3

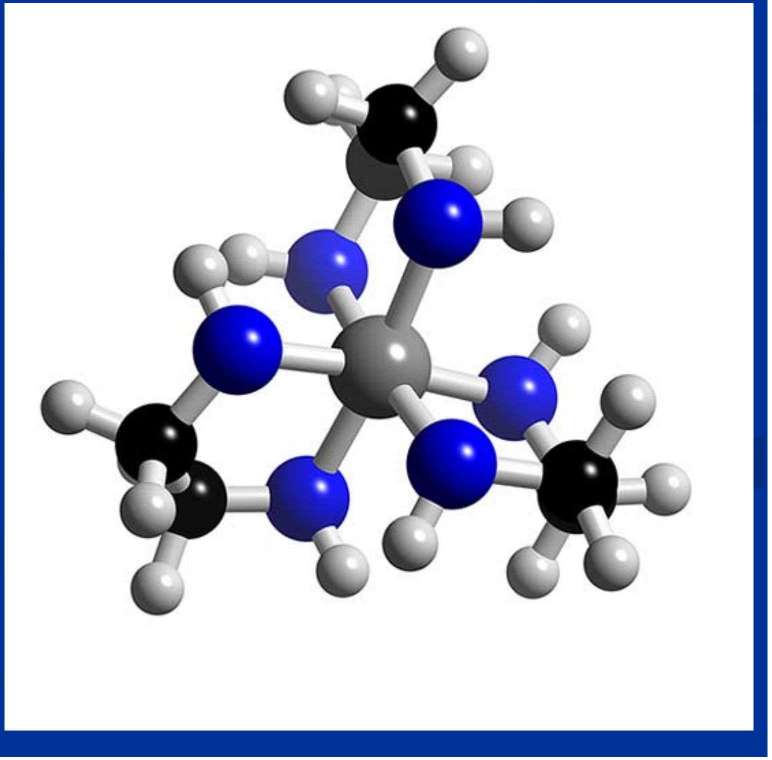




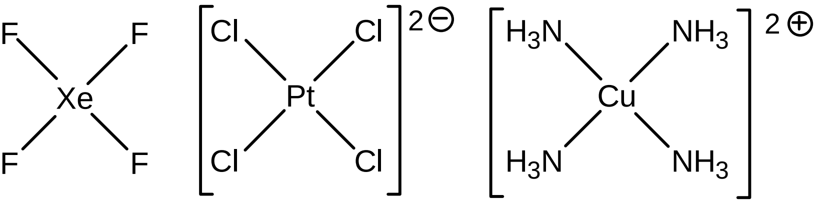


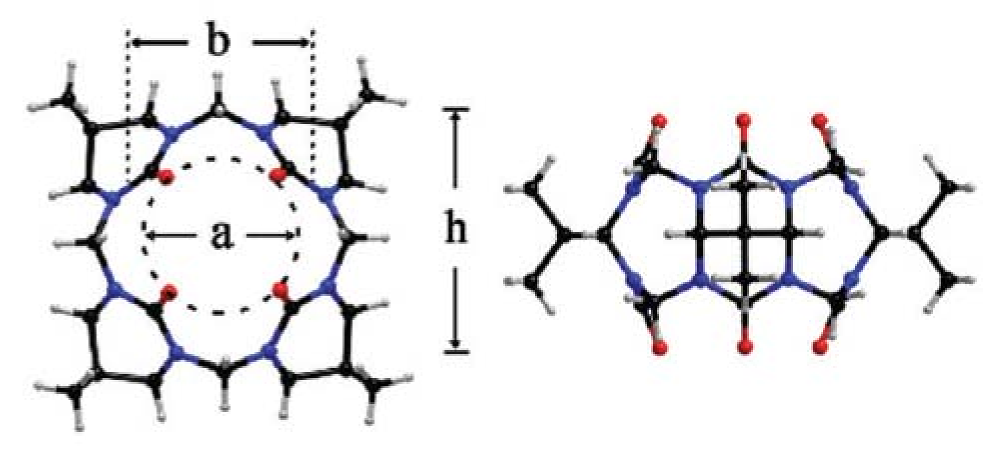
Calix[3]carbazole (1)

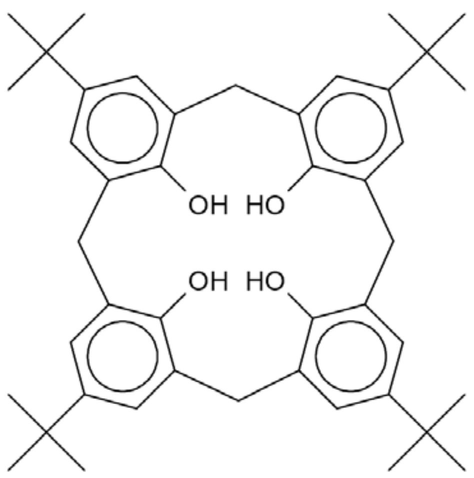


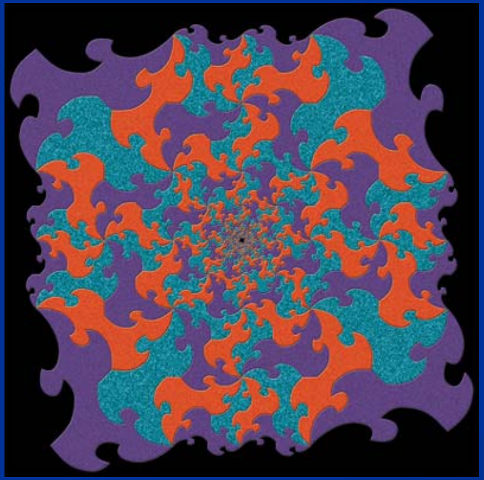


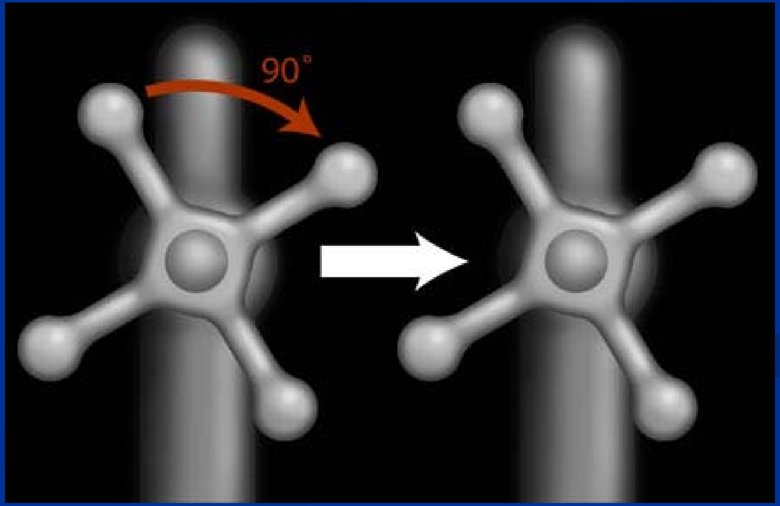
Rotation Axis C_4





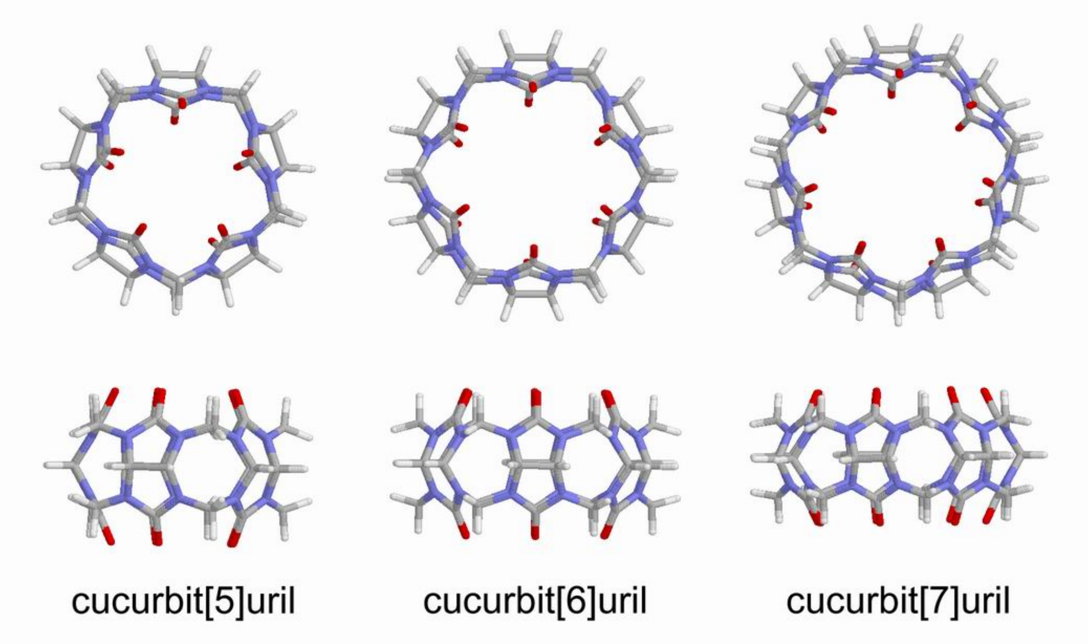




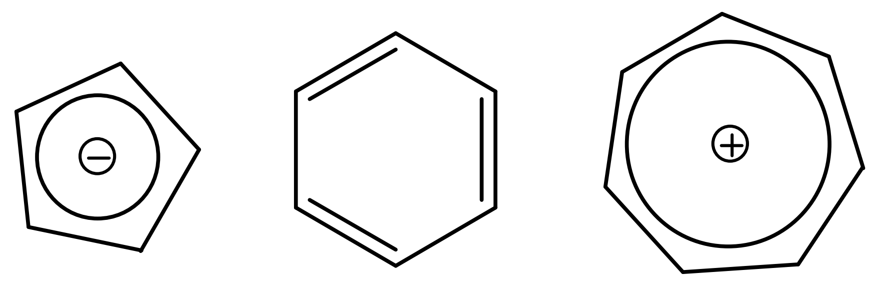


$C_4^1 \rightarrow C_4^2 \rightarrow C_4^3 \rightarrow C_4^4 = E$

Rotation Axis C_n


cucurbit[5]uril cucurbit[6]uril cucurbit[7]uril

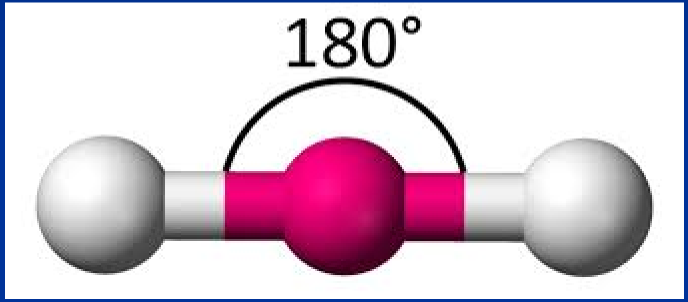
$C_5, C_6, C_7, \ldots\ldots C_\infty$

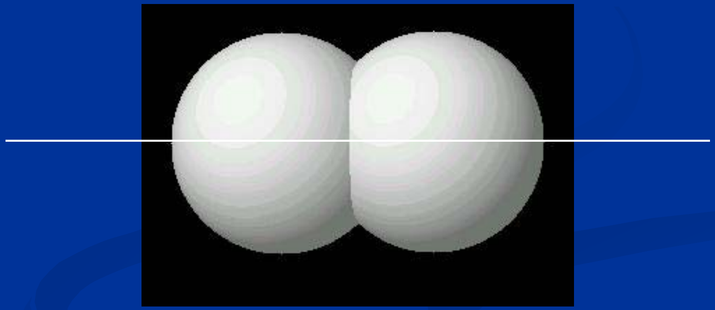


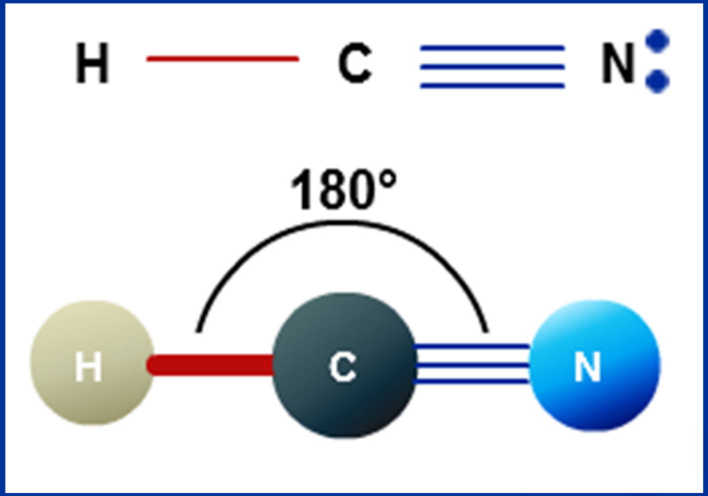
$$C_n^{1} \rightarrow C_n^{2} \rightarrow C_n^{3} \rightarrow C_n^{4} \ldots\ldots \rightarrow C_n^{n} = E$$

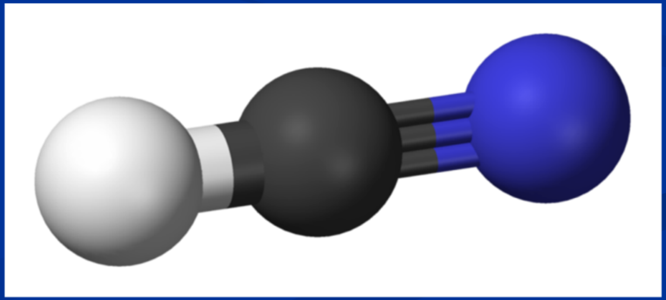
Rotation Axis C_∞

Linear molecules

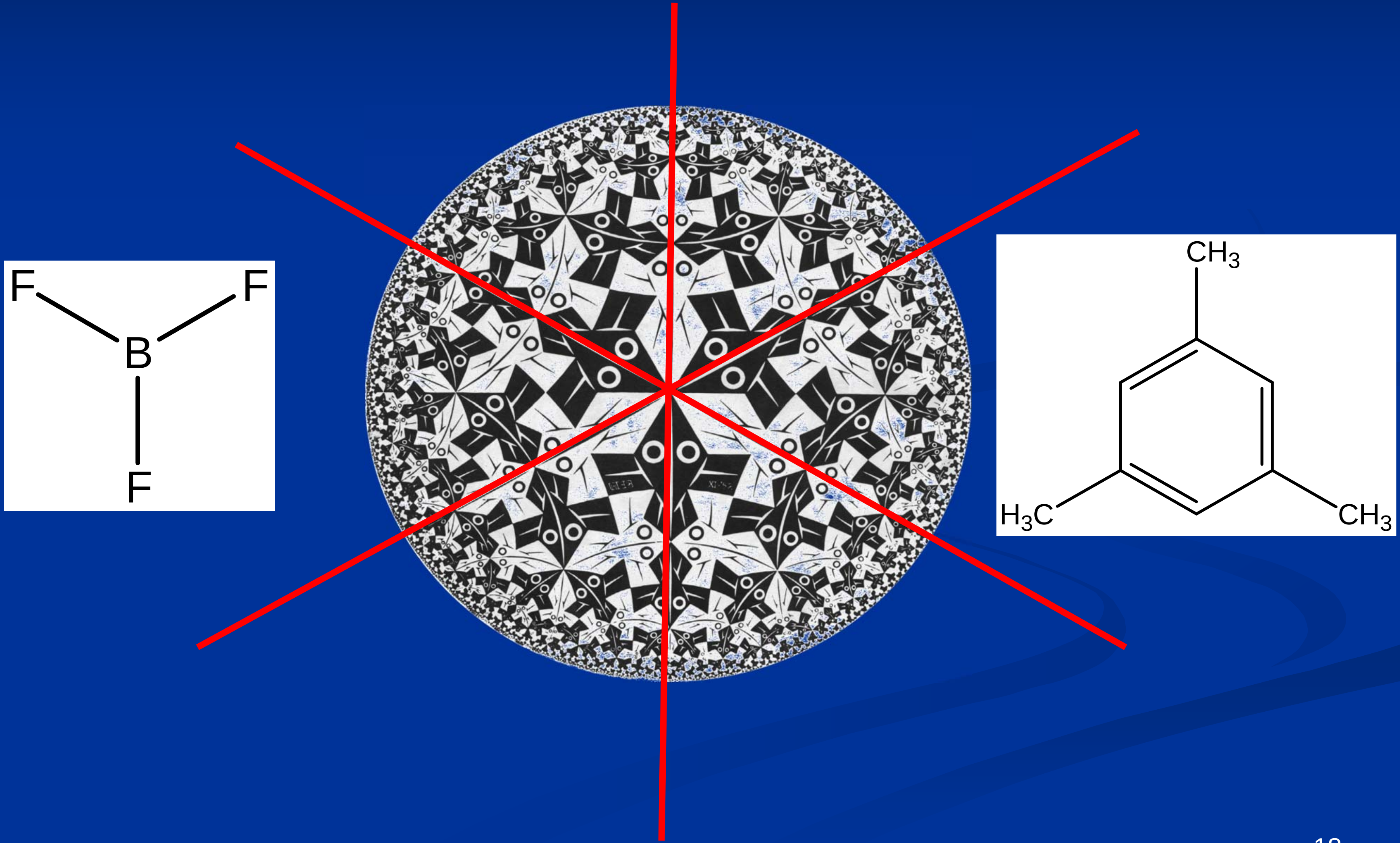








Plane of Symmetry σ



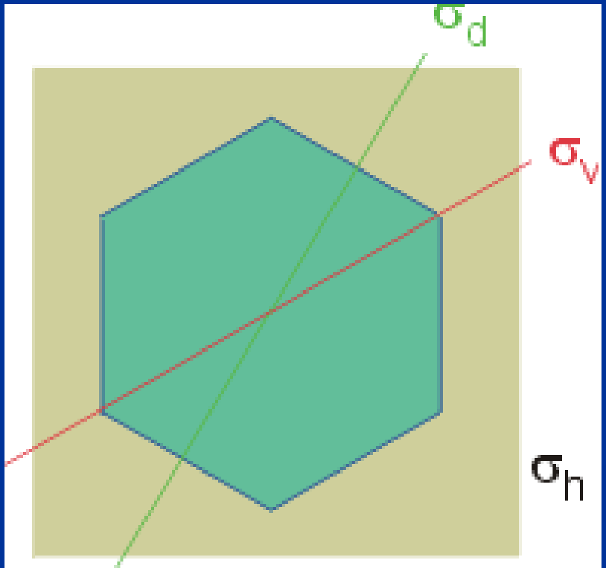
Plane of Symmetry σ

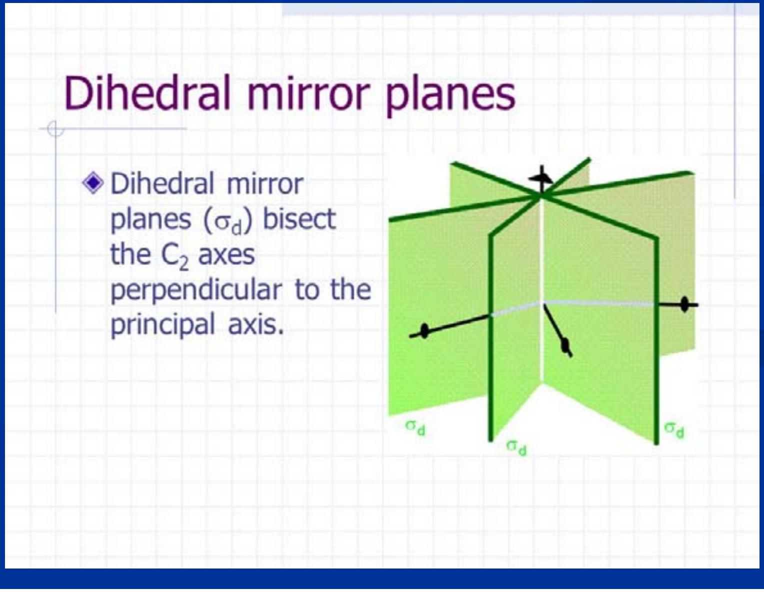
Planar molecules – symmetry plane of the molecule

σ_h = horizontal plane, perpendicular to principal axis C_n

σ_v = vertical plane, parallel to principal axis, bisects the most atoms

σ_d = dihedral plane, colinear with principal axis C_n, bisecting two C_2'

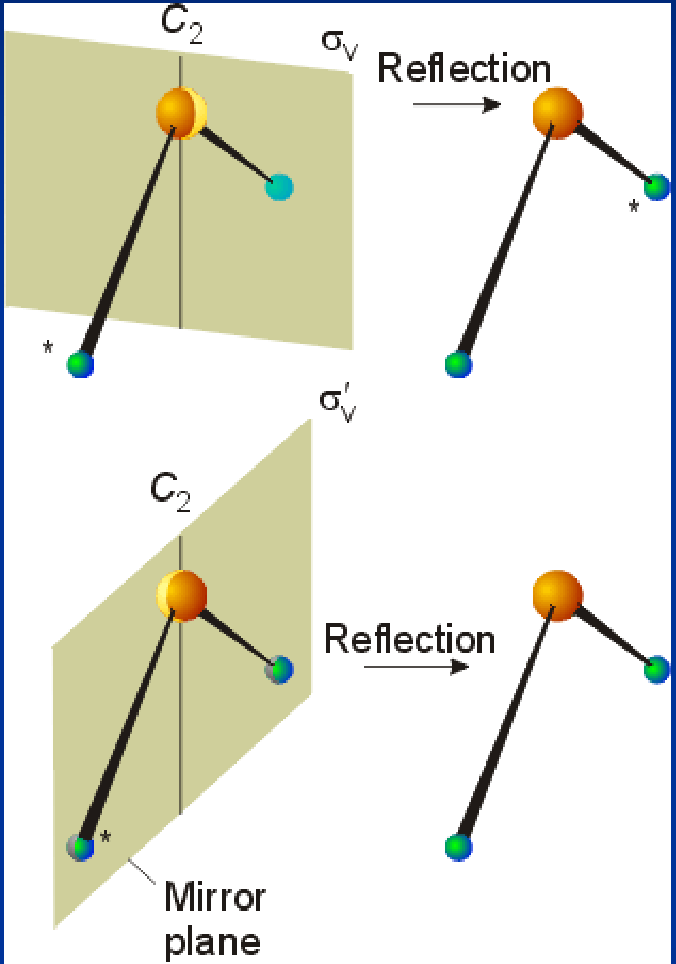


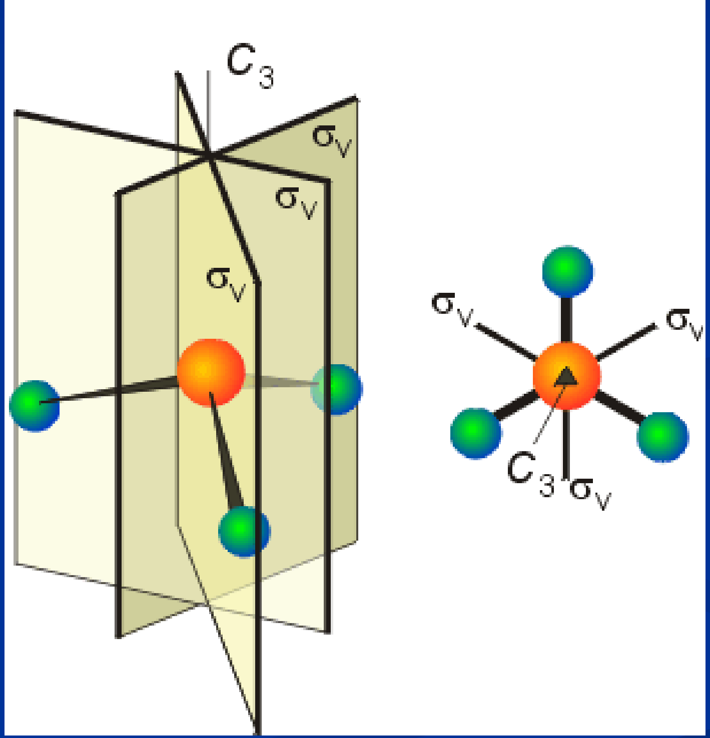


Dihedral mirror planes

- Dihedral mirror planes (σ_d) bisect the C_2 axes perpendicular to the principal axis.

Plane of Symmetry σ

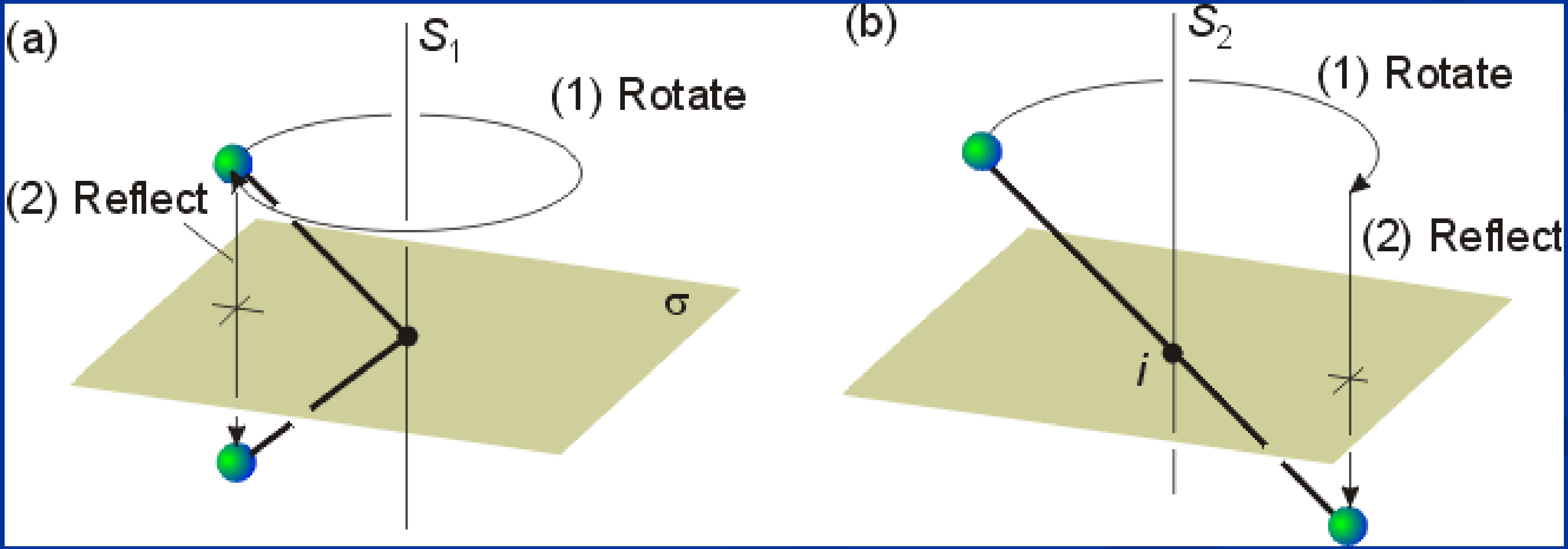




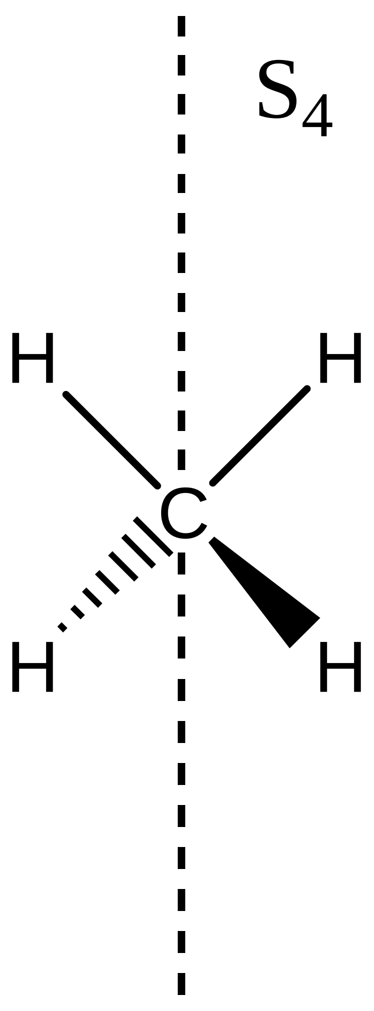
Improper Axis S_n

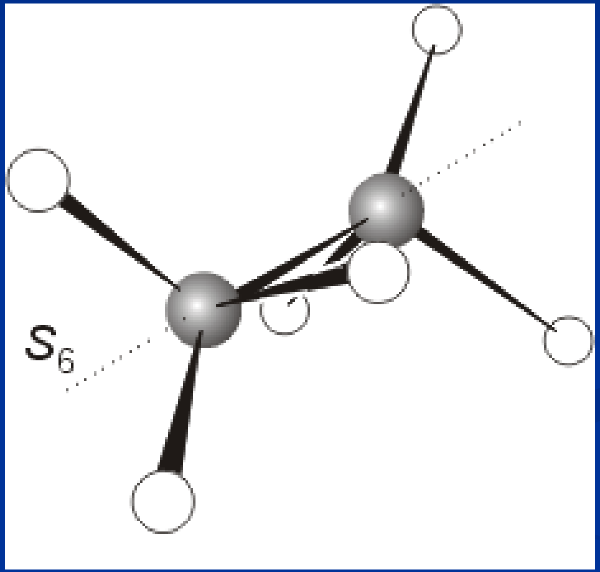
Rotation-reflection = a compound operation, rotation (C_n) followed by a reflection through a plane perpendicular to the C_n axis

$$\mathbf{S_1 = C_1 \times \sigma = \sigma} \qquad \mathbf{S_2 = C_2 \times \sigma = i}$$



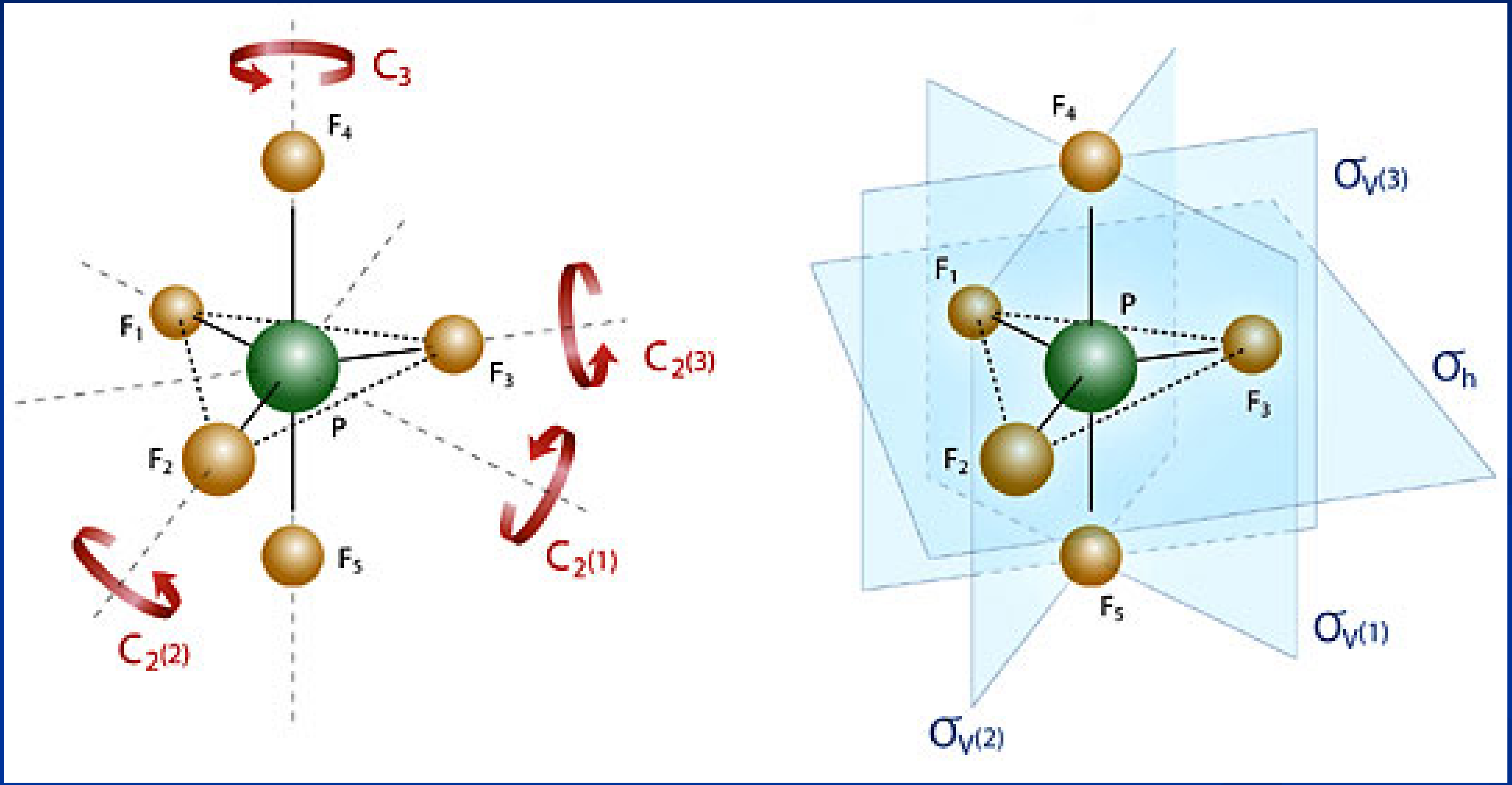
Improper Axis S_n





BF_3, C_6H_6

Symmetry Elements in a Molecule



Equivalent atoms = exchanged by symmetry operations

$F_4 = F_5$ $F_1 = F_2 = F_3$

Chirality

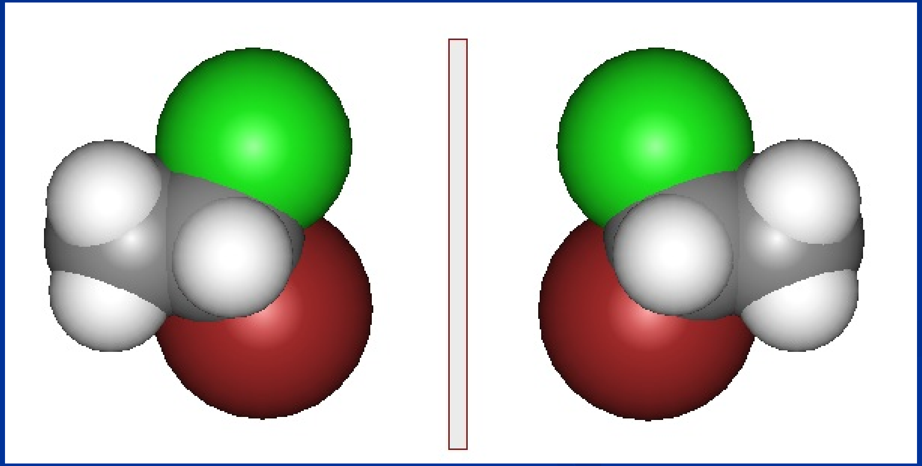
Figure 2. The Founding Fathers. R. M. Barrer (1910–1996) (right) and R. M. Milton (1920–2000) photographed

Chirality

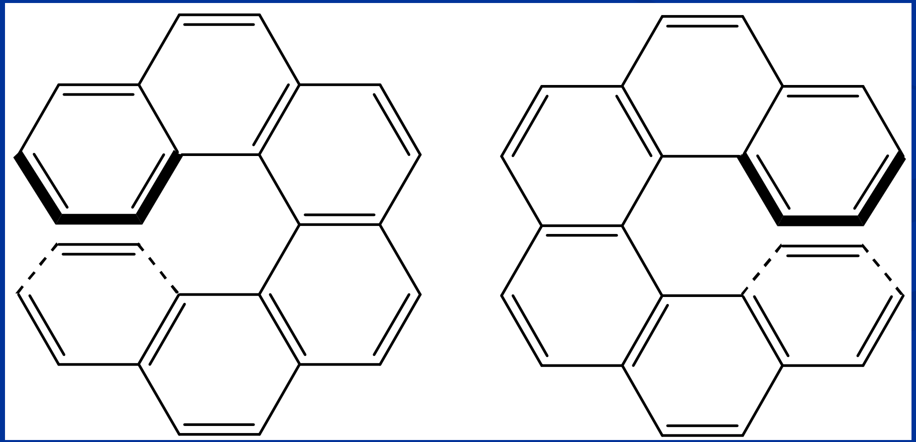
Condition of chirality: no S_n present in a molecule

$S_1 = \sigma$

$S_2 = i$



C_2 →



Chemical Shift

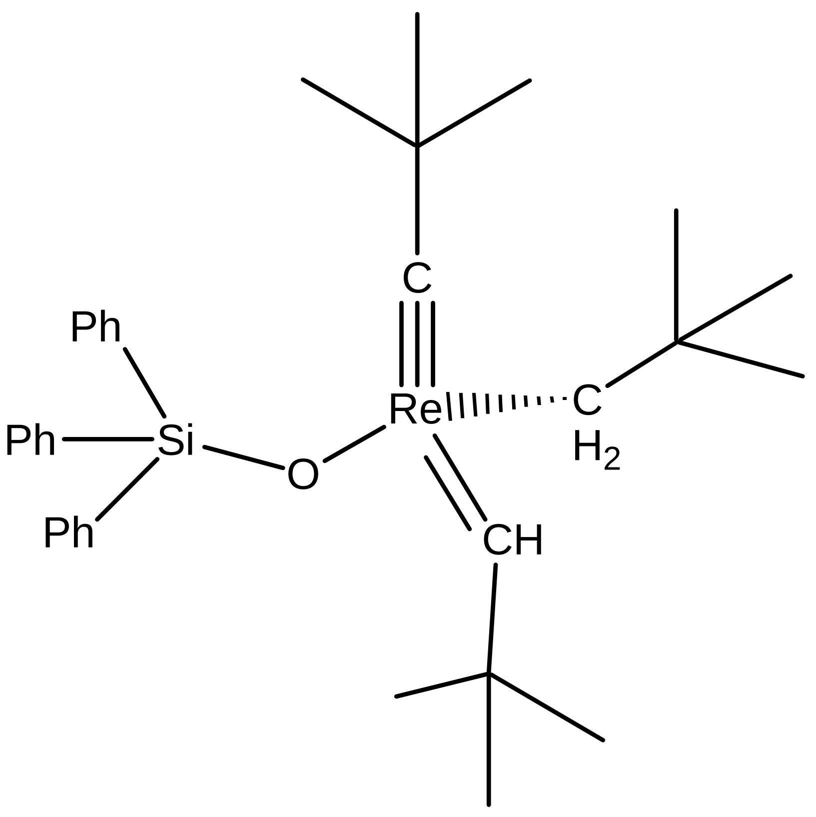
Number of signals = nonequivalent nuclei

Chemically different atoms

^{13}C NMR

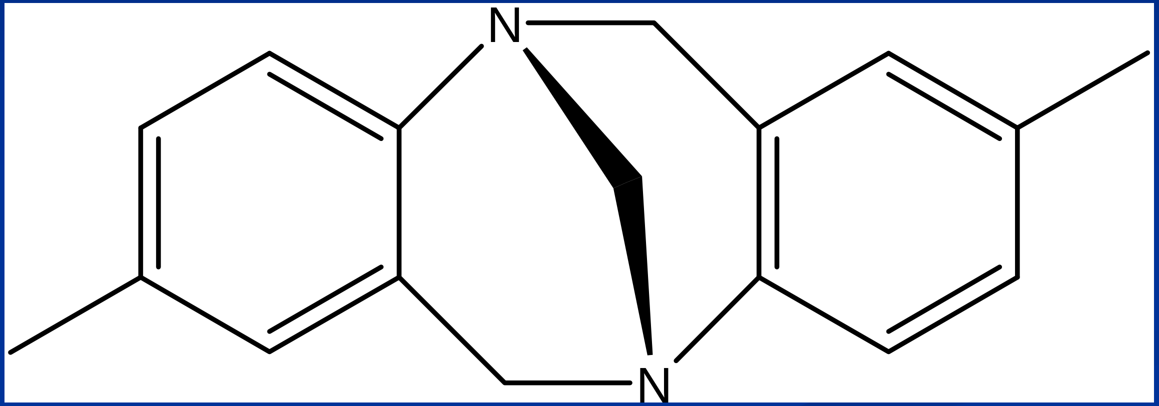
3 x t-Bu groups

No C_3 axis



Geometrical difference = chemical difference

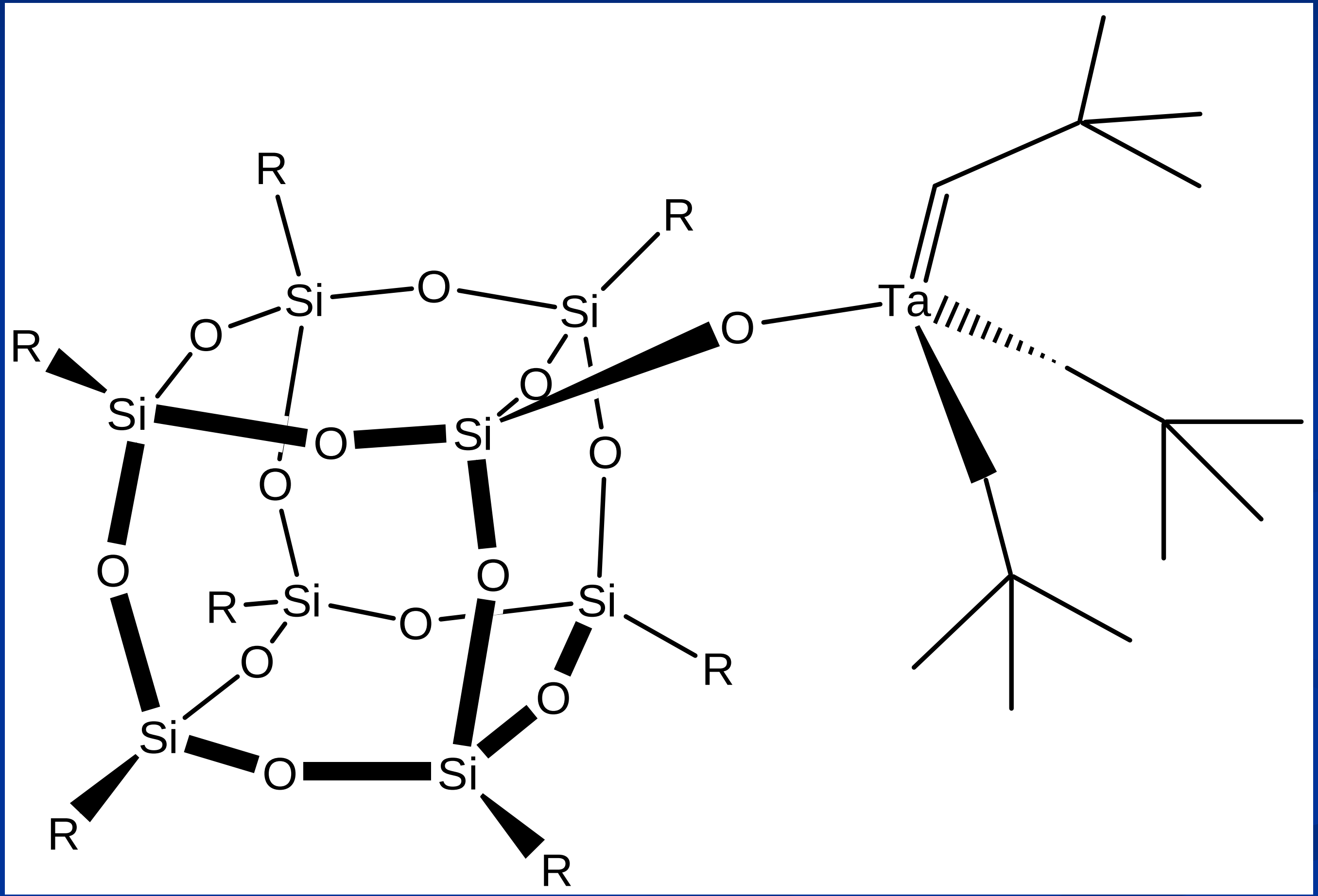
Molecular Symmetry



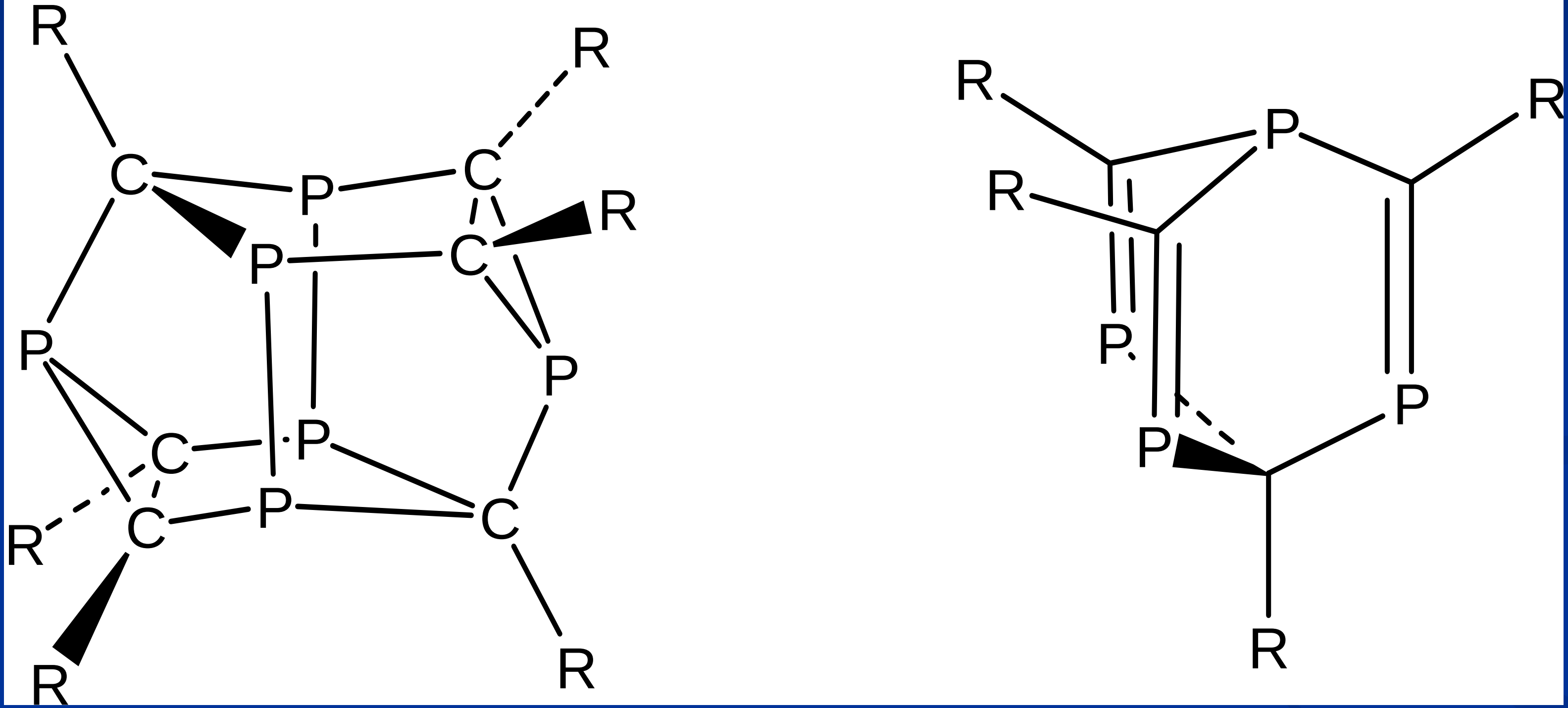
C_2 axis

1 x Me group signal
1 x NCH_2
1 x H_2CN_2

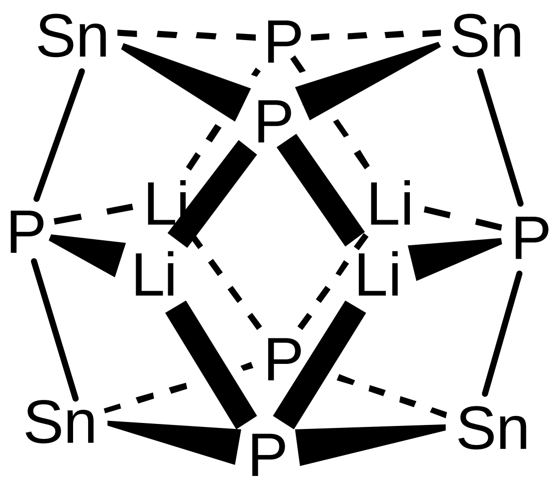
Chemical Shift

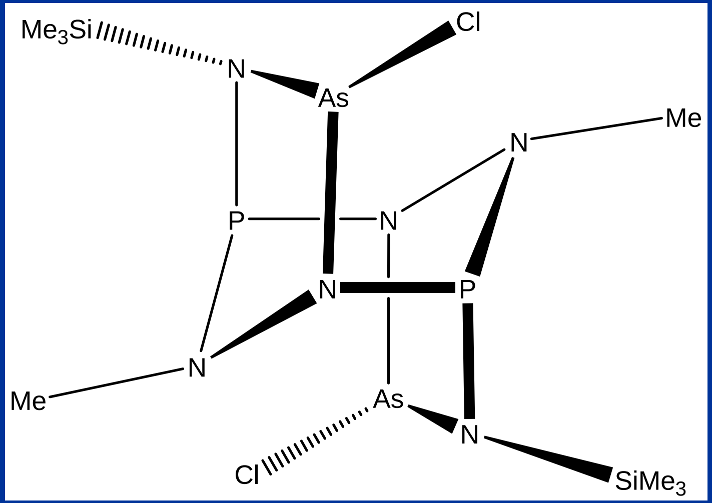


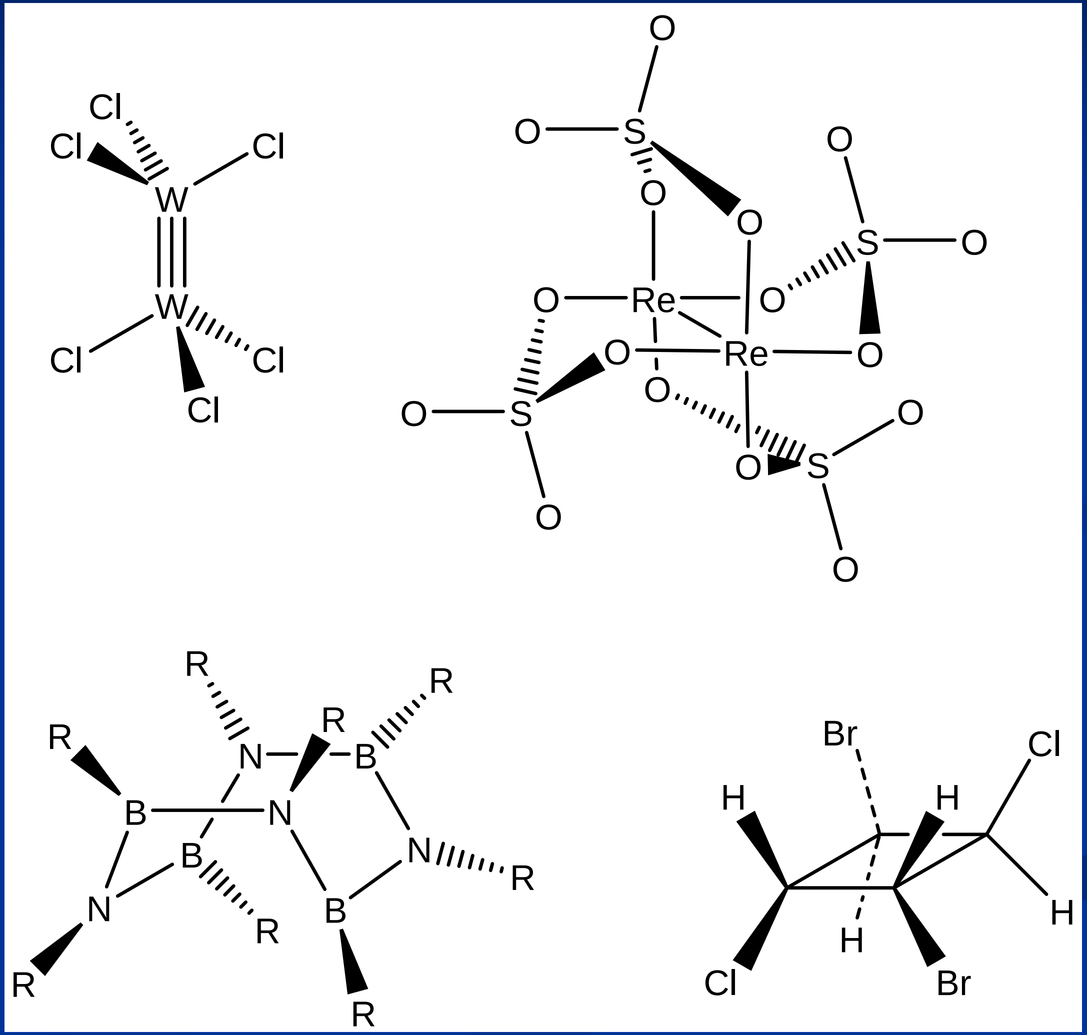
Chemical Shift



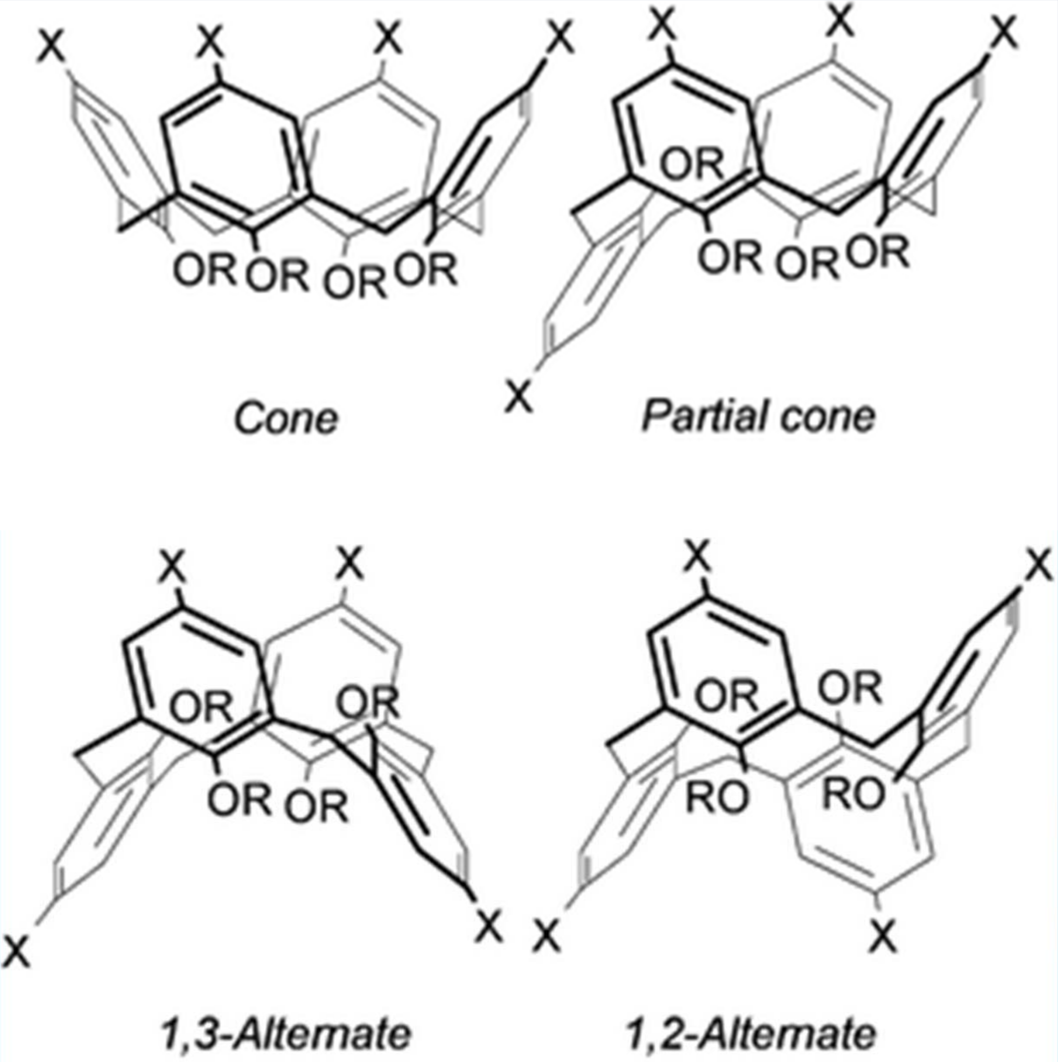
Chemical Shift



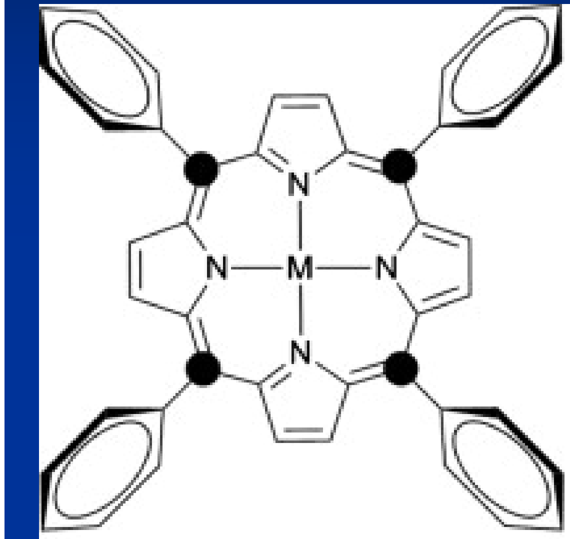




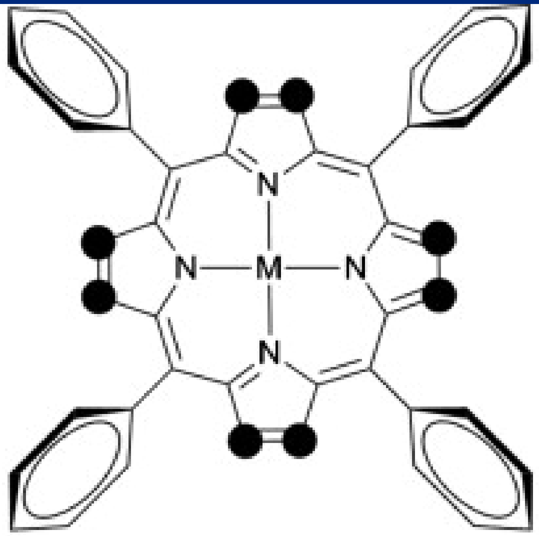
Chemical Shift



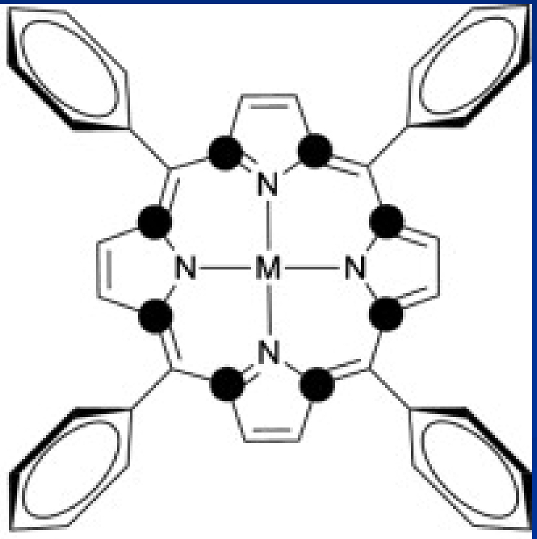
Chemical Shift



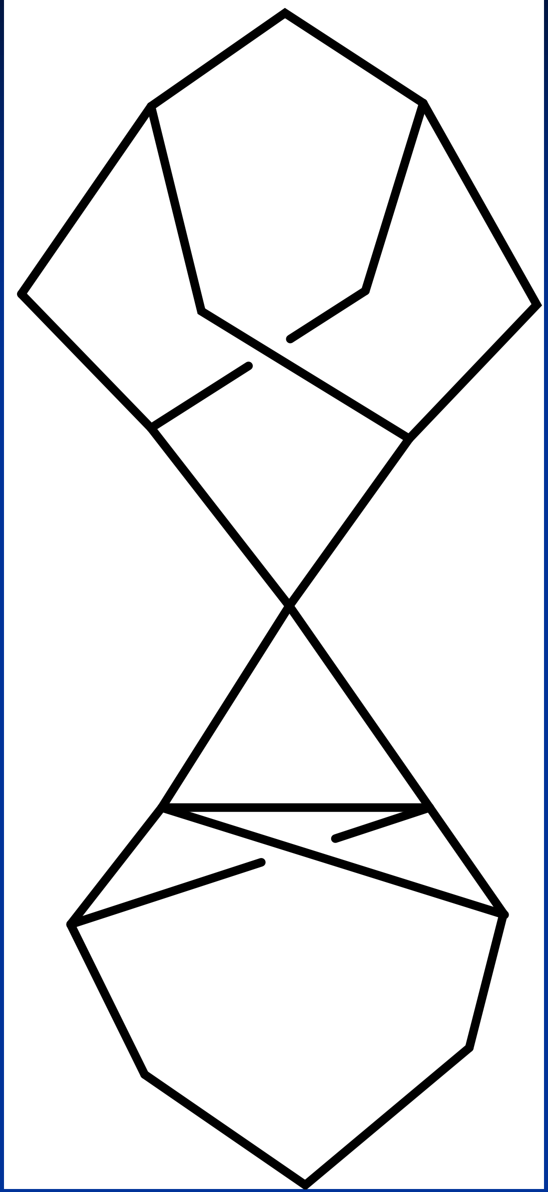
C1



C2



C3

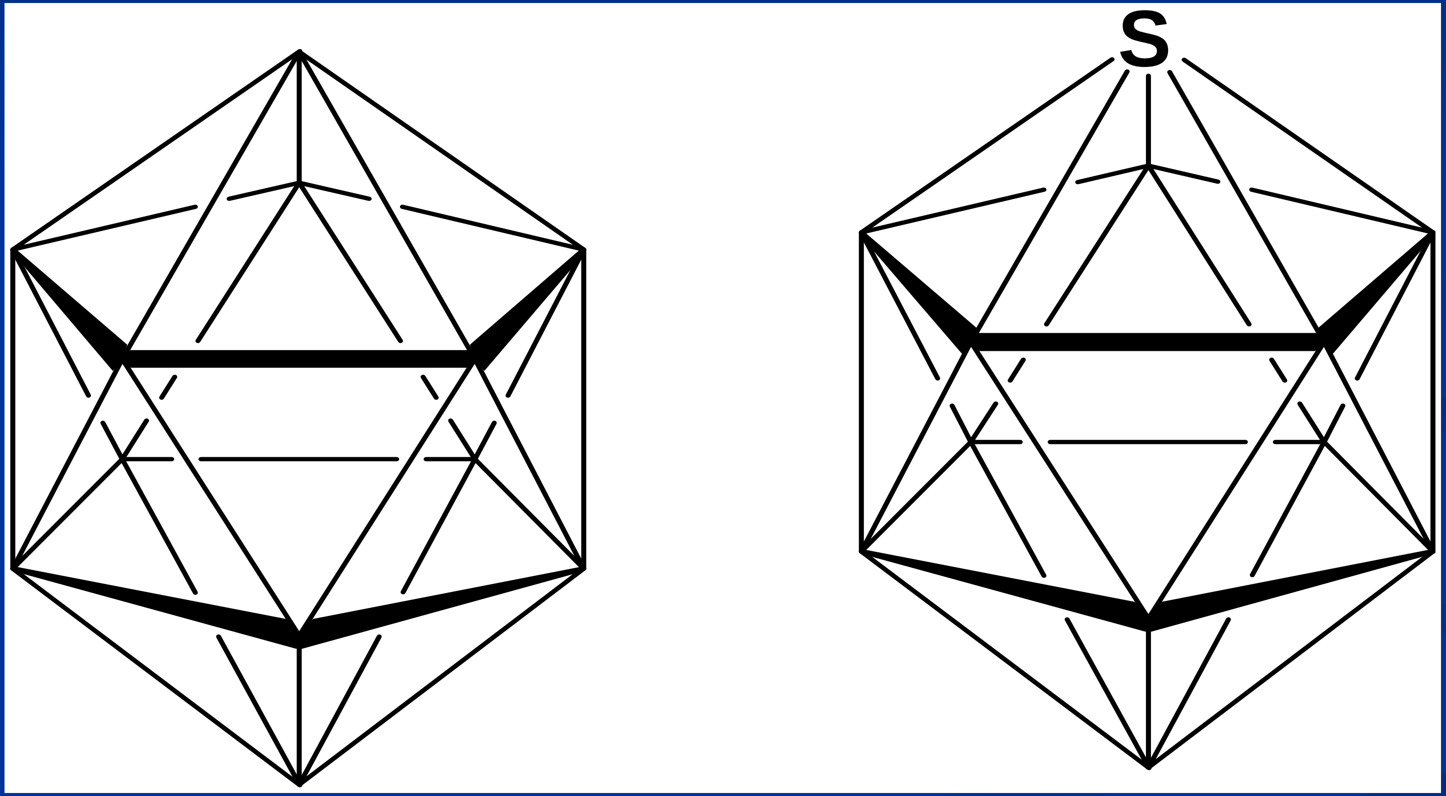


^{1}H NMR (600 MHz, $CDCl_3$, TMS):
3.25 (s, 2H, H-2’ and H-6’),
1.70 (br s, 2H, H-1 and H-3),
1.57 (br s, 2H, H-5 and H-7),
1.55 (br s, 4H, H-4, 8, 9, 10),
1.45 (m, 6H, H-4, 8, 9, 10 and H-6),
1.34 (m, 4H, H-3’ and H-5’),
0.96 ppm (m, 2H, H-4’)

^{13}C NMR (75 MHz, $CDCl_3$, TMS):
102.2 (C-8’=C-2),
80.8 (2C, C-2’ and C-6’),
40.0 (4C, C-4, 8, 9, 10),
39.1 (C-6),
29.2 (2C, C-5 and C-7),
28.7 (2C, C-1 and C-3),
22.3 (2C, C-3’ and C-5’),
20.8 (C-4’),
20.2 ppm (2C, C-1’ and C-7’).

Chemical Shift

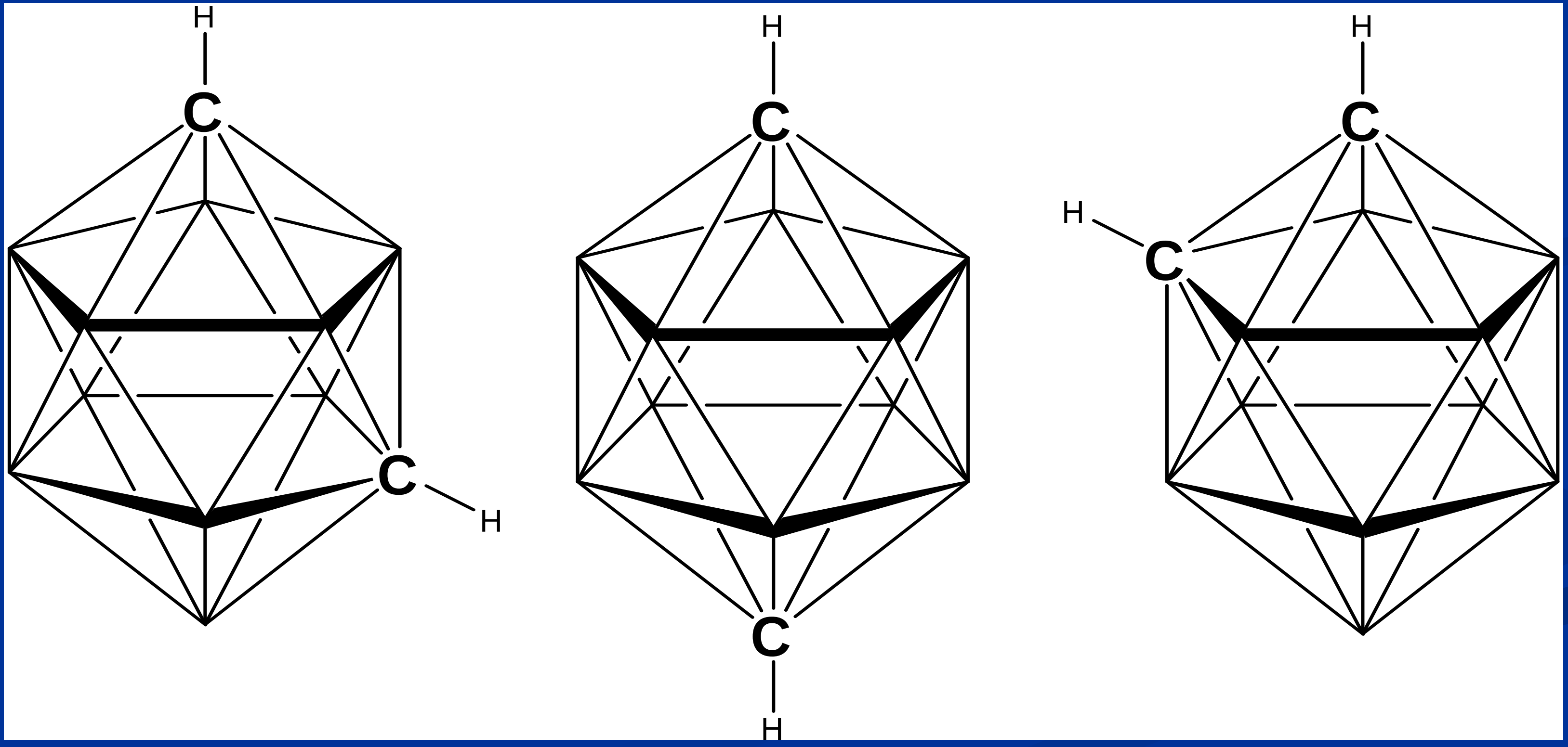
^{11}B NMR



Chemical Shift

^{11}B NMR

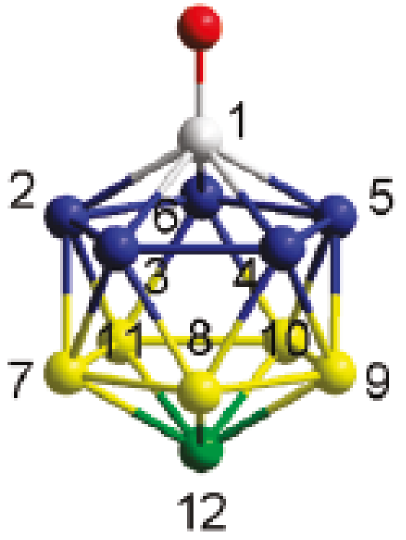
Isomers of $B_{10}H_{10}C_2H_2$

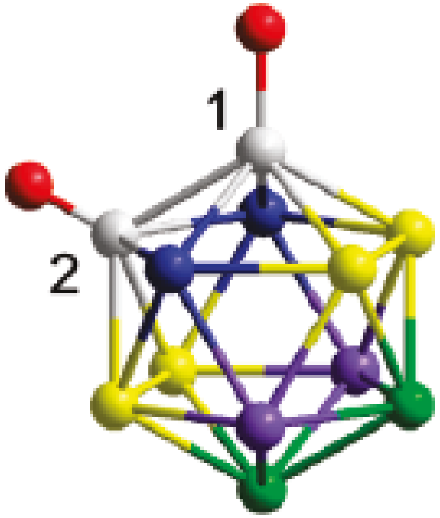


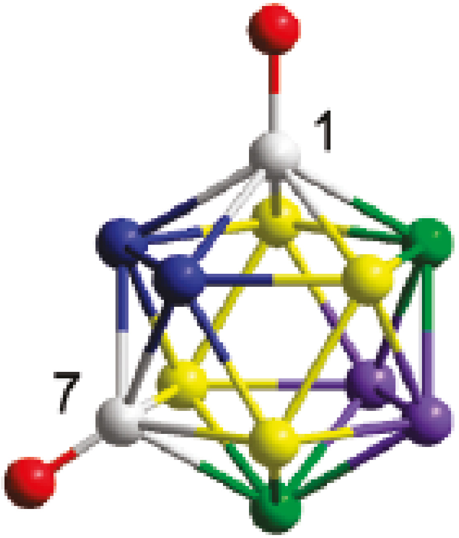
Chemical Shift

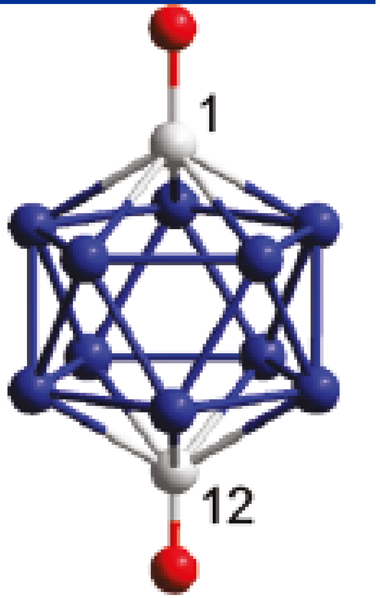
^{11}B NMR

Mono- and Disubstituted $B_{12}H_{12}^{2-}$ Molecules with Identical Substituents





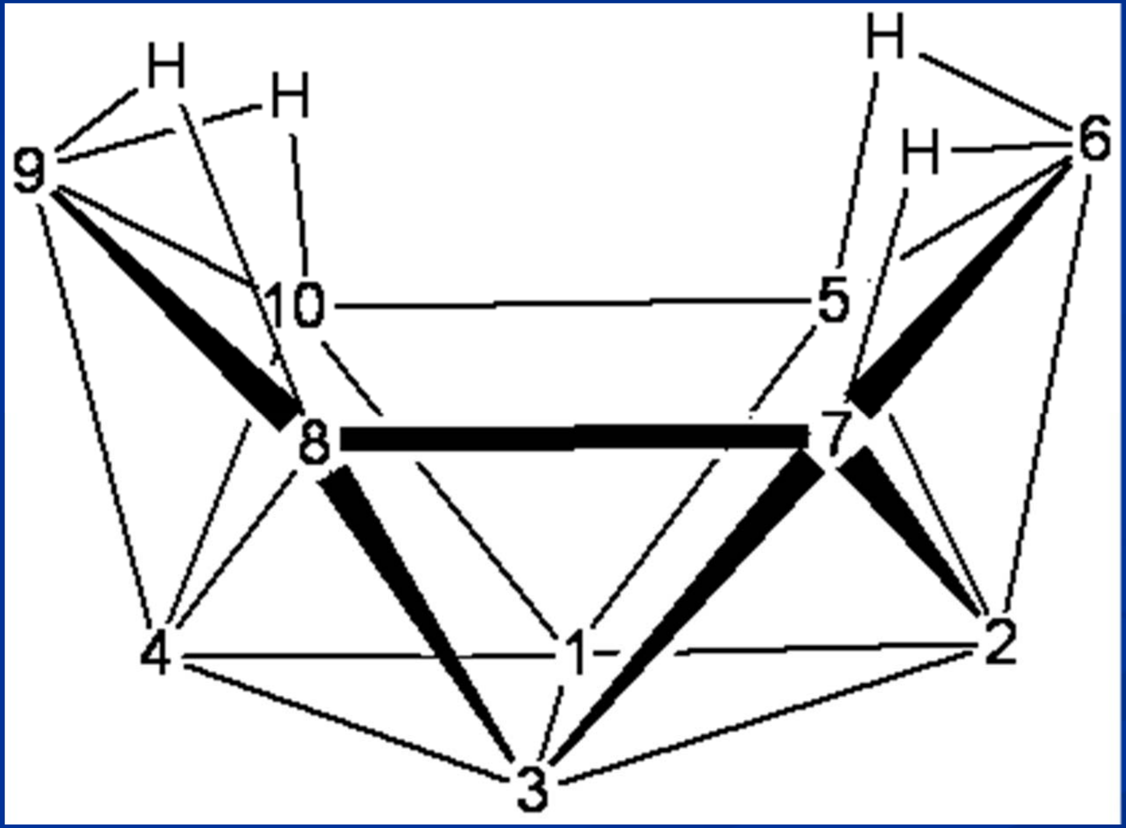




C_{5v}	C_{2v}	C_{2v}	D_{5d}
1 : 5 : 5 : 1	2 : 2 : 4 : 2 : 2	2 : 2 : 4 : 2 : 2	2 : 10

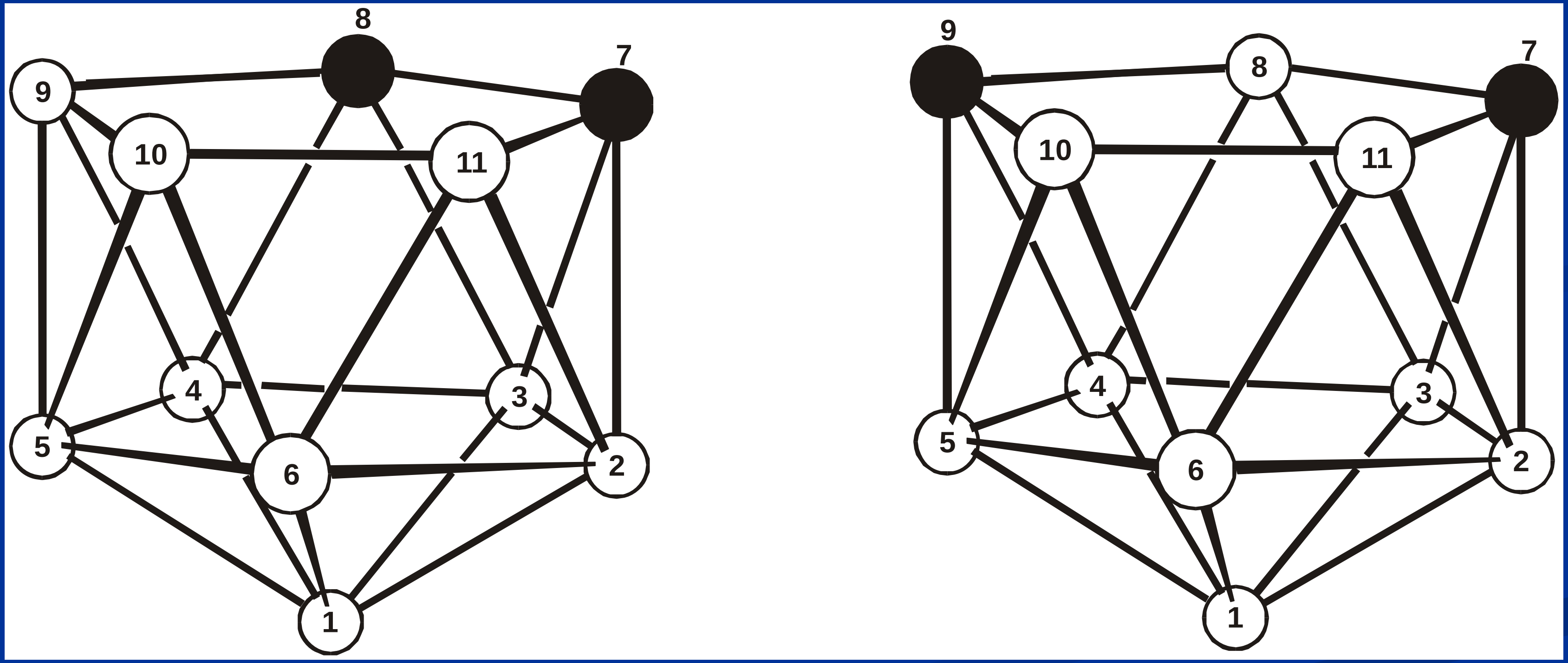
Chemical Shift

^{11}B NMR

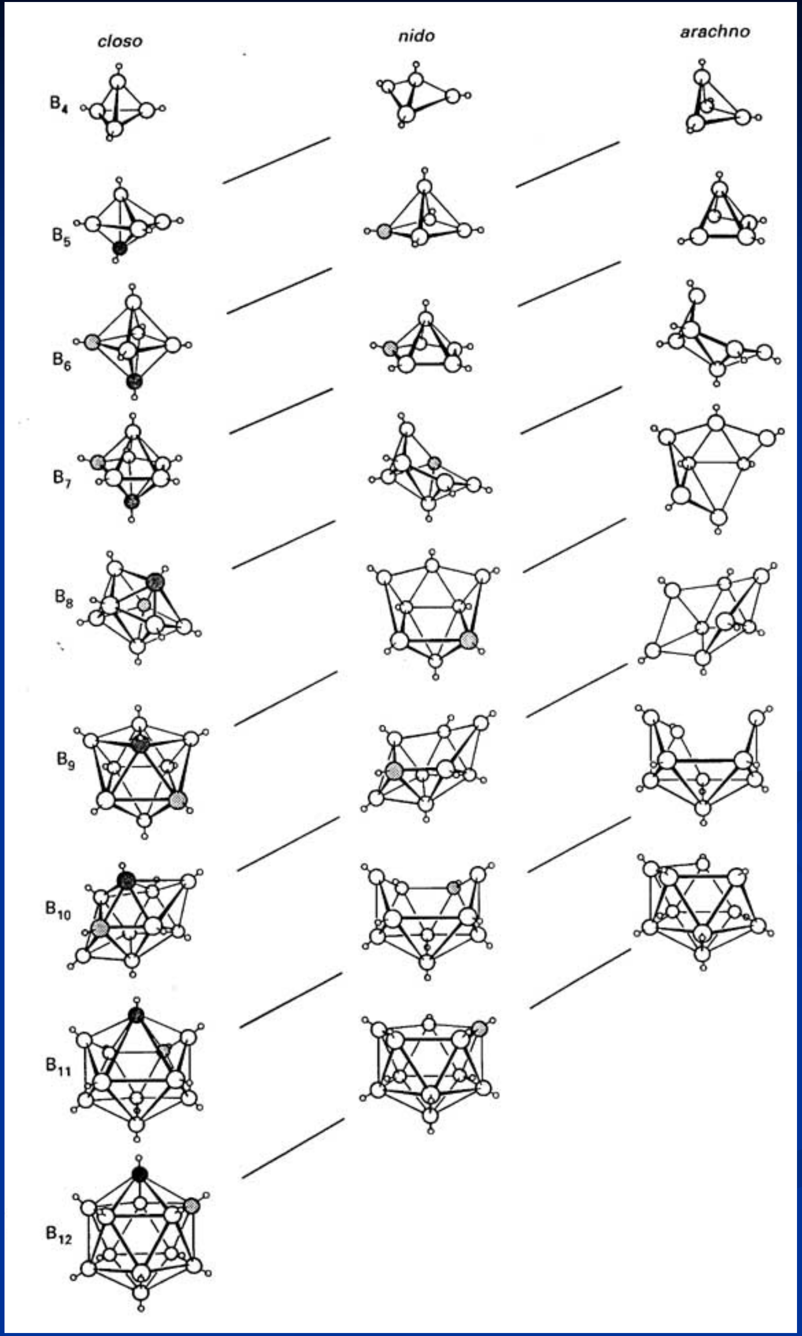


Chemical Shift

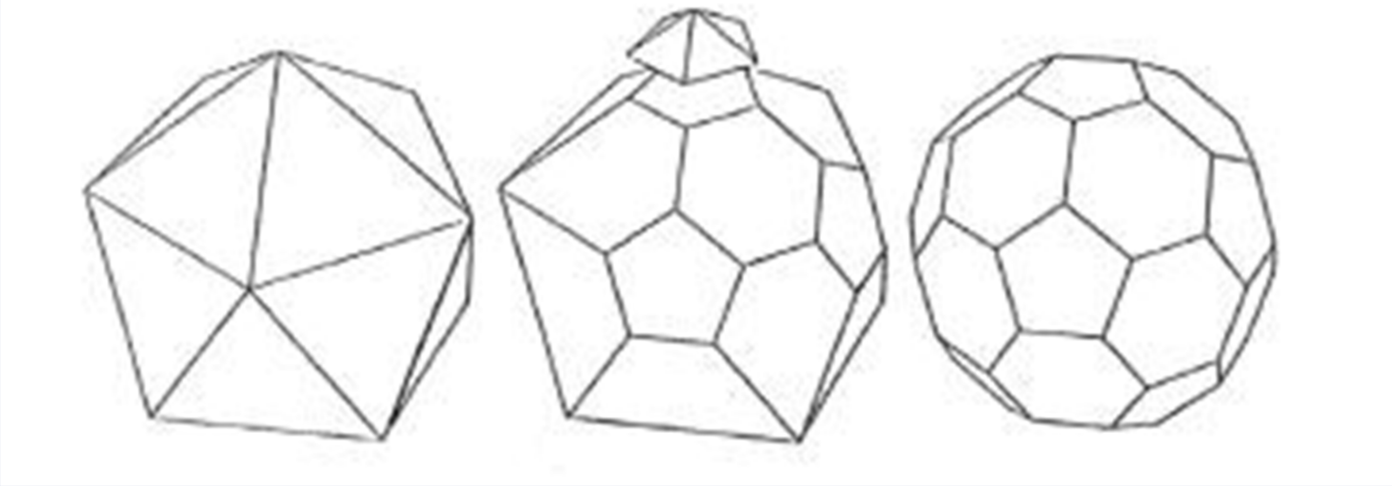
^{11}B NMR



^{11}B NMR



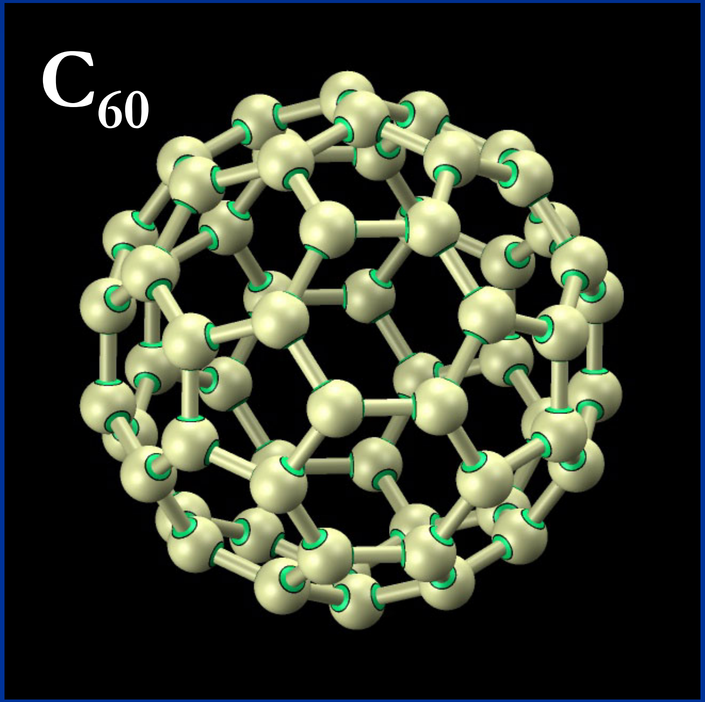
Fullerenes

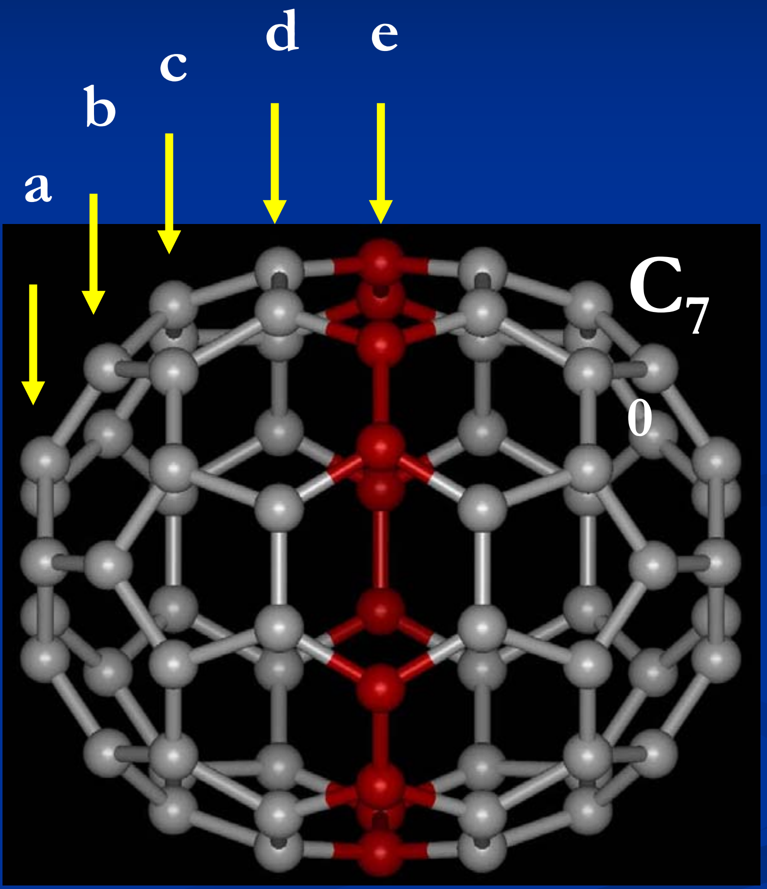


Icosahedron

Truncated icosahedron

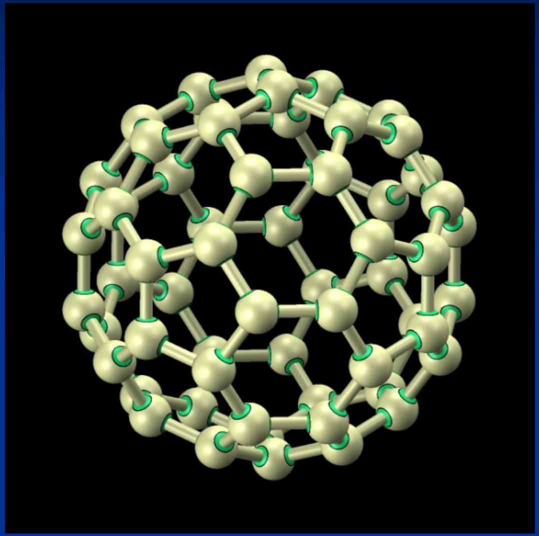
Chemical Shift



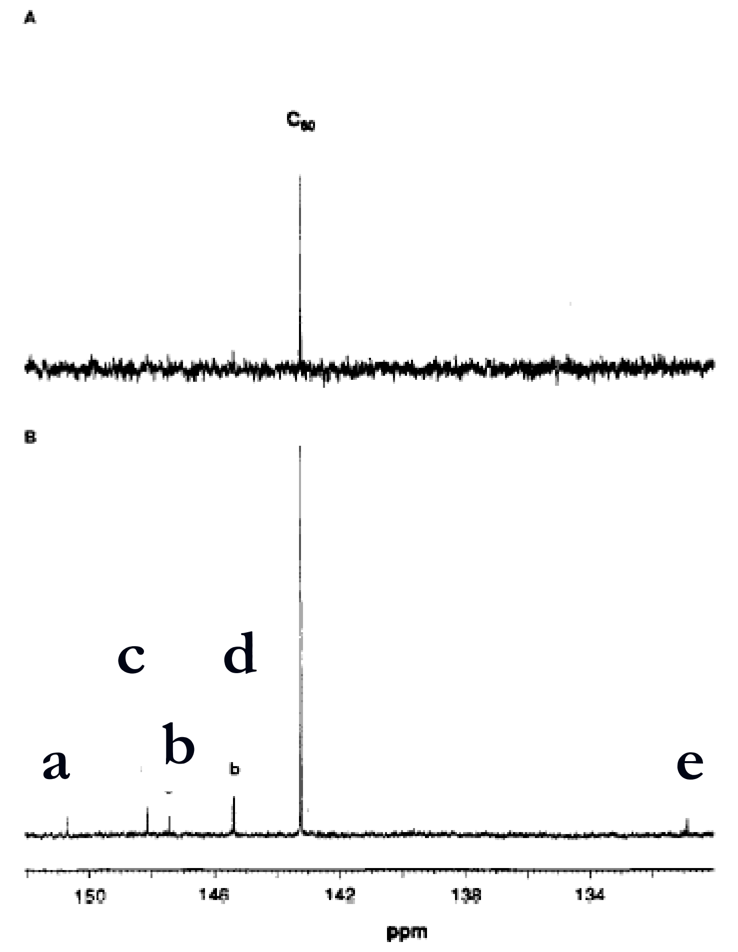


δ (^{13}C) = 143 ppm

Chemical Shift



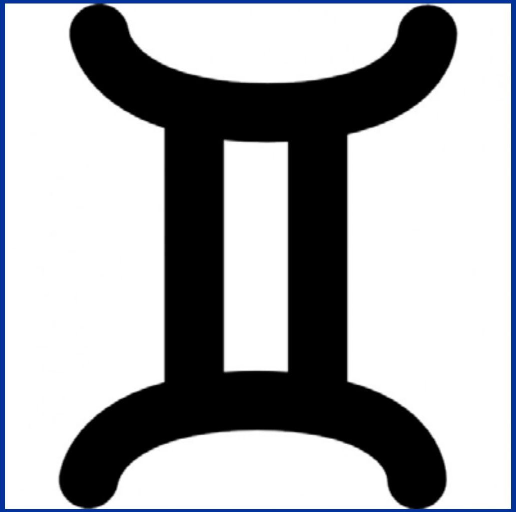
δ (^{13}C)	ppm
a	150.07
c	147.52
b	146.82
d	144.77
e	130.28



Geminal Groups

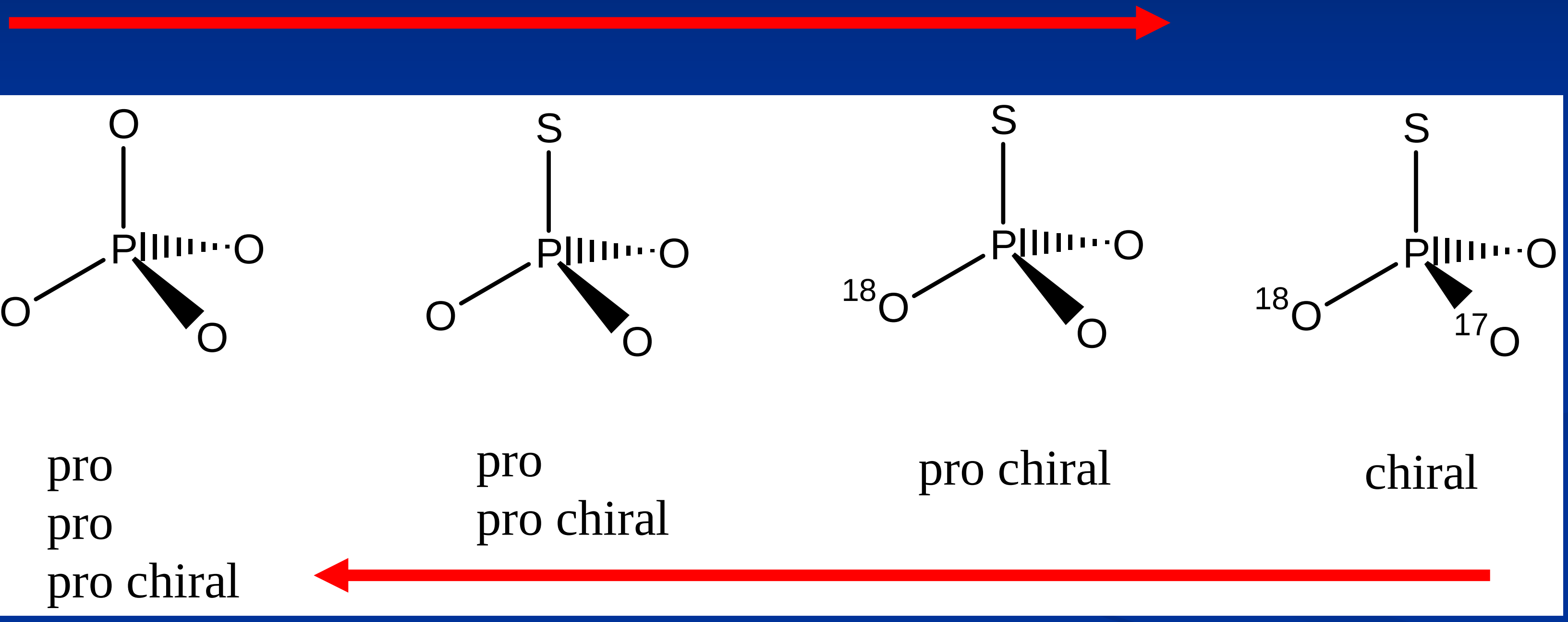
Geminal groups – paired ligands

Y-E-Y: CH_2, $C(CH_3)_2$, CF_2, $SiMe_2$, $P(CH_3)_2$, …



Prochiral Groups

Substitution



pro
pro
pro chiral

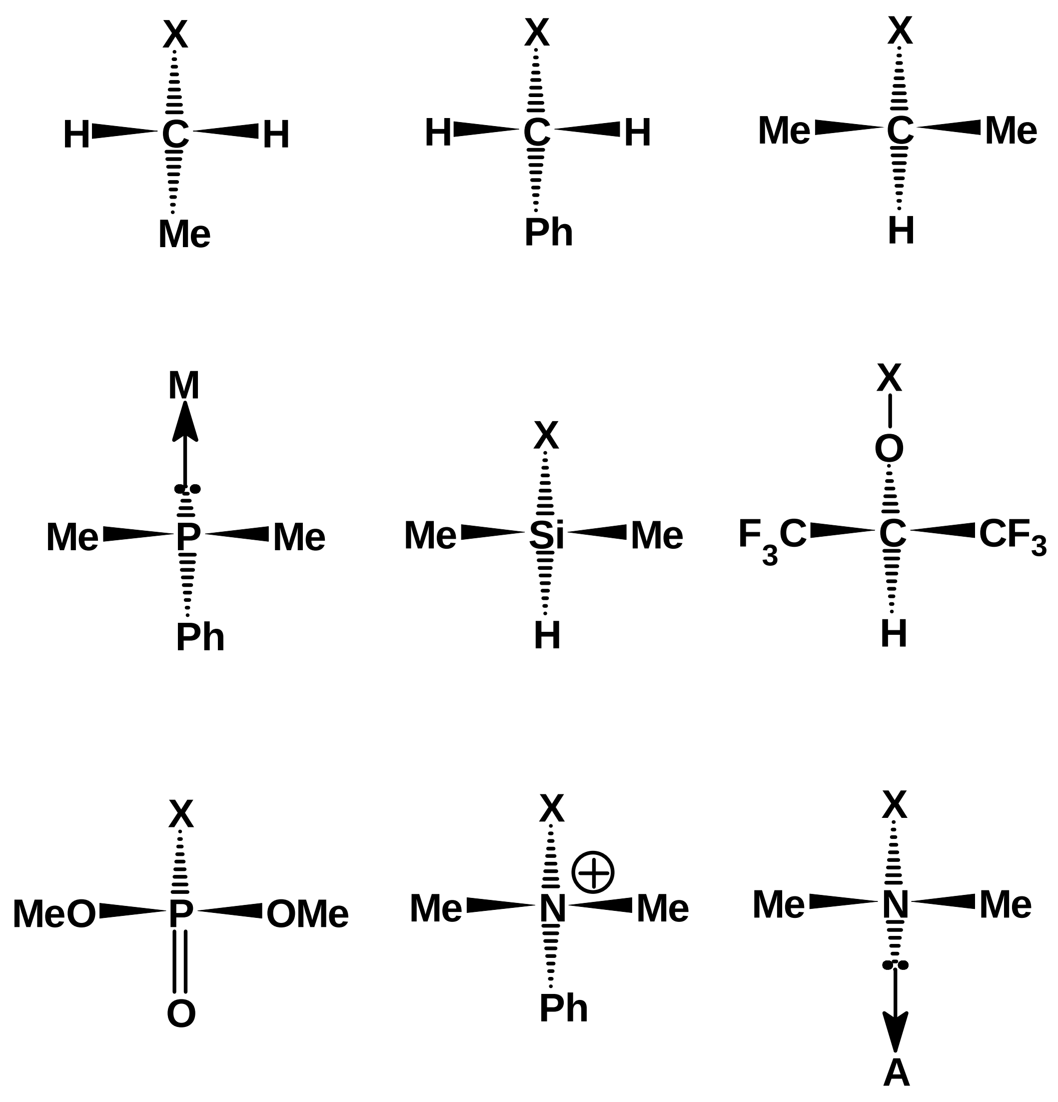
pro
pro chiral

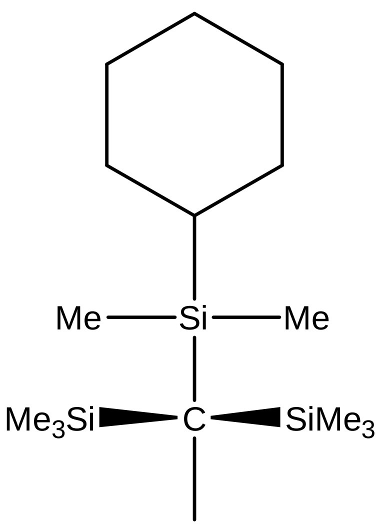
pro chiral

chiral

Symmetry

Geminal groups in Prochiral Groups



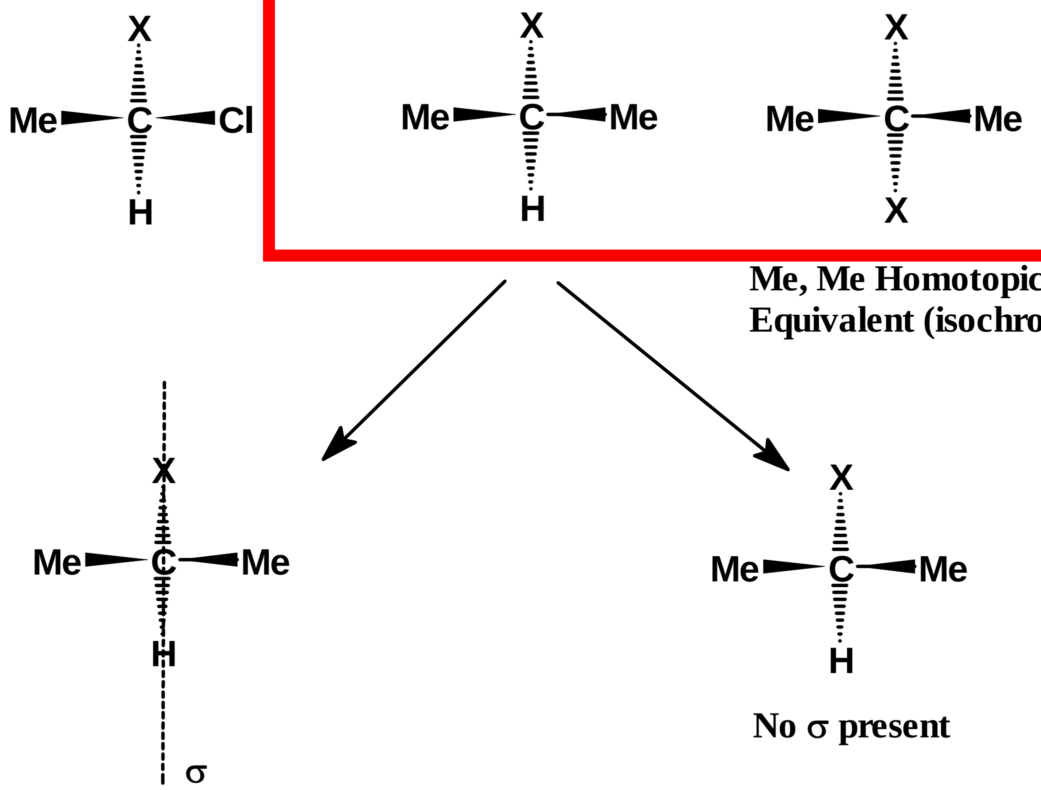


X = rest of the molecule

M = transition metal fragment

A = Lewis acid

Chemical Shift Nonequivalence of Geminal Ligands in Prochiral Groups



Chiral Group

Prochiral Group

C_2 Group

Geminal groups

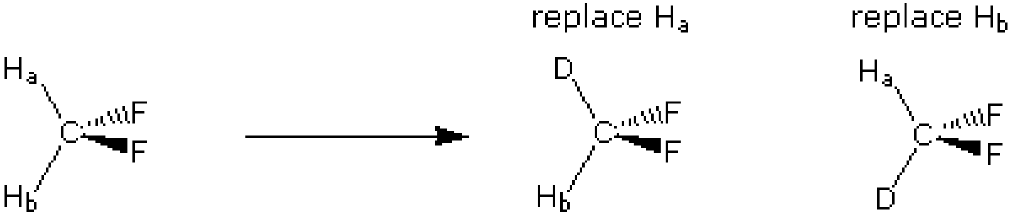
Me, Me Homotopic
Equivalent (isochronous)

No σ present

Me, Me Enantiotopic
Equivalent (isochronous) in achiral media
Nonequivalent (anisochronous) in chiral media

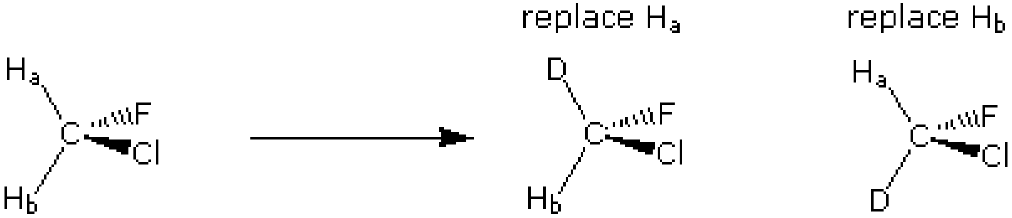
Me, Me Diastereotopic
Nonequivalent (anisochronous)
If X is chiral, the paired ligands in a prochiral group are always diastereotoppic

Substitution Test of Geminal Groups



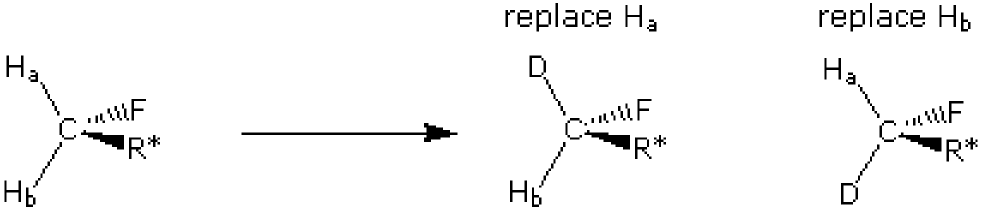
same compound

$\Longrightarrow$ H_a and H_b are homotopic



enantiomers

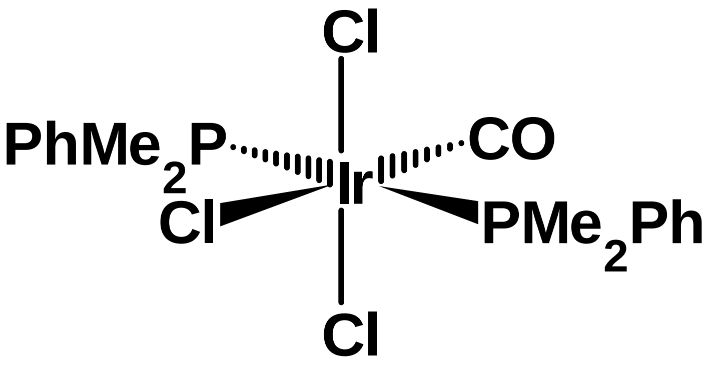
$\Longrightarrow$ H_a and H_b are enantiotopic



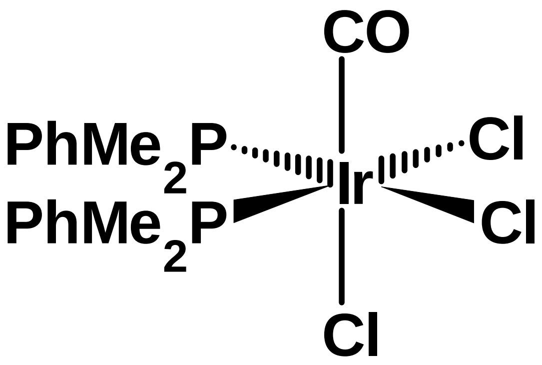
diastereomers

$\Longrightarrow$ H_a and H_b are diastereotopic

Chemical Shift Nonequivalence in Prochiral Groups

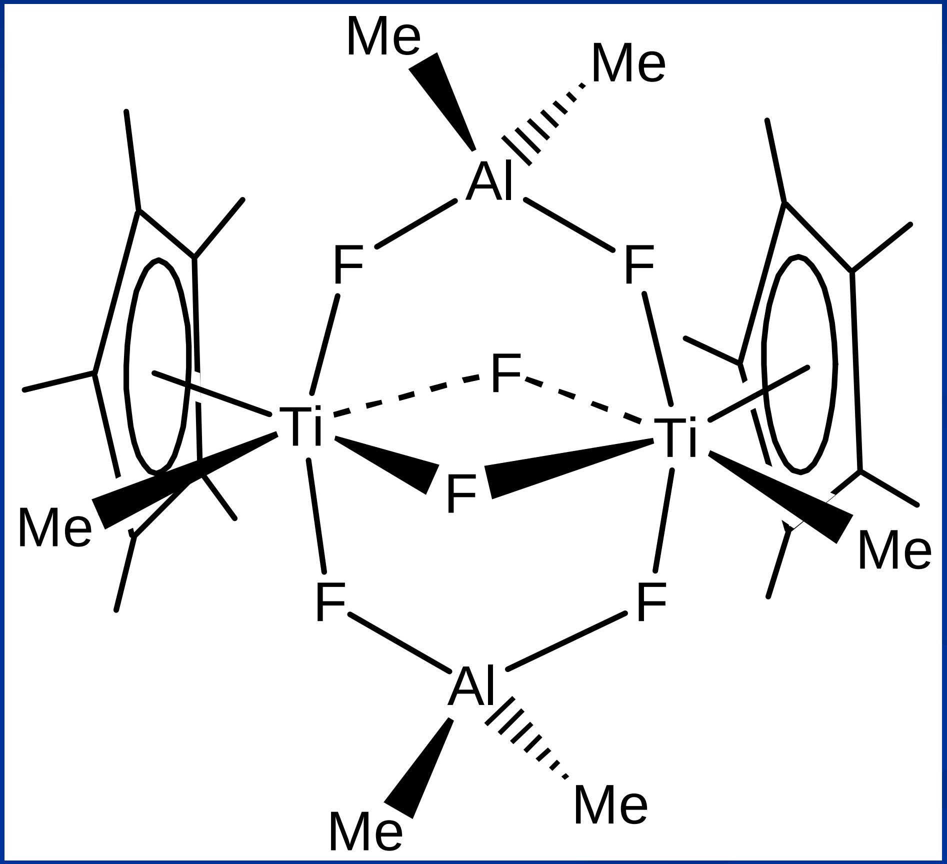


mer-Cl, trans-P



fac-Cl, cis-P

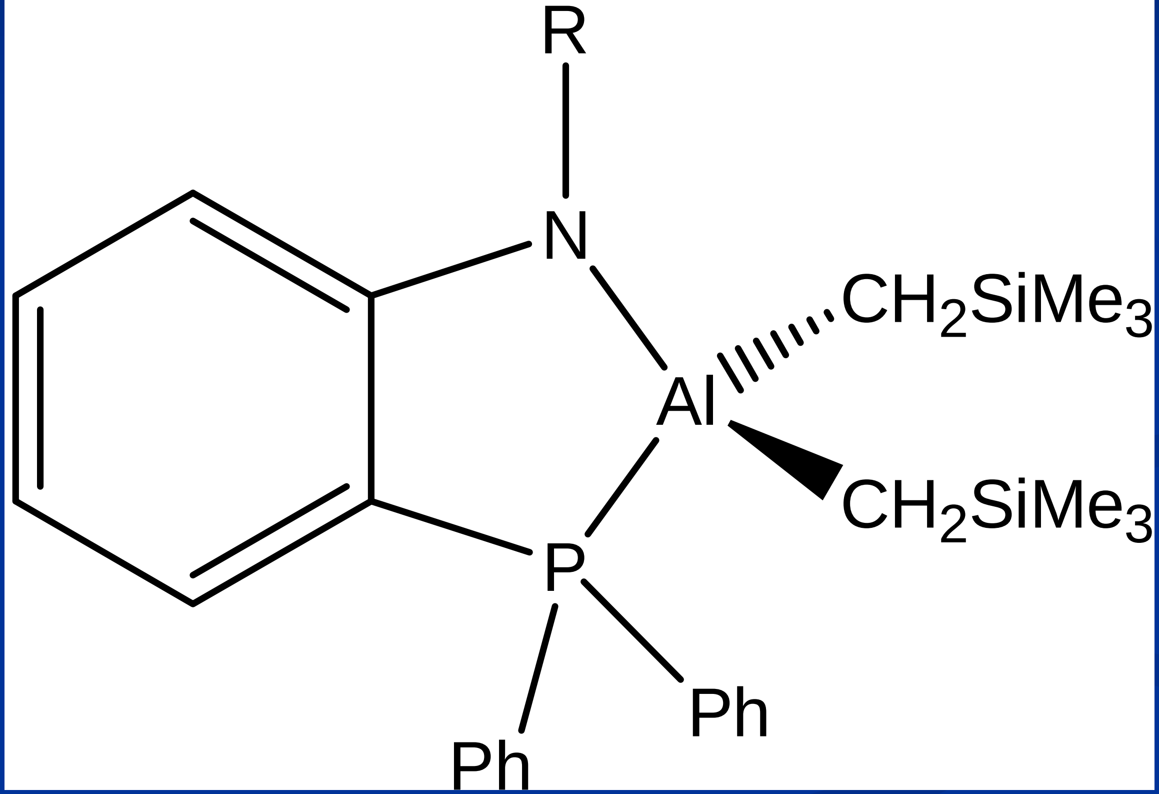
Chemical Shift Nonequivalence in Prochiral Groups



Chemical Shift Nonequivalence in Prochiral Groups

R = Me

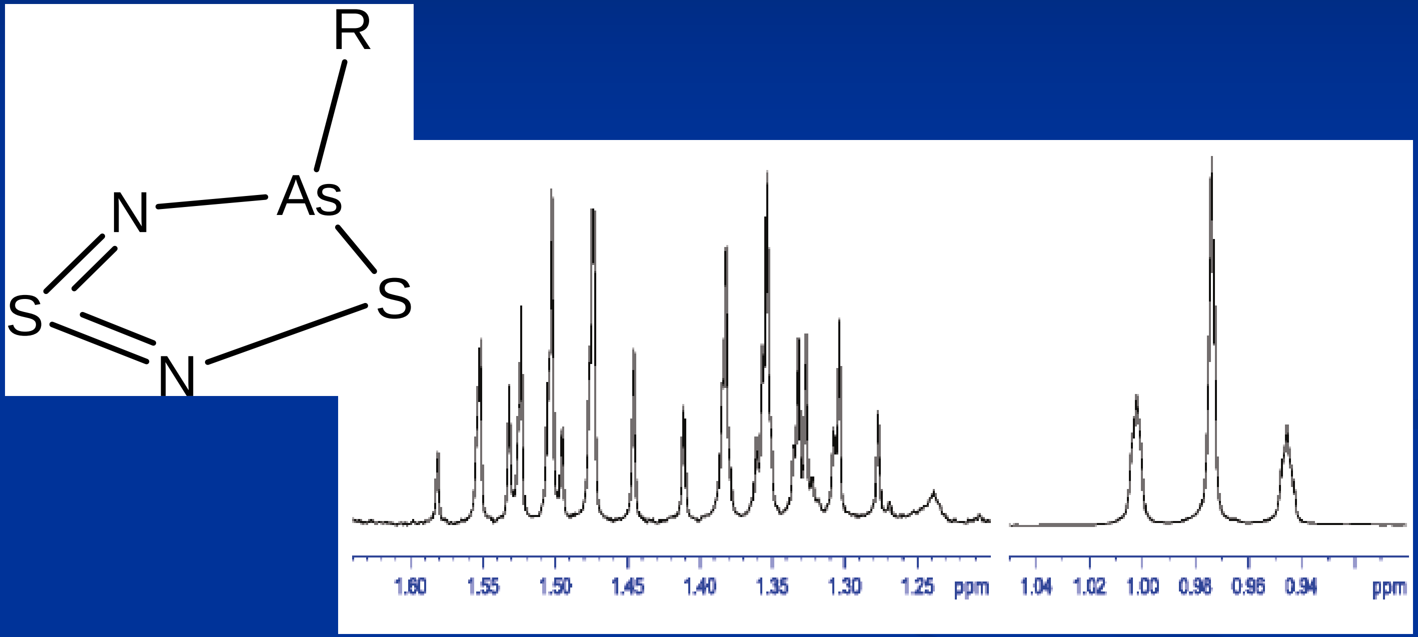
R = 2-butyl



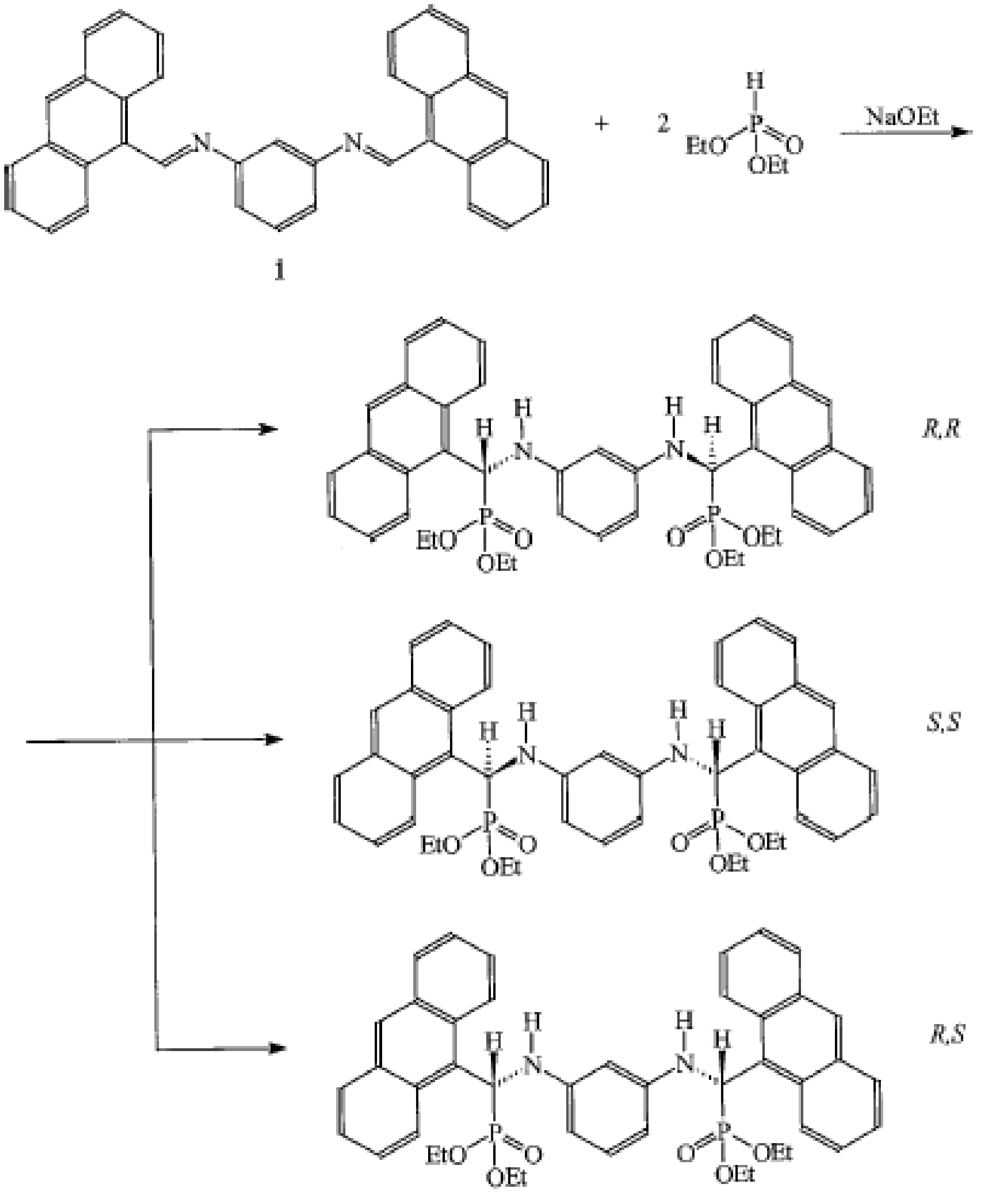
Pyramidal N - Fast inversion on N

Chemical Shift Nonequivalence in Prochiral Groups

R = Et



R = ^{i}Pr



2: *R,R*; *S,S*; *R,S*

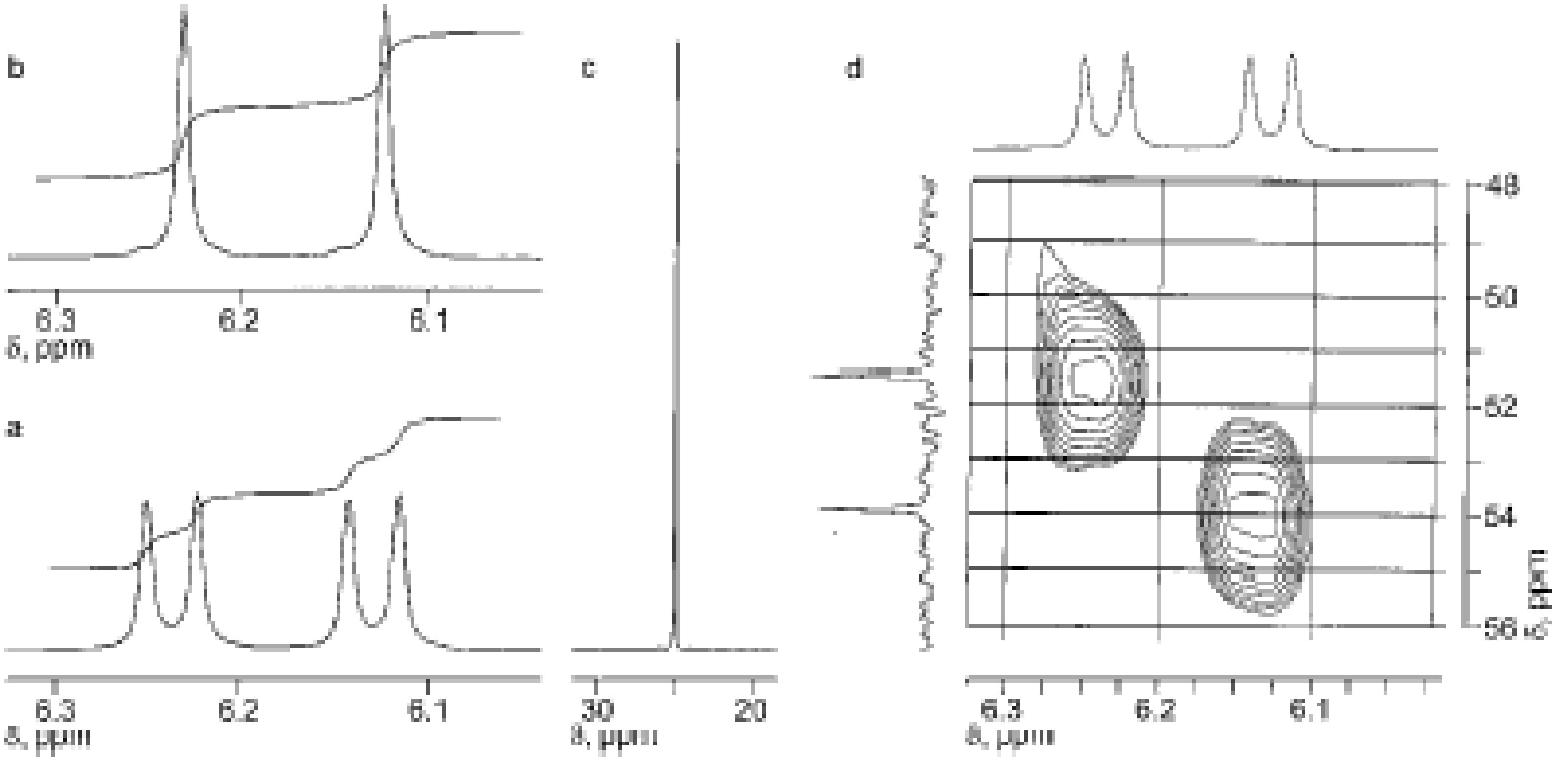
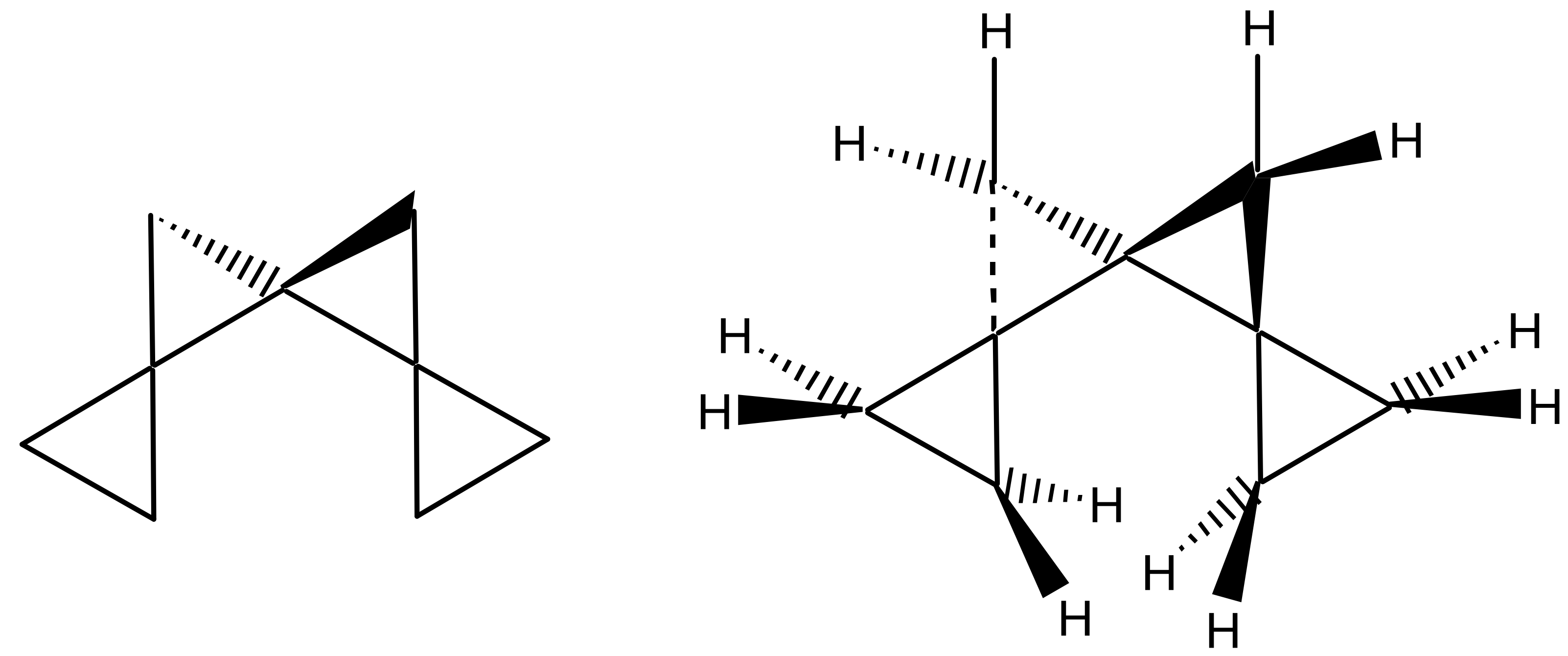
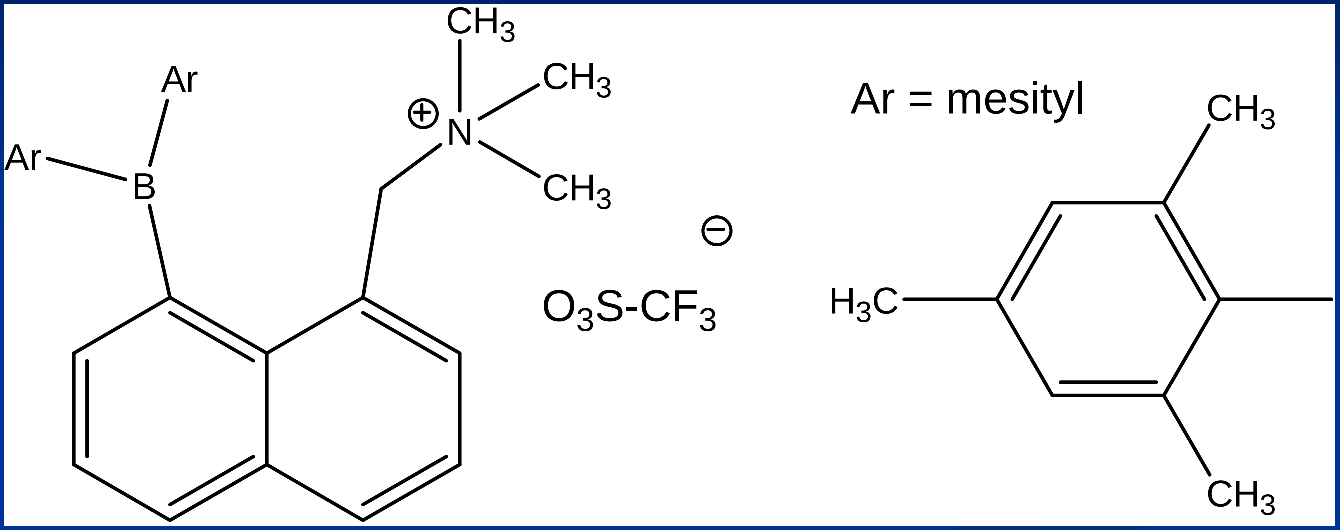


FIGURE 1 NMR spectra of CH(P) moiety of compound **2**: a), b) ^1H NMR spectra in $CDCl_3$ and $CDCl_3$, D_2O respectively; c) $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$; d) CH COSY diagram in $CDCl_3$.

[4] triangulane



Prochiral Groups



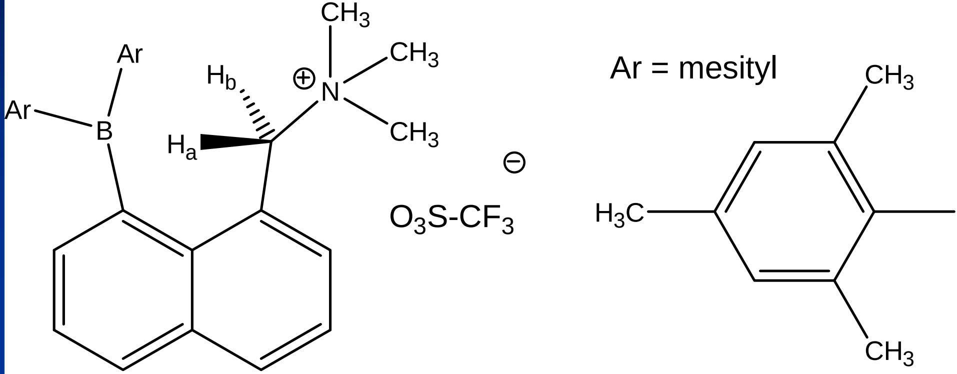
^{1}H NMR spectrum

6 CH aromatic signals

How many CH_2 signals ?

6 CH_3 mesityl signals

Prochiral Groups



steric congestion

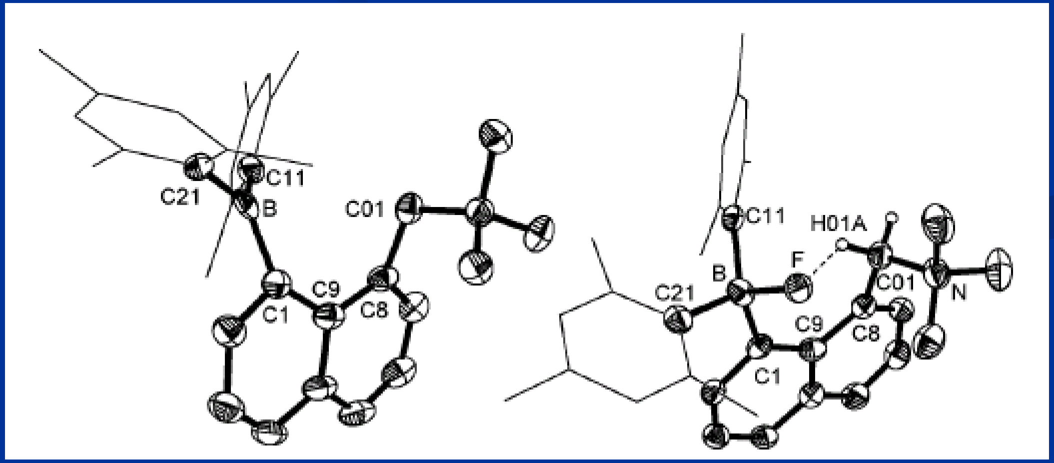
^{1}H NMR spectrum

6 CH aromatic signals

6 CH_3 mesityl signals

The methylene hydrogens are diastereotopic

two signals at 3.69 and 4.81 ppm



Chemical Shift

Chemical shift for a given molecule:

- Number of signals = nonequivalent nuclei
molecular symmetry

- Relative intensity = number of nuclei

- Position in the spectrum = shielding/chemical shift
electronic structure

- Multiplicity = connectivity of atoms and groups

Integration

Quantitative conditions – Relaxation time vs. Recycle delay

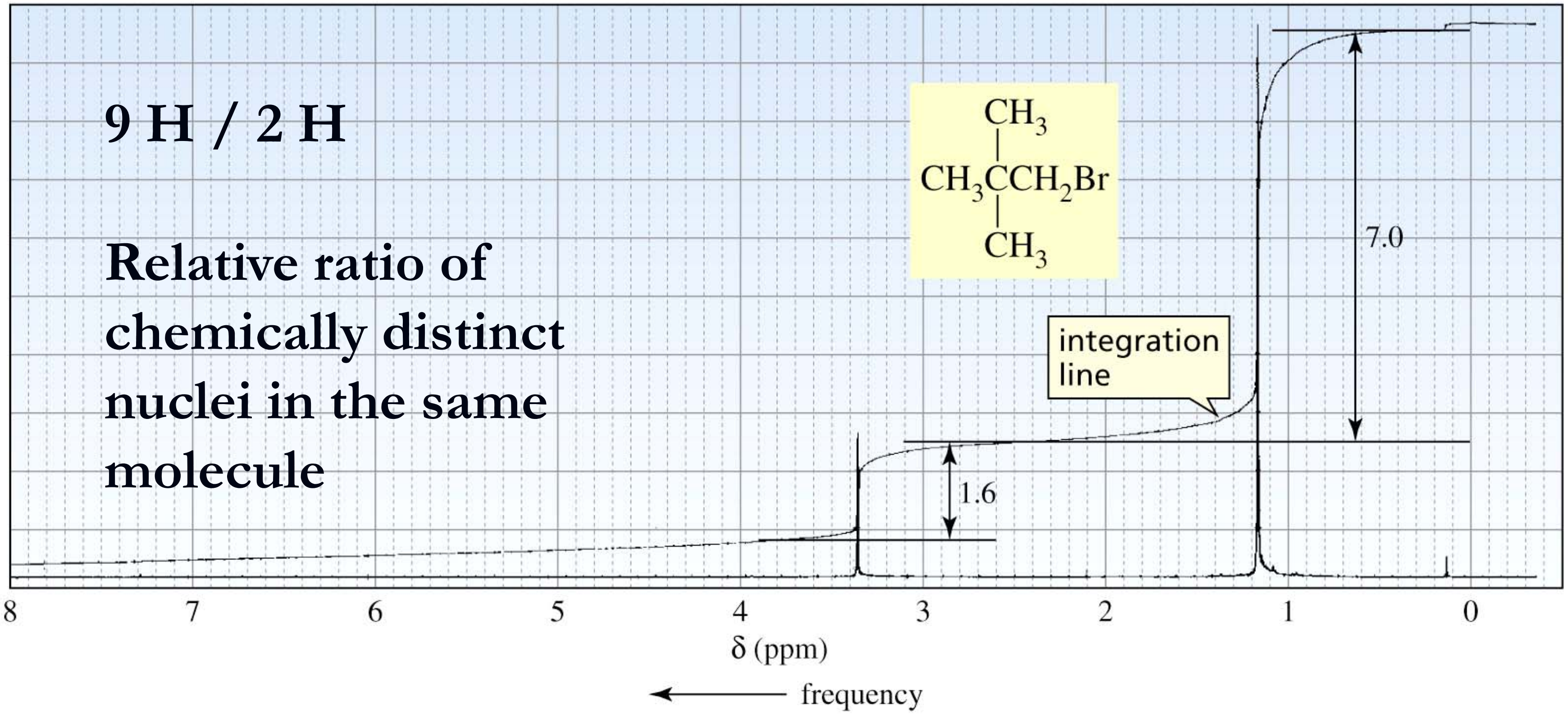
Phasing and Baseline correction applied

The area under each signal is proportional to the number of nuclei that give rise to that signal

The height of each integration step is proportional to the area under a specific signal

The integrated intensity tells us the relative number of nuclei that give rise to each signal, not absolute number

Relative Signal Intensity

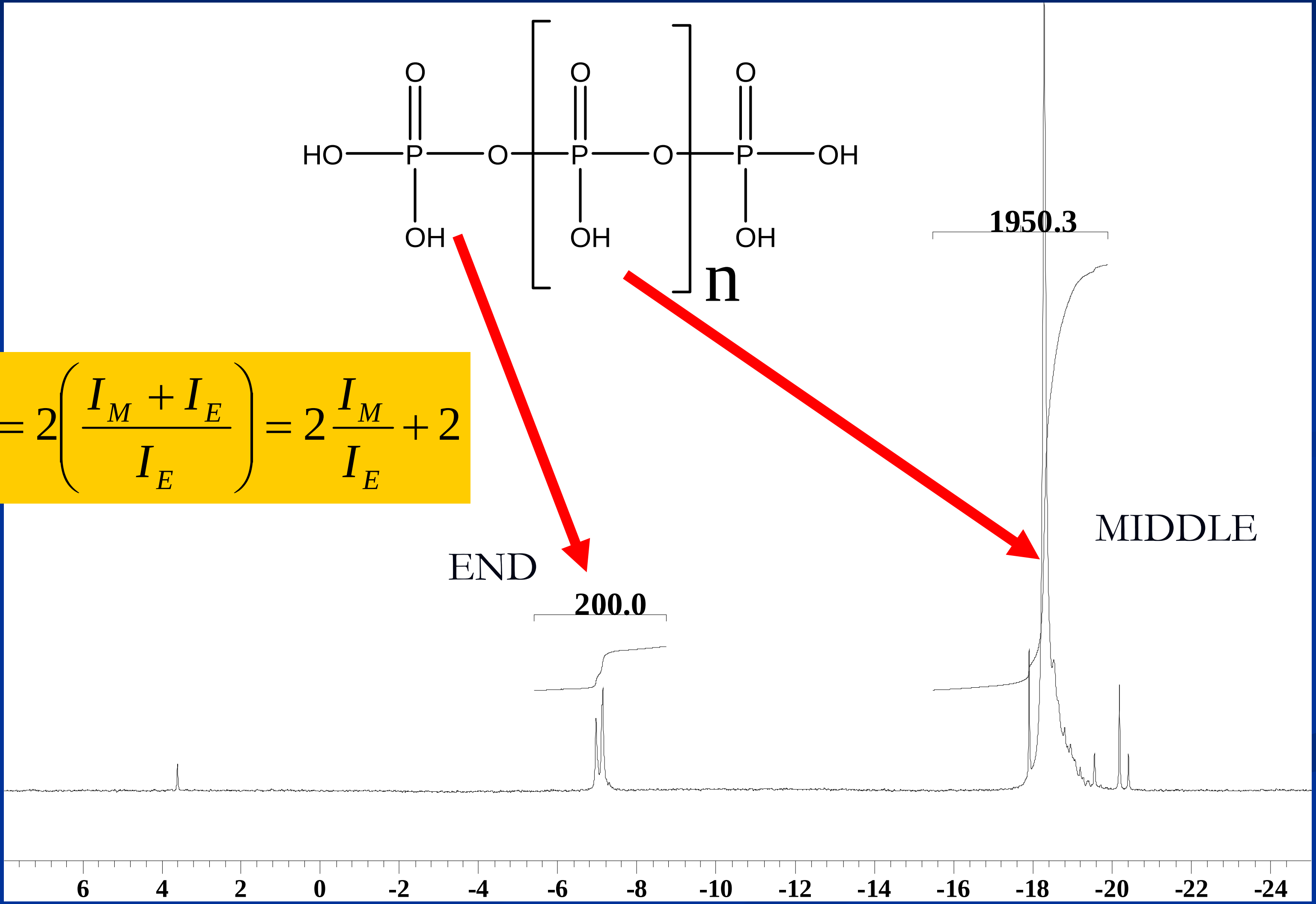


9 H / 2 H

Relative ratio of chemically distinct nuclei in the same molecule

Polyphosphate Chain Length

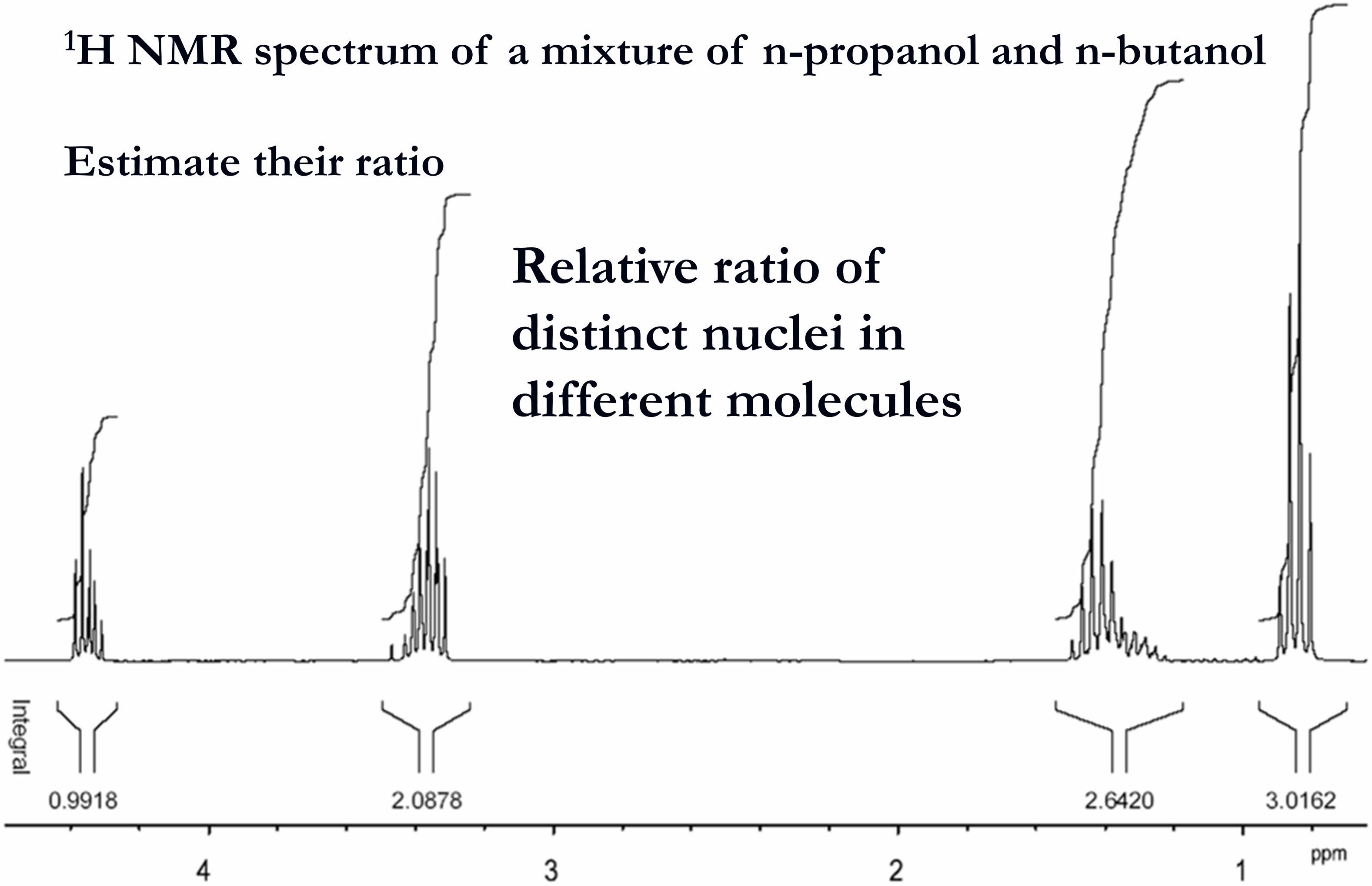
$$n = 2\frac{P_{TOTAL}}{P_{END}} = 2\left(\frac{I_M + I_E}{I_E}\right) = 2\frac{I_M}{I_E} + 2$$



Relative Signal Intensity

^{1}H NMR spectrum of a mixture of n-propanol and n-butanol

Estimate their ratio

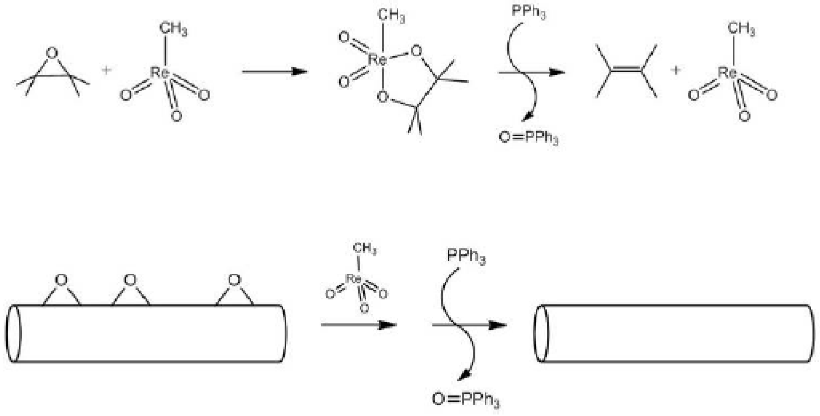


Relative ratio of distinct nuclei in different molecules

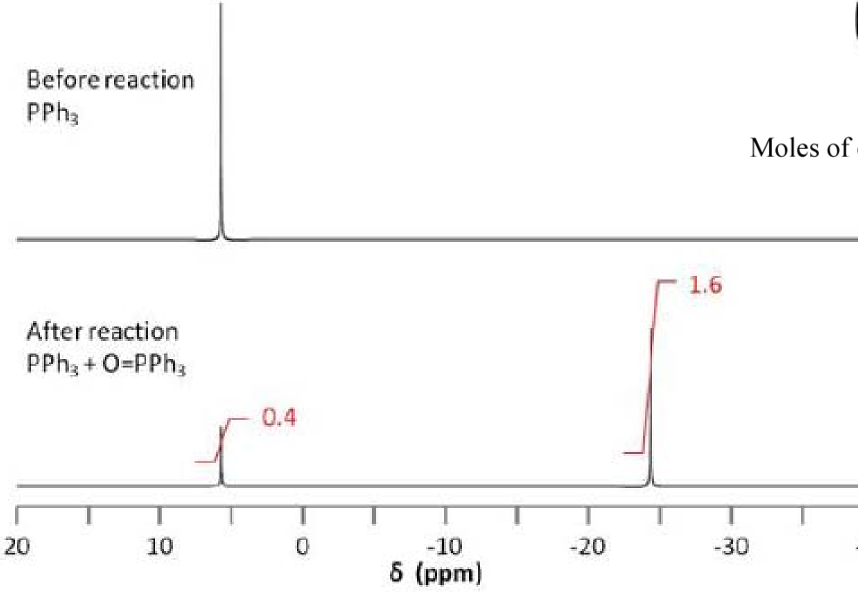
Relative Signal Intensity

Measuring the amount of epoxide on nanomaterials such as carbon nanotubes and fullerenes by monitoring a catalytic reaction of methyltrioxorhenium and PPh_3.

The relative amounts of PPh_3 and $OPPh_3$ can be used to stoichiometrically determine the amount of epoxide on the nanotube by determining the relative amounts of of PPh_3 and $OPPh_3$

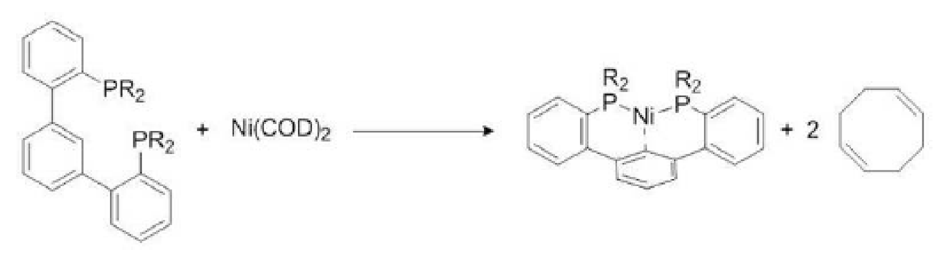


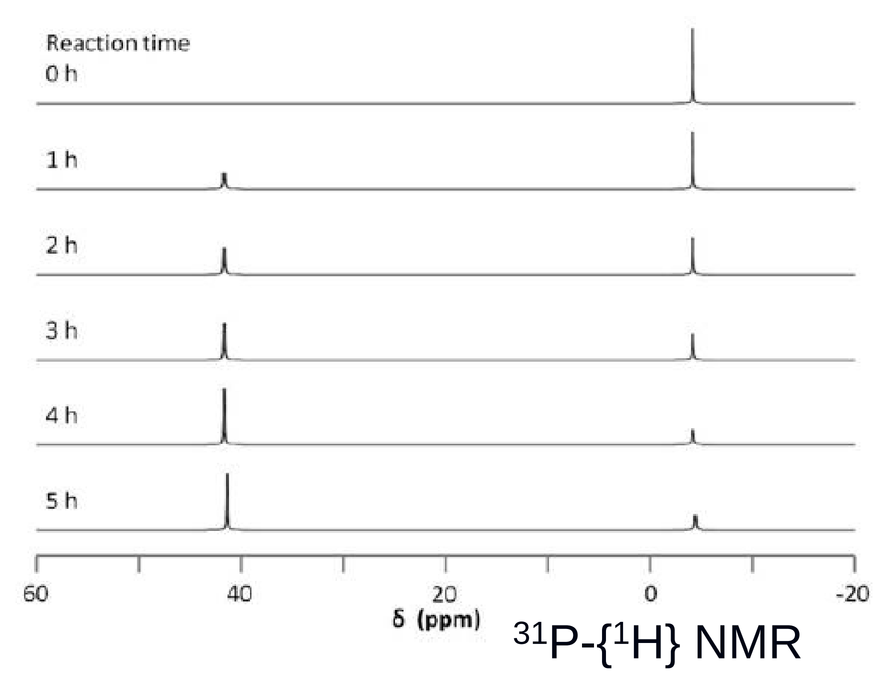
$$\text{Moles of epoxide} = \frac{\text{area of } OPPh_3 \text{ peak}}{\text{area of } PPh_3 \text{ peak}} \times \text{moles } PPh_3$$



Relative Signal Intensity

Monitoring a reaction course





The reaction is followed by ^{31}P NMR by taking a small aliquot from the reaction mixture at diferent reaction times.

The changing peak intensity can be used to monitor the reaction.

The reaction begins with a single signal at -4.40 ppm, corresponding to the free diphosphine ligand.

After an hour, a new signal appears at 41.05 ppm, corresponding the the diphosphine nickel complex.

The downfield peak grows as the reaction proceeds relative to the upfield peak. No change is observed between 4 and 5 hours, suggesting the conclusion of the reaction.