

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

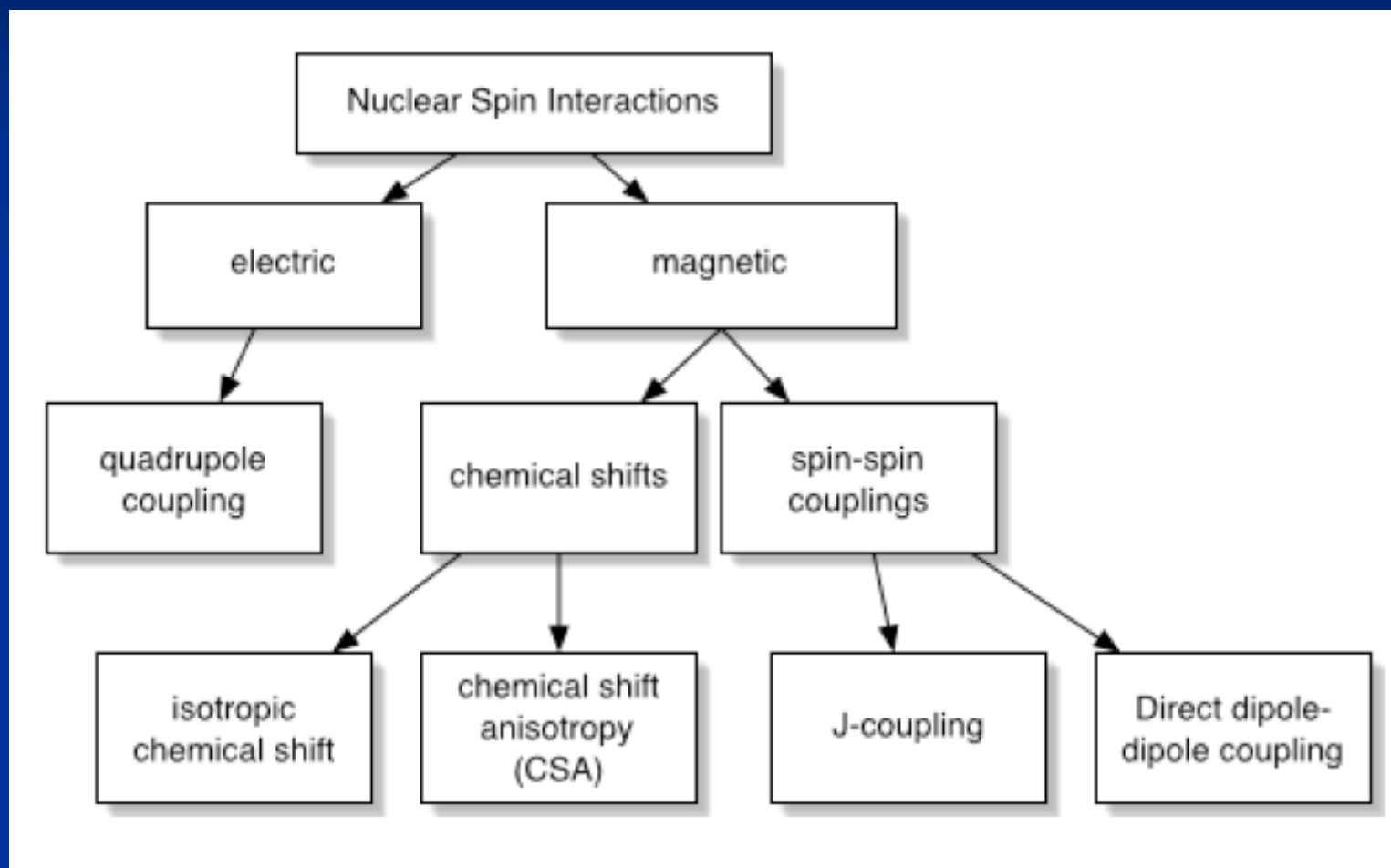
3) Electric field gradient

distribution of nuclei (positive charge) and electrons (negative charge)
quadrupolar nuclei

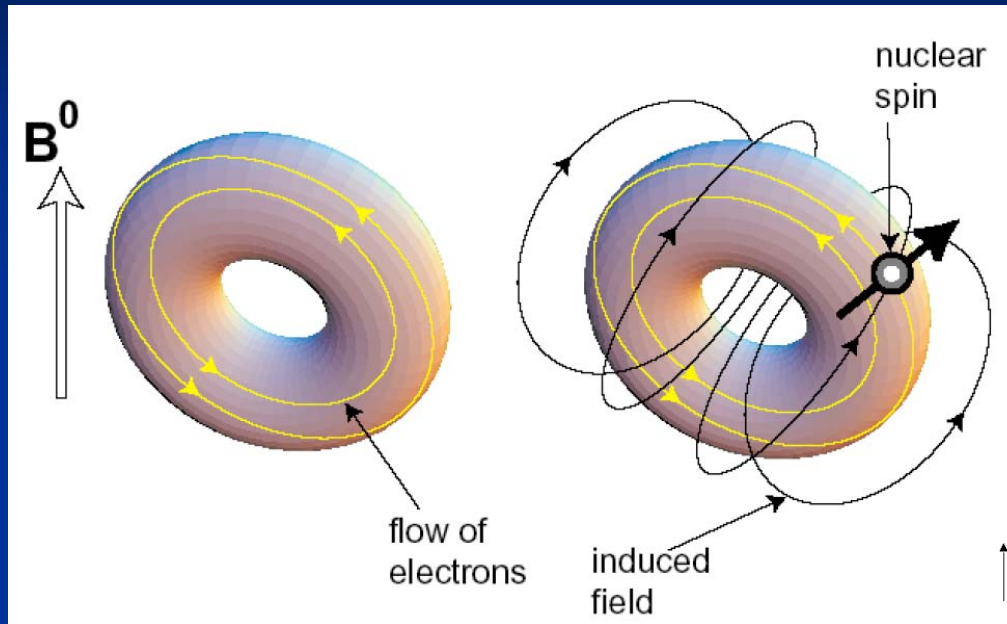
4) Scalar coupling

dipolar interactions through electrons in molecules, bonds

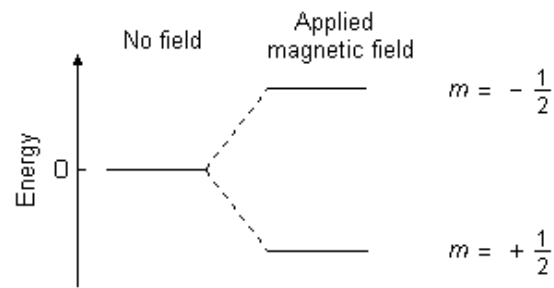
Nuclear Spin Interactions



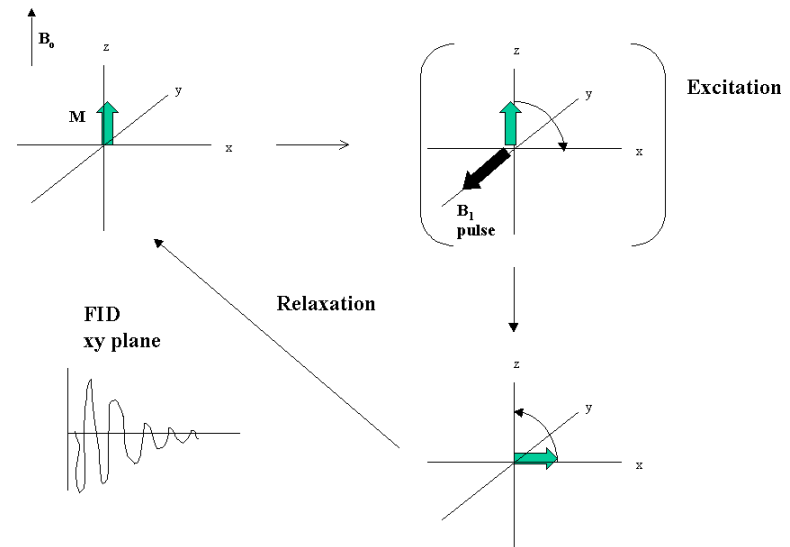
Shielding, Chemical shift



Energy levels for a nucleus with spin quantum number 1/2



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

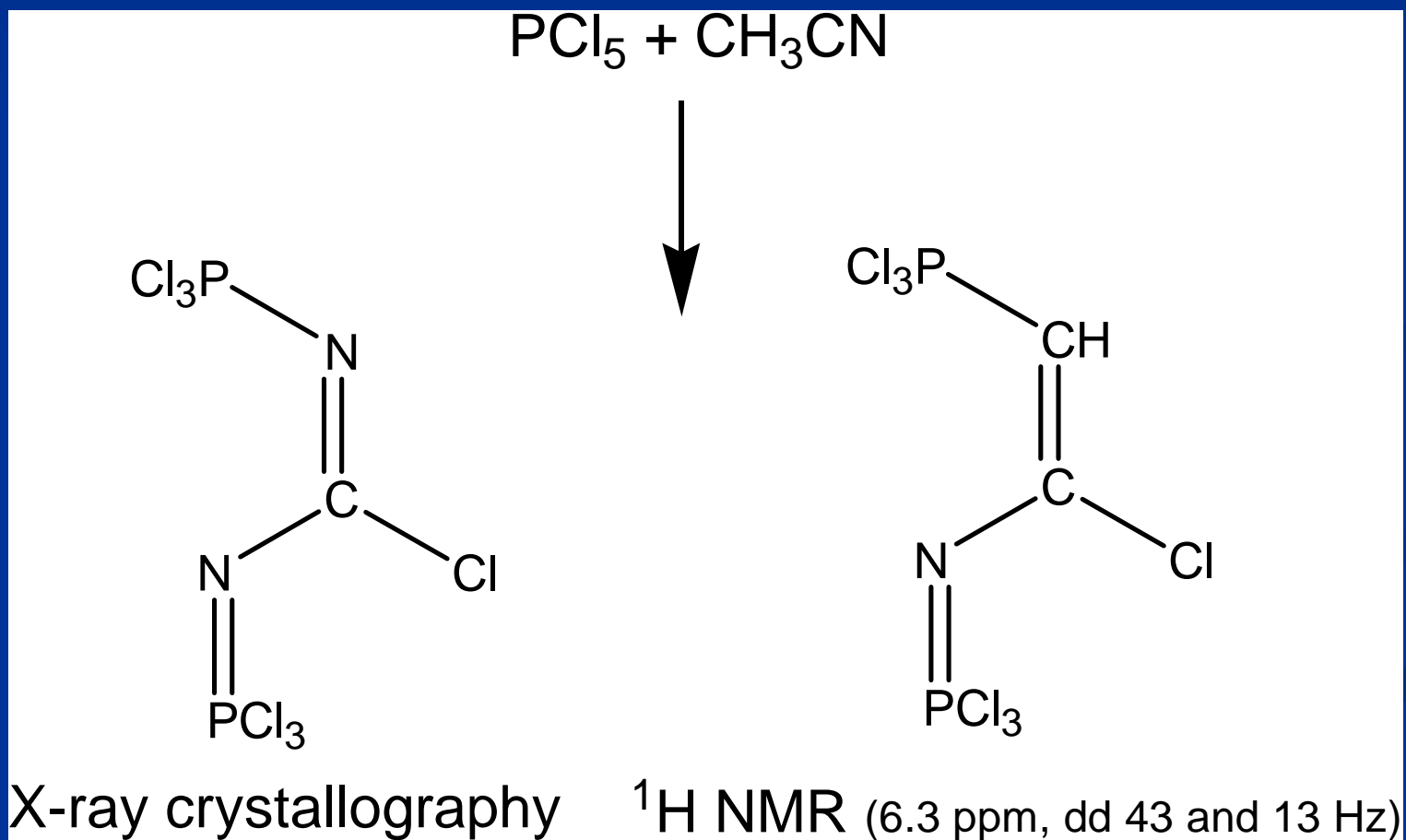


Chemical Shift Information

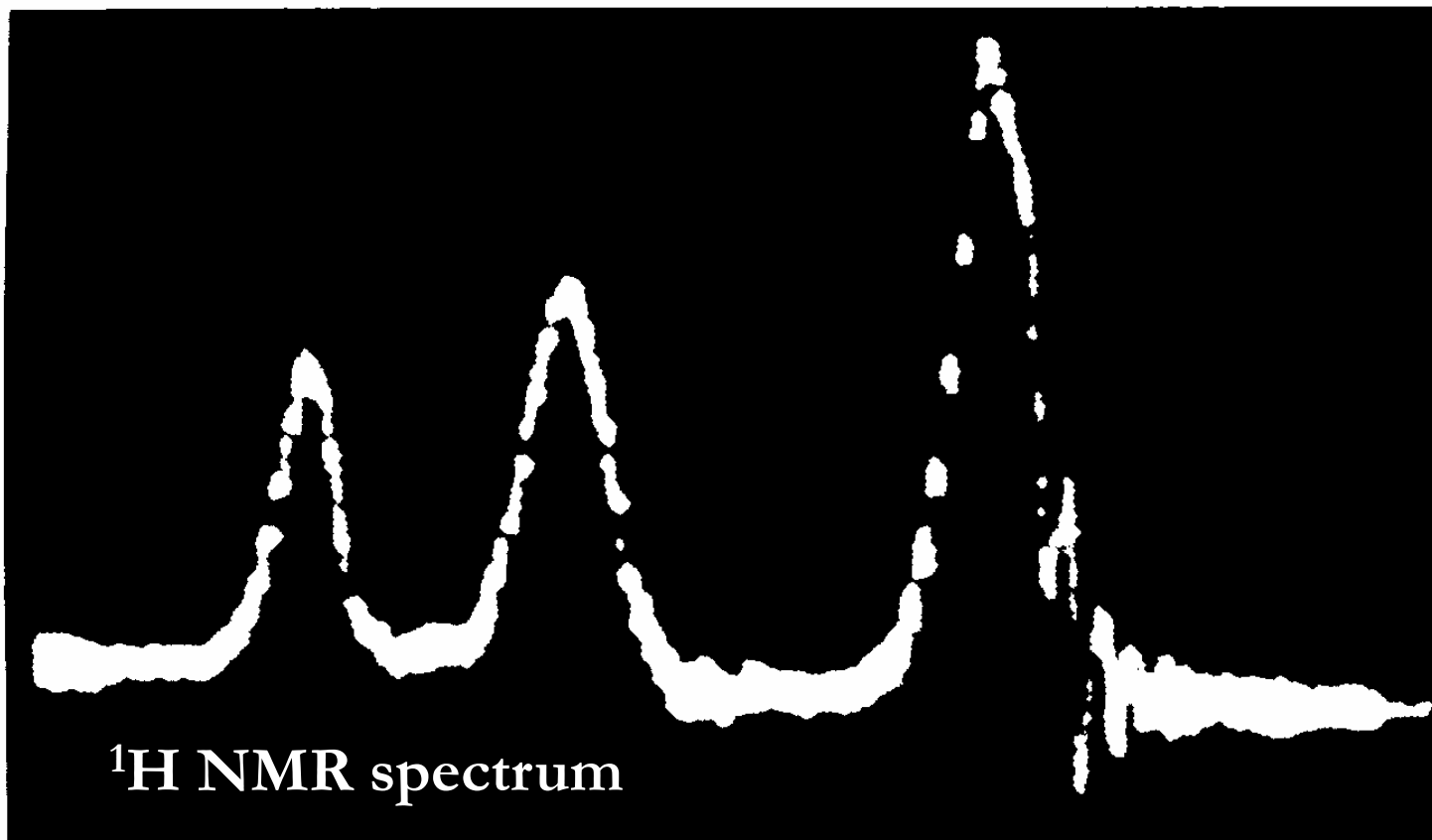
- (The presence of an element in the sample)
- **Number of signals** = number of chemically different atoms
Symmetry of the molecule
- **Relative intensity** = ratio of atoms – integration
- **Position** = chemical shielding / shift – electronic environment, type of bonds, oxidation state, coordination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

Chemical Shift Information

The presence of an element in the sample



Chemical Shift

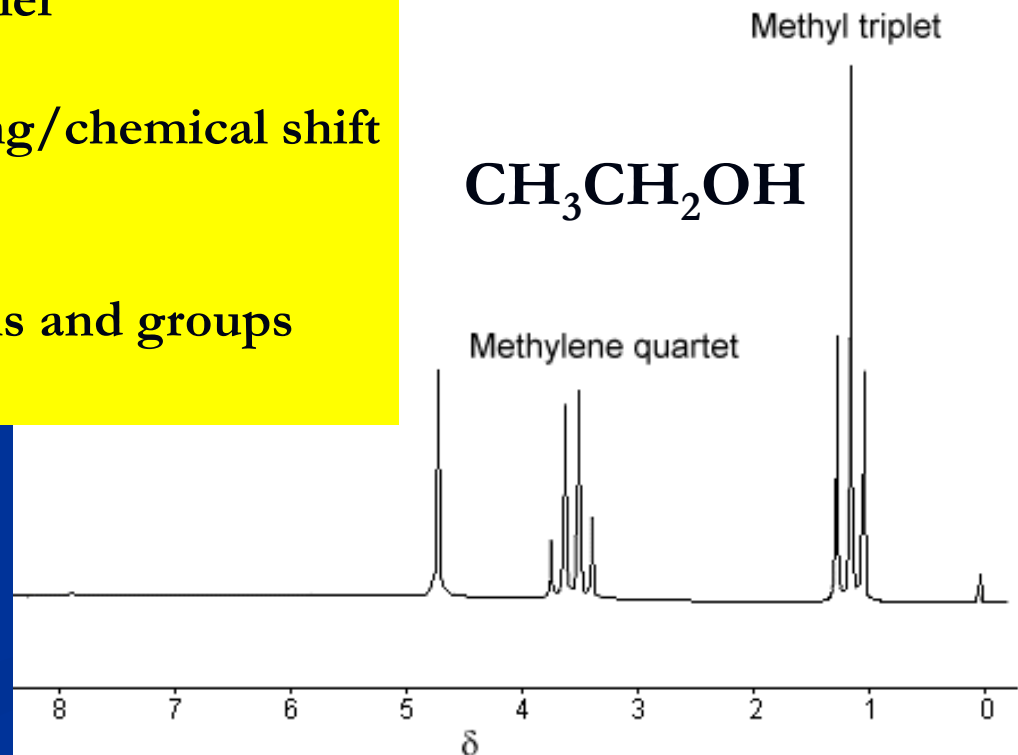


The three peaks of ethyl alcohol as first observed in 1951 at Stanford University.

Chemical Shift

Chemical shift for a given molecule:

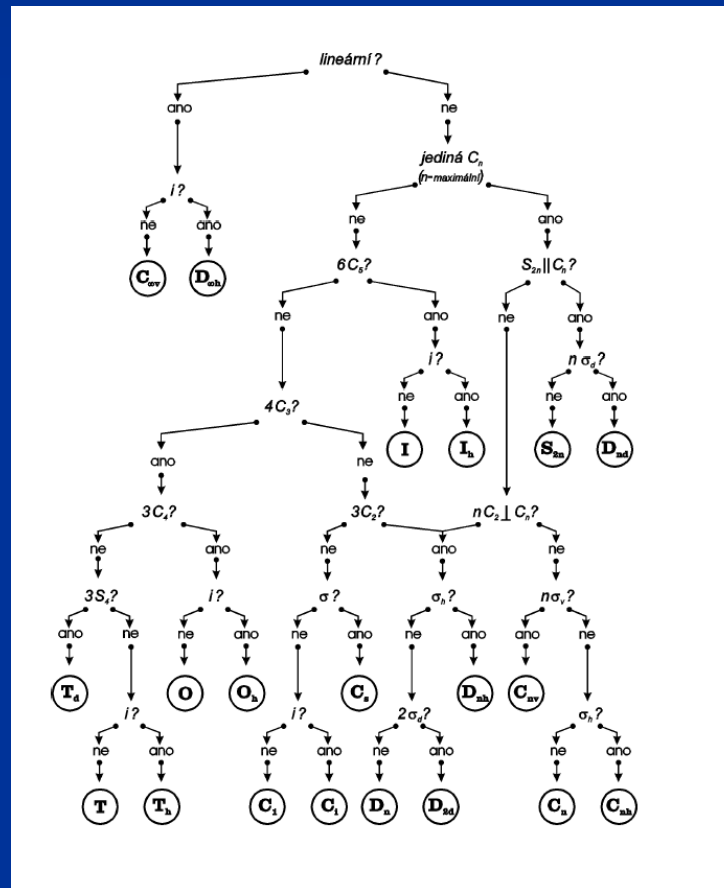
- **Number of signals** = nonequivalent nuclei
molecular symmetry
- **Relative intensity** = number of nuclei
- **Position in the spectrum** = shielding/chemical shift
electronic structure
- **Multiplicity** = connectivity of atoms and groups



Molecular Symmetry

Number of signals = nonequivalent nuclei, molecular symmetry

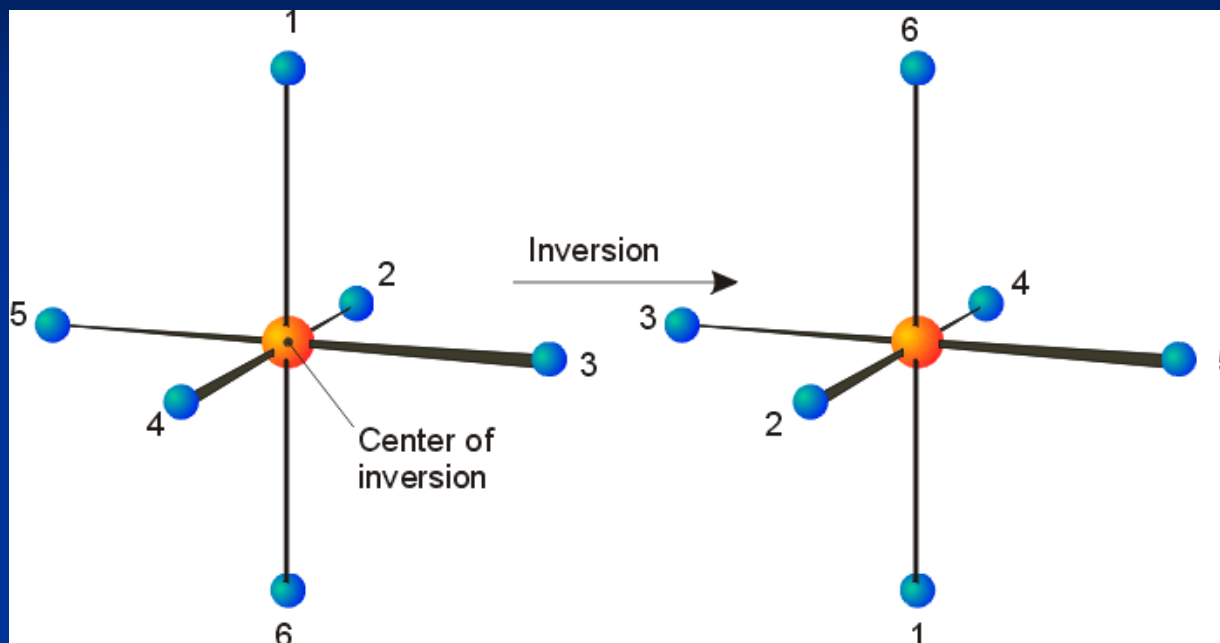
Flow chart for point group determination



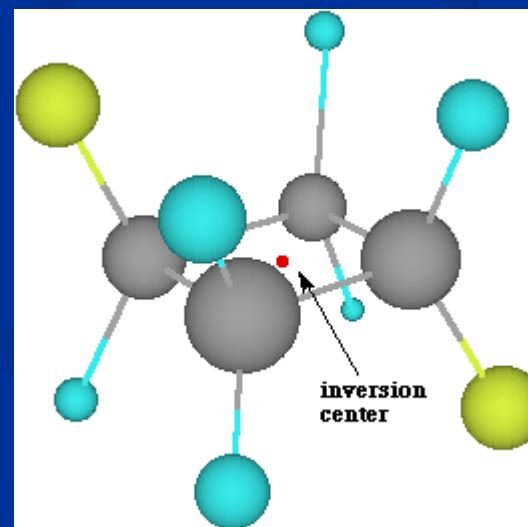
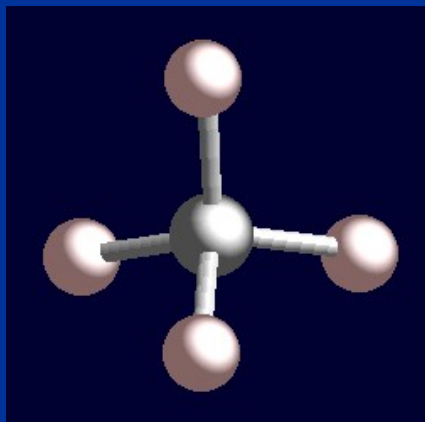
Symmetry Elements and Operations

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

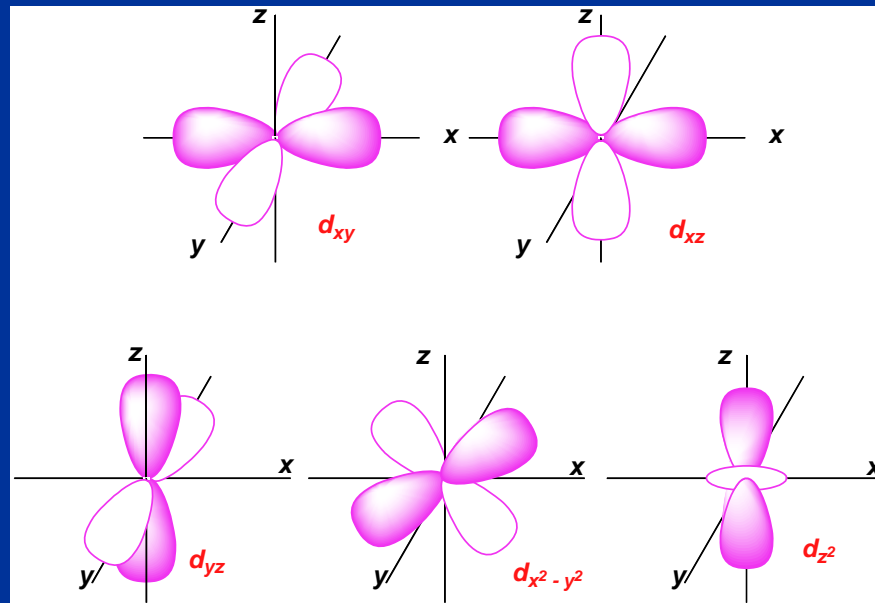
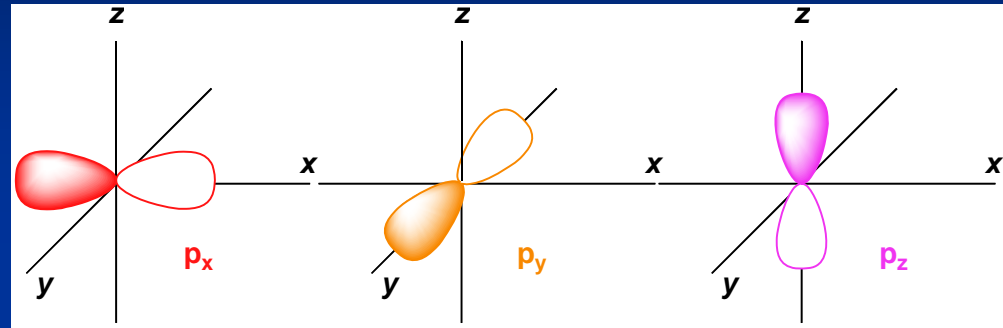
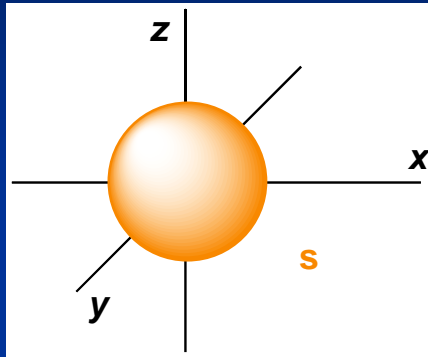
Inversion Center



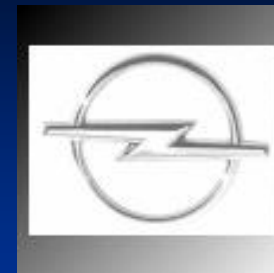
NO inversion center



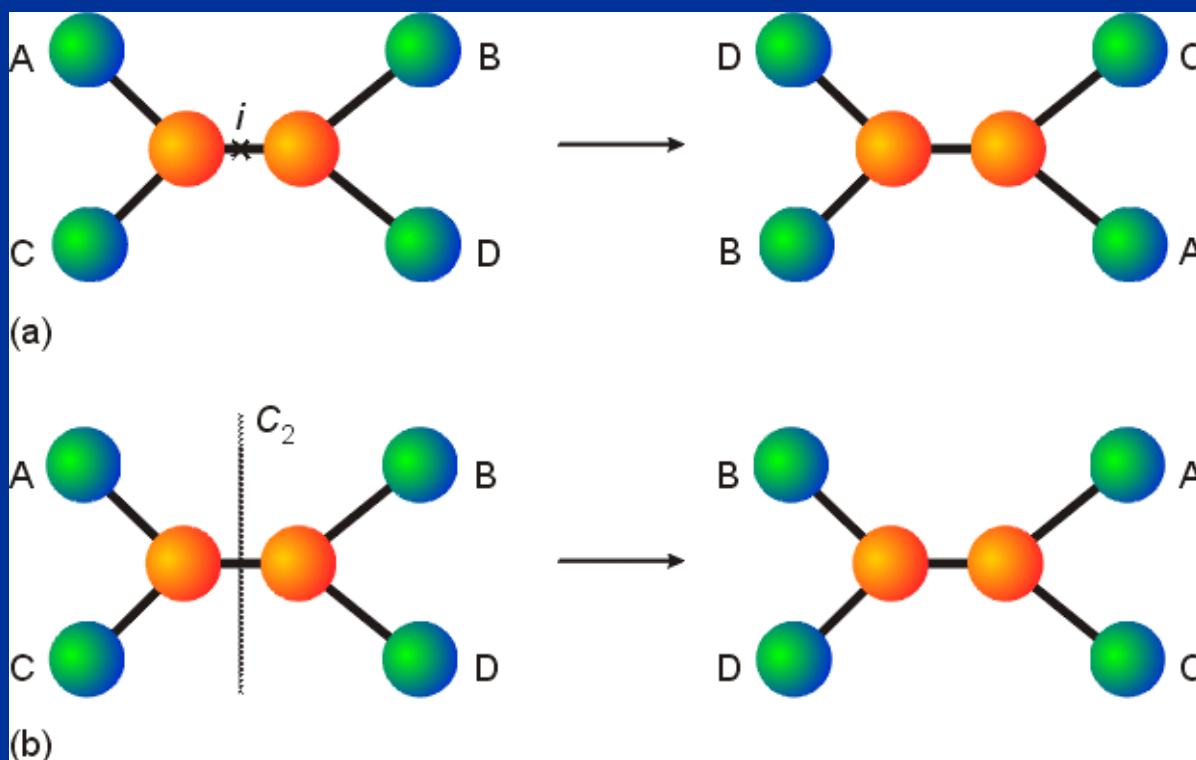
Inversion Center



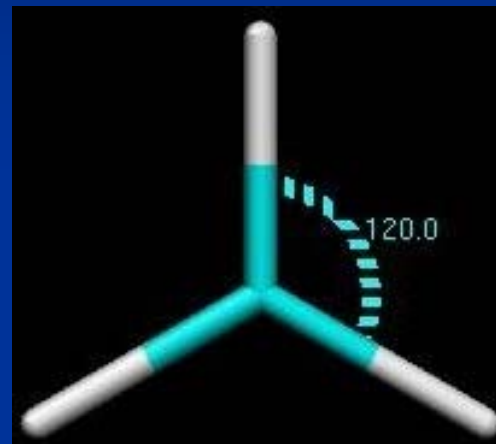
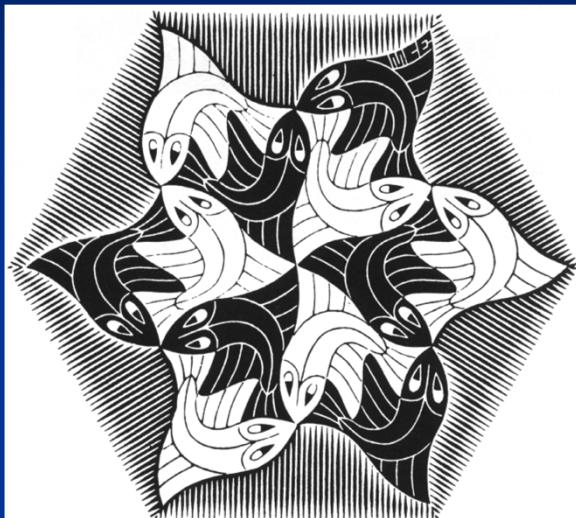
Rotation Axis C_2



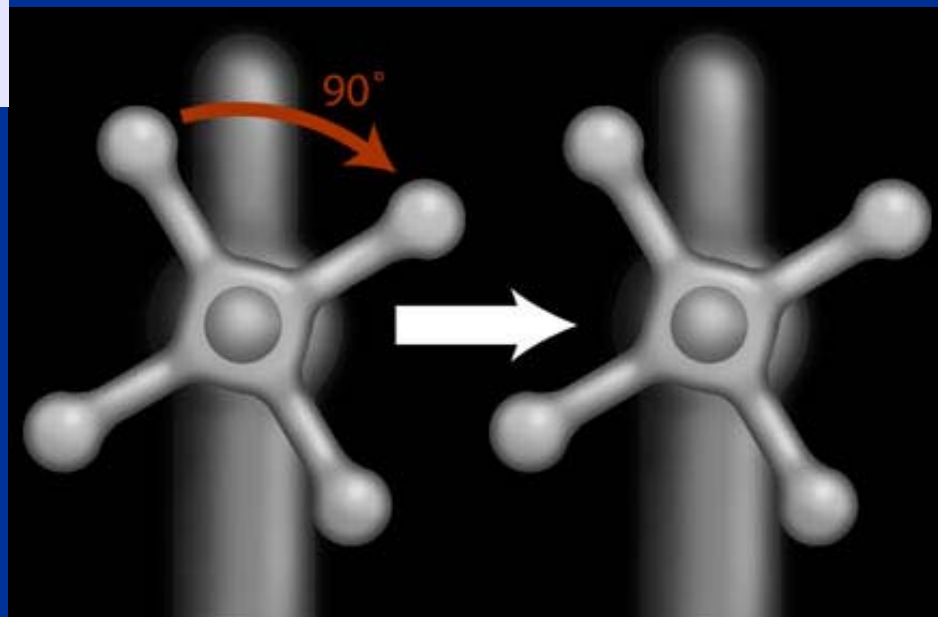
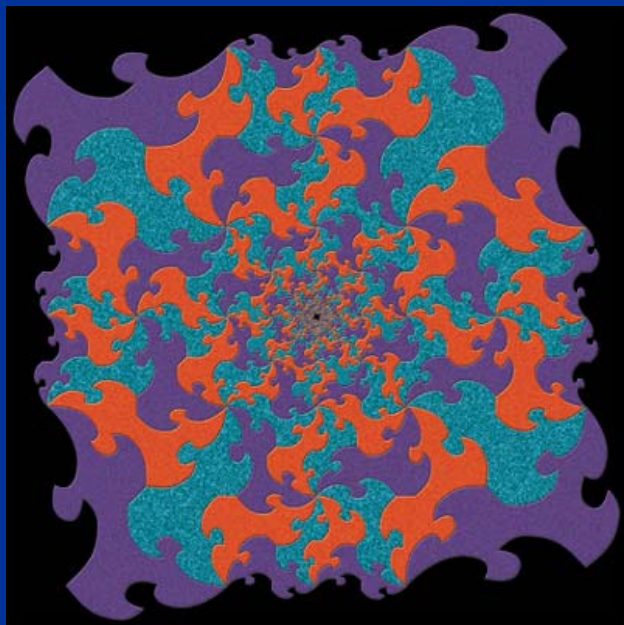
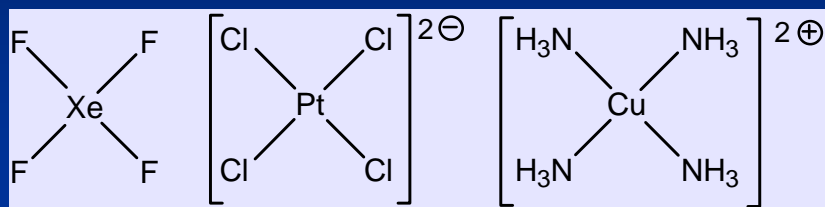
Rotation by $360/n$ about C_n brings the object to an indistinguishable position from the original



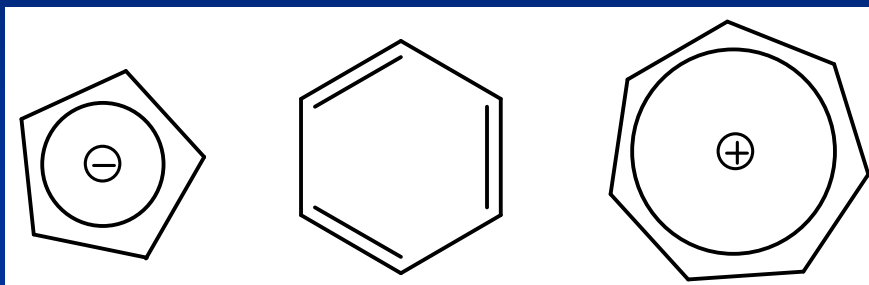
Rotation Axis C_3



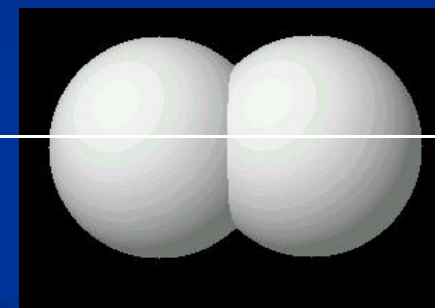
Rotation Axis C_4



Rotation Axis C_∞



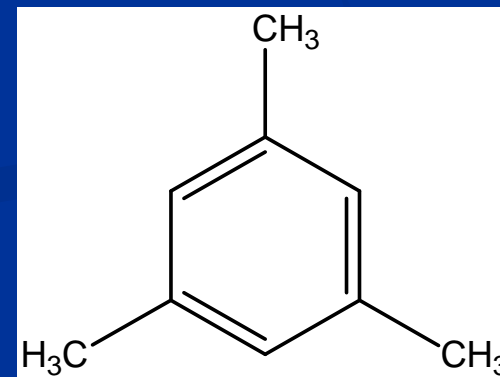
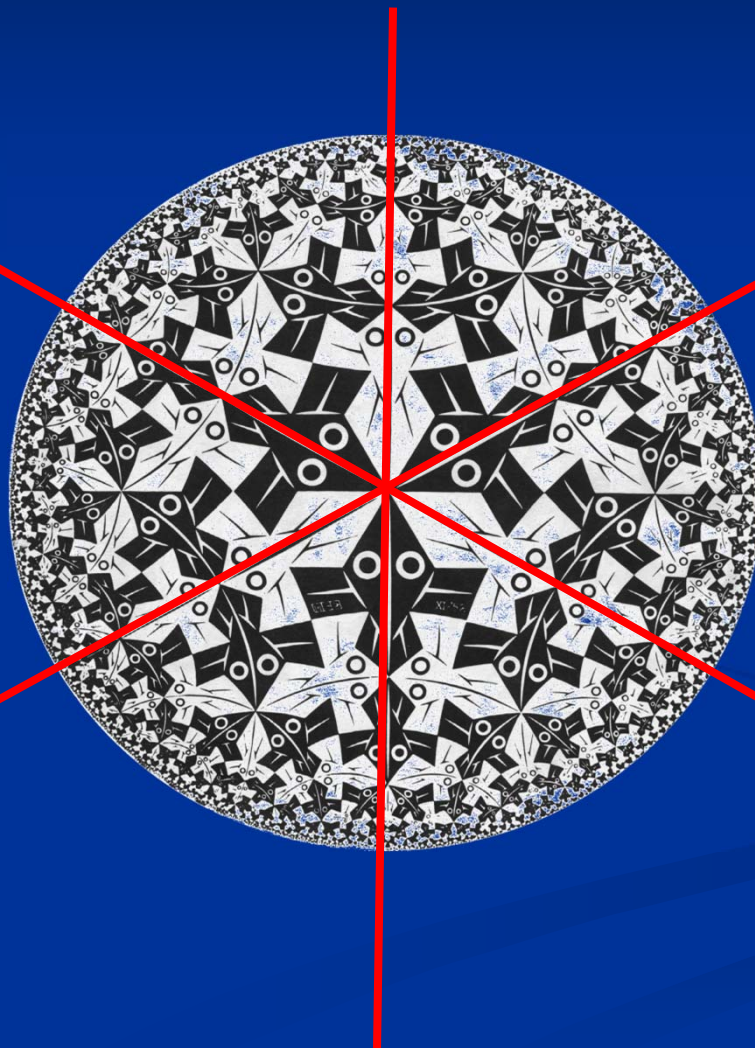
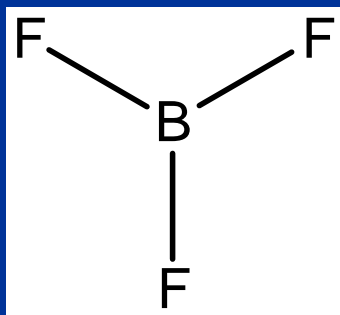
$C_5, C_6, C_7, \dots, C_\infty$



Linear molecules



Plane of Symmetry σ



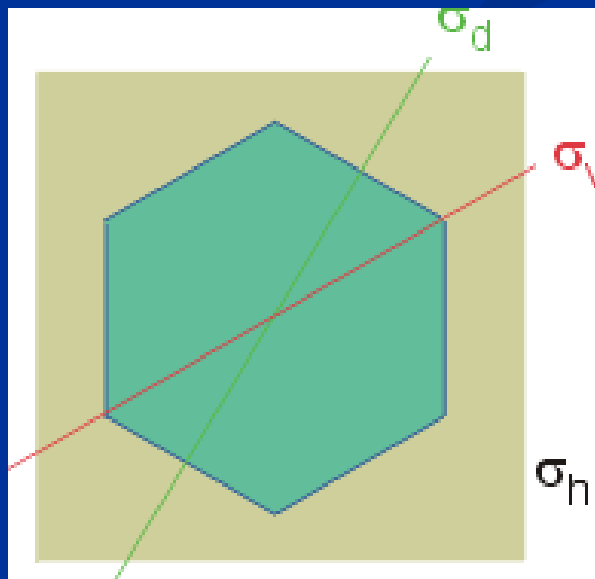
Plane of Symmetry σ

Planar molecules – symmetry plane of the molecule

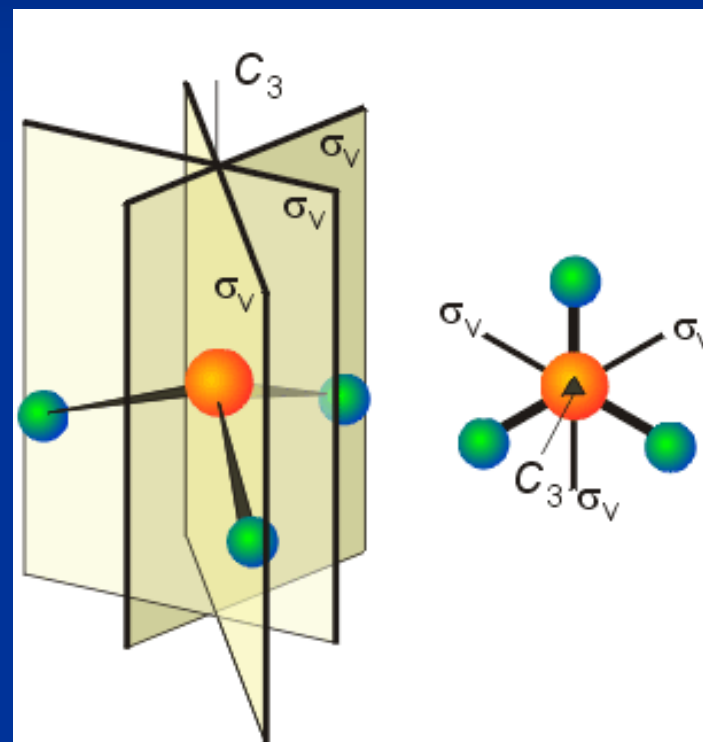
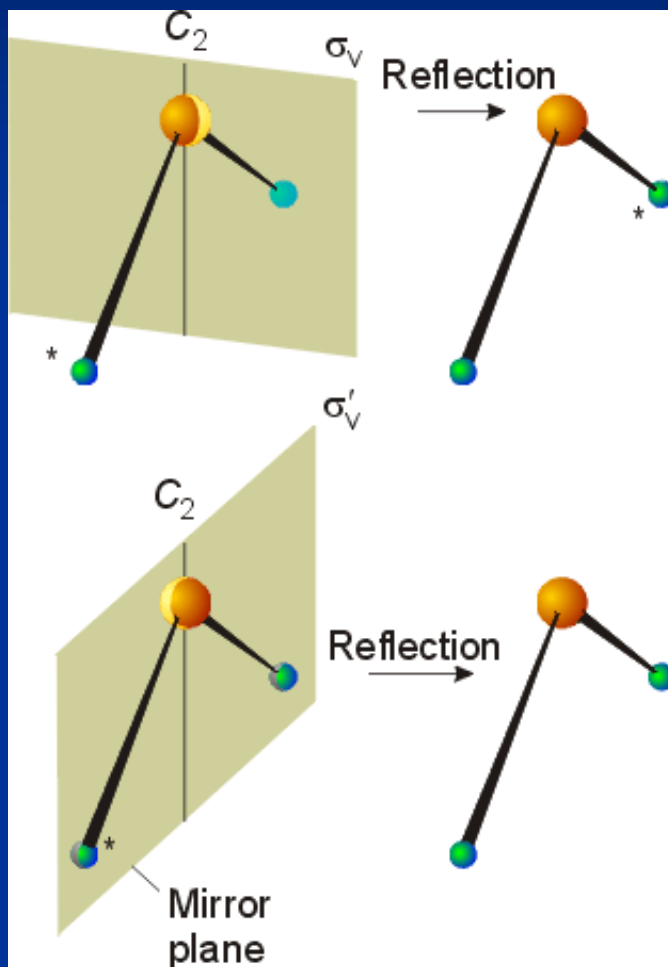
σ_h = horizontal plane, perpendicular to principal axis

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

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



Plane of Symmetry σ

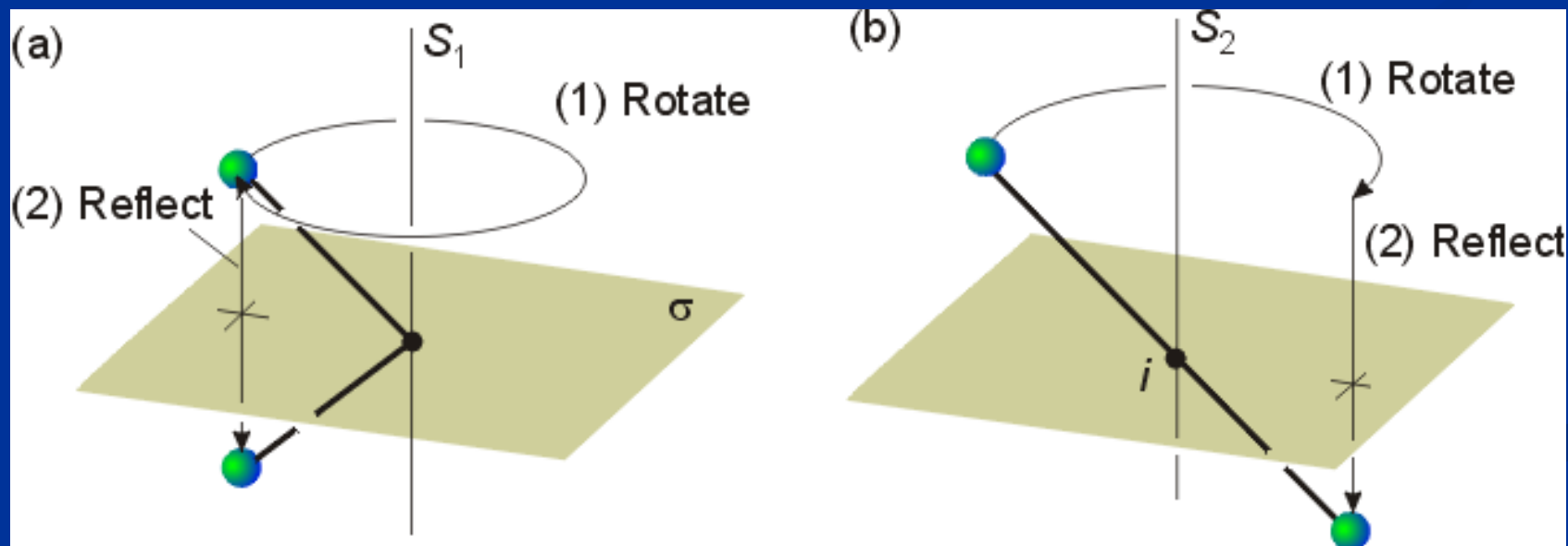


Improper Axis S_n

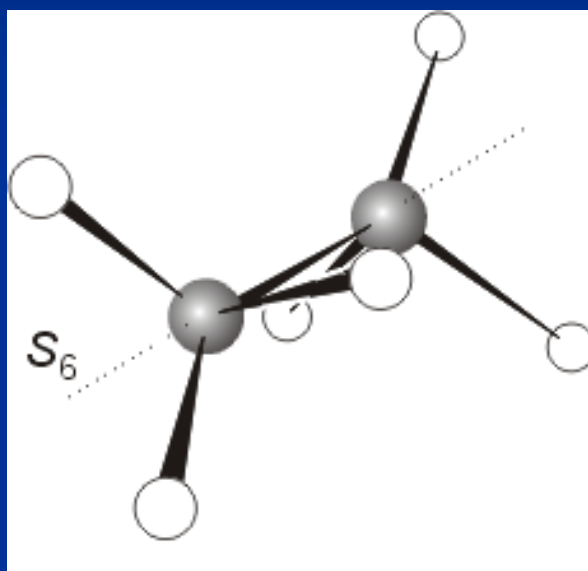
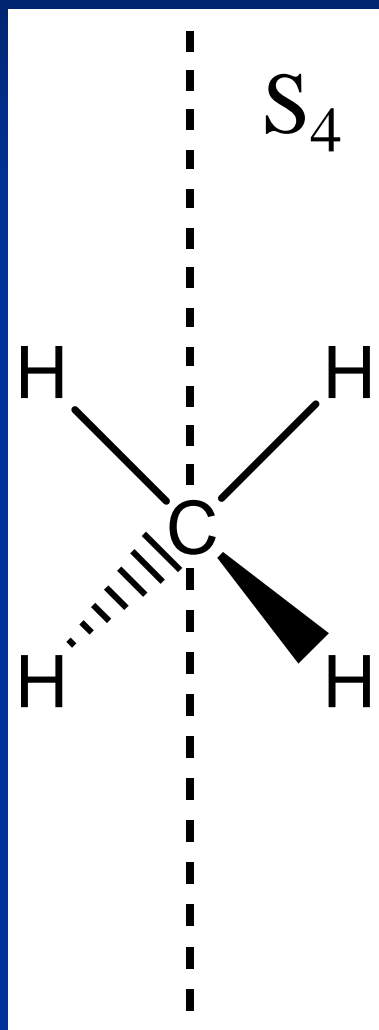
Rotation-reflection = a compound operation, rotation (C_n) followed by a reflection through a plane perpendicular to the C_n axis

$$S_1 = C_1 \times \sigma = \sigma$$

$$S_2 = C_2 \times \sigma = i$$

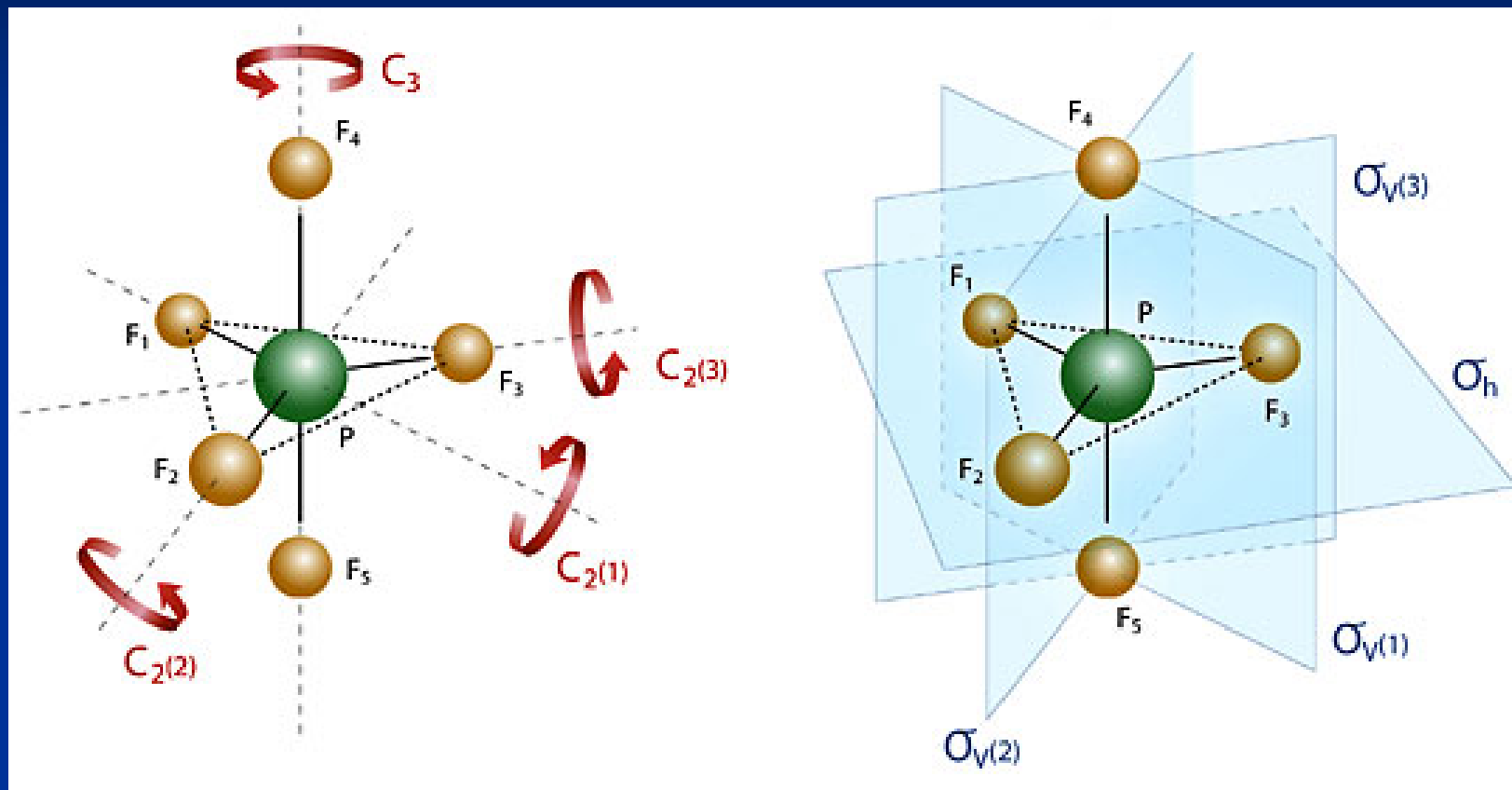


Improper Axis S_n



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



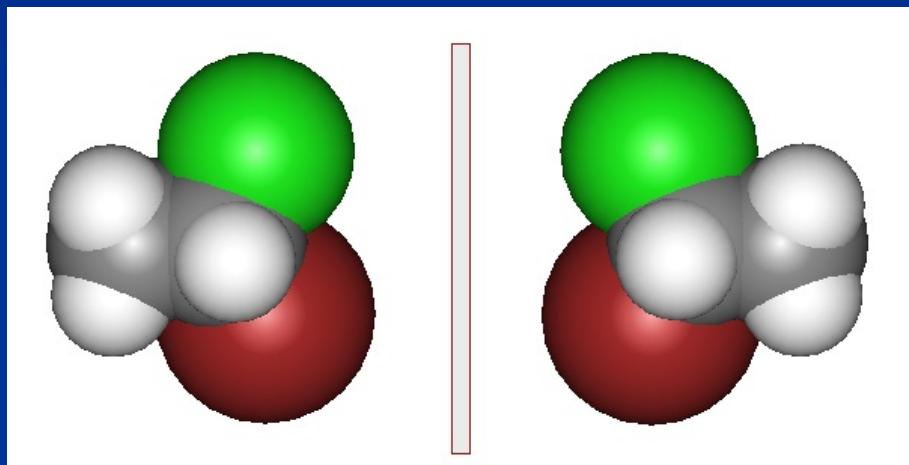
Figure 2. The Founding Fathers. R. M. Barrer (1910–1996) (right) and R. M. Milton (1920–2000) photographed

Chirality

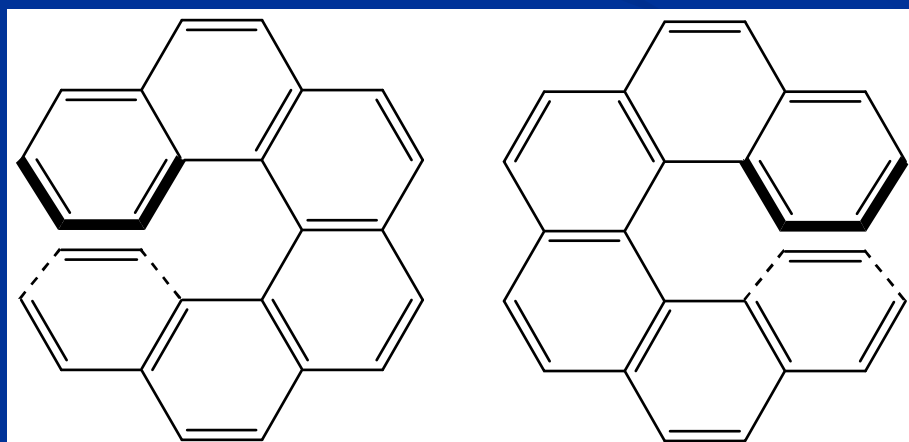
Condition of chirality: no S_n present in a molecule

$$S_1 = \sigma$$

$$S_2 = i$$



C_2



Chemical Shift

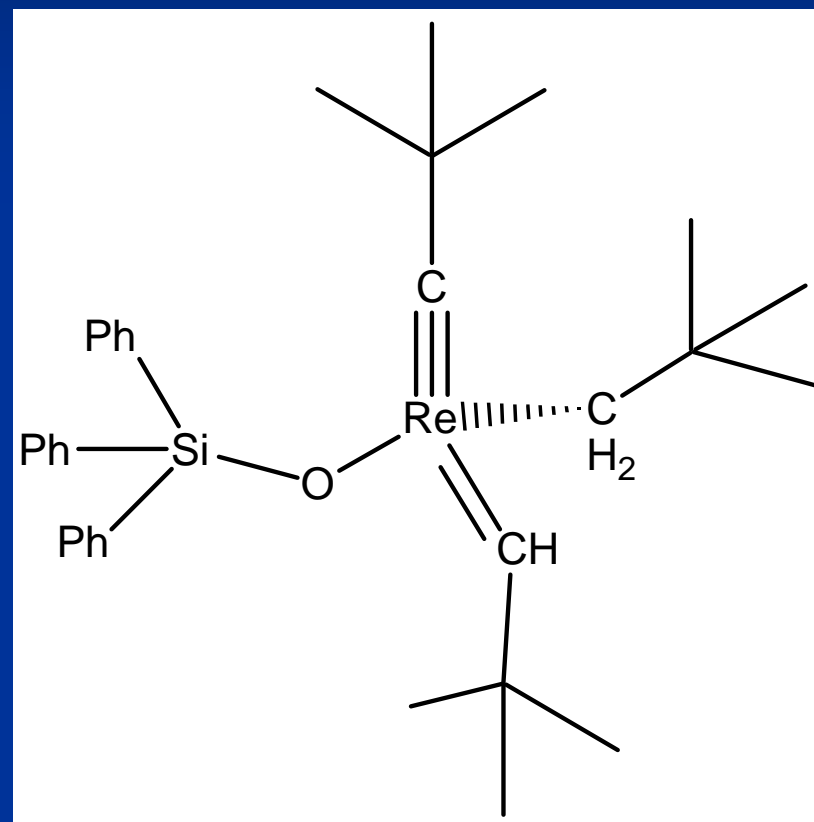
Number of signals = nonequivalent nuclei

Chemically different atoms

^{13}C NMR

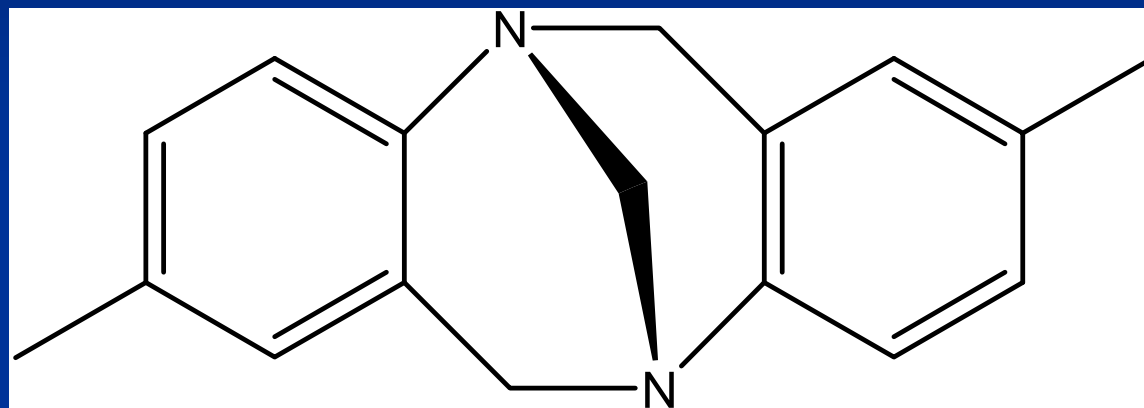
3 x t-Bu groups

No C_3 axis



Geometrical difference = chemical difference

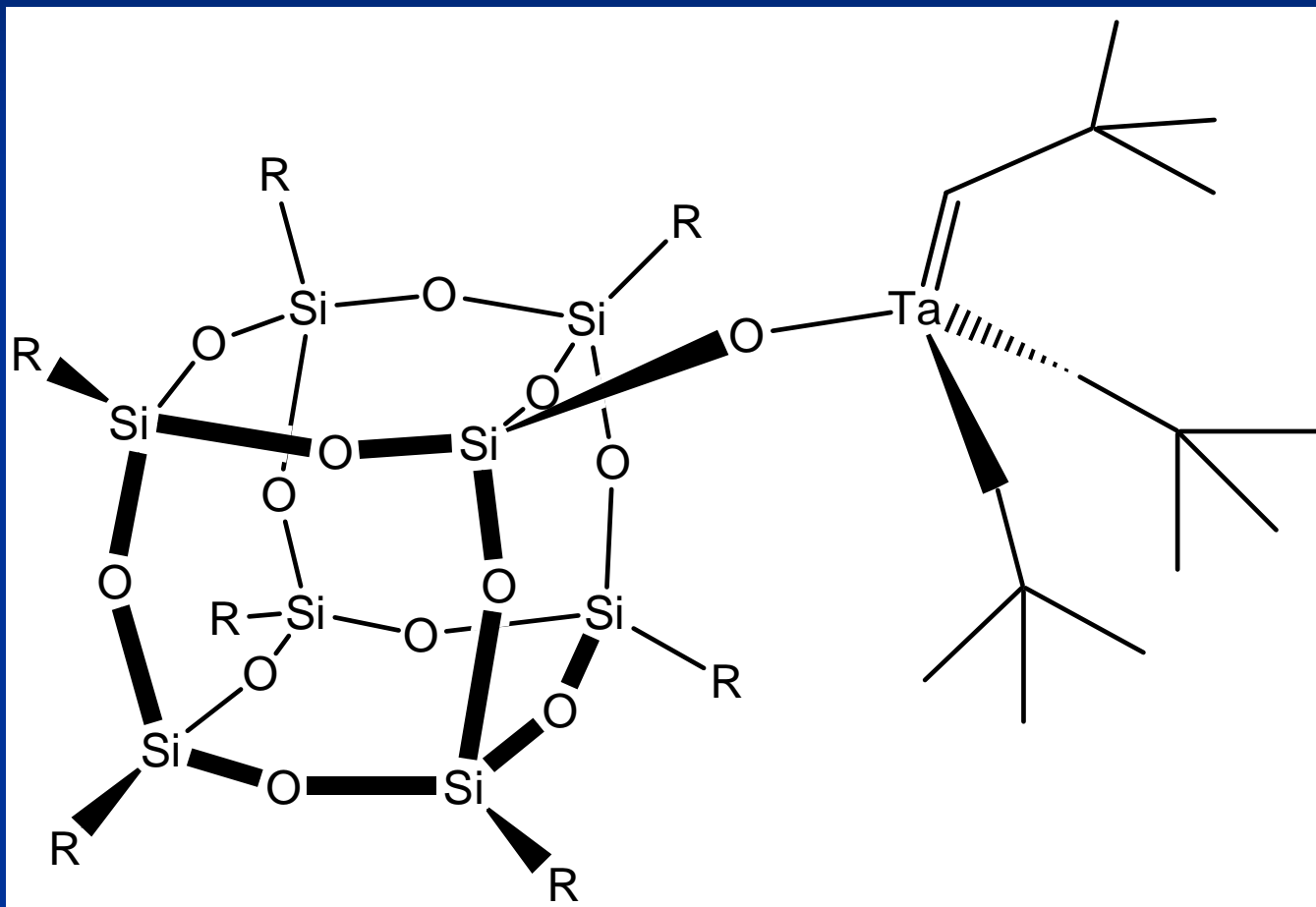
Molecular Symmetry



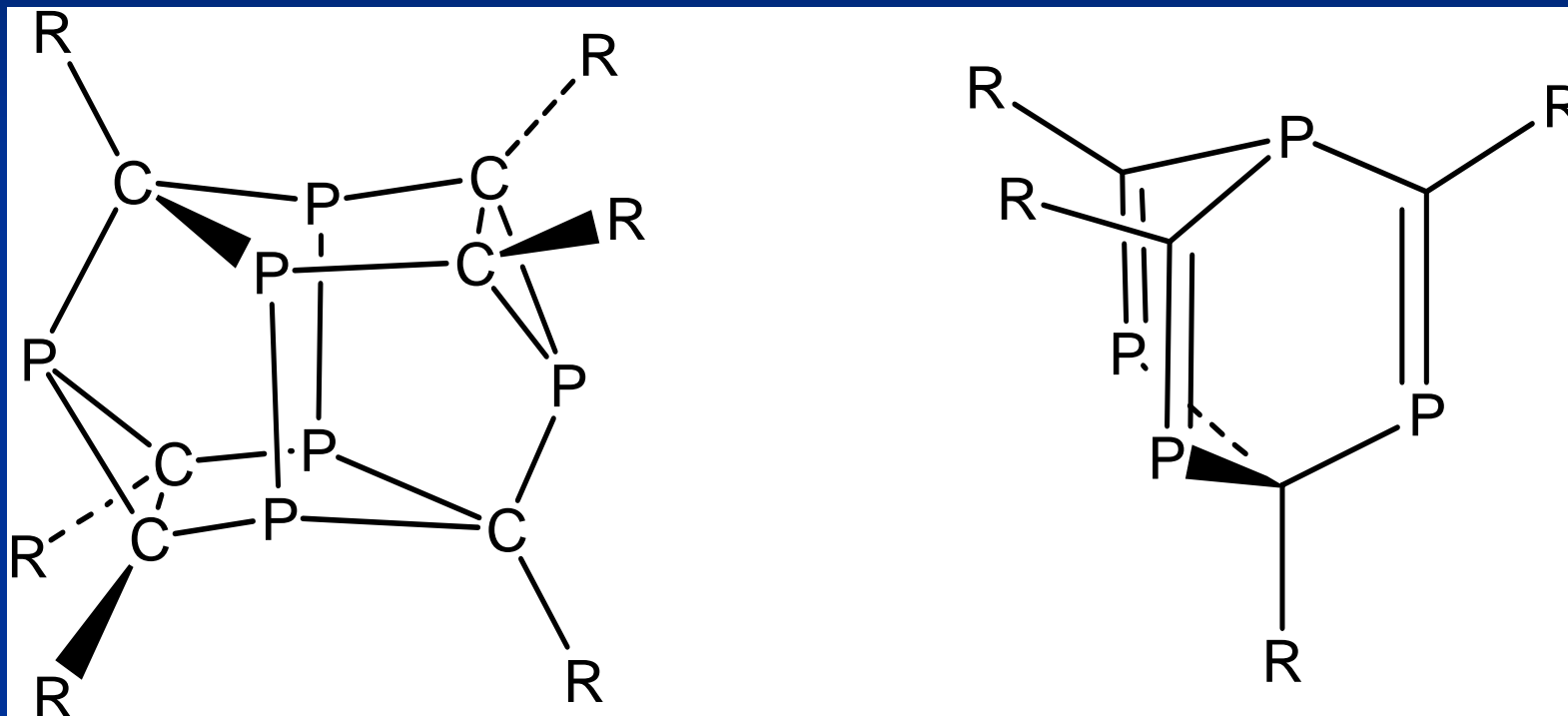
1 x Me group signal

C_2 axis

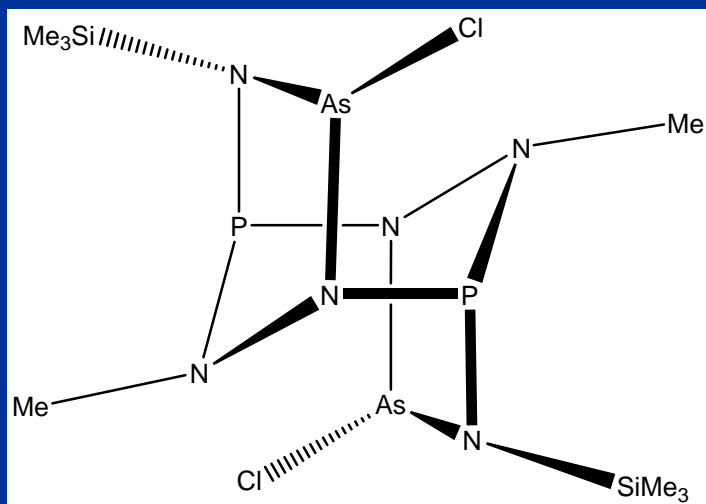
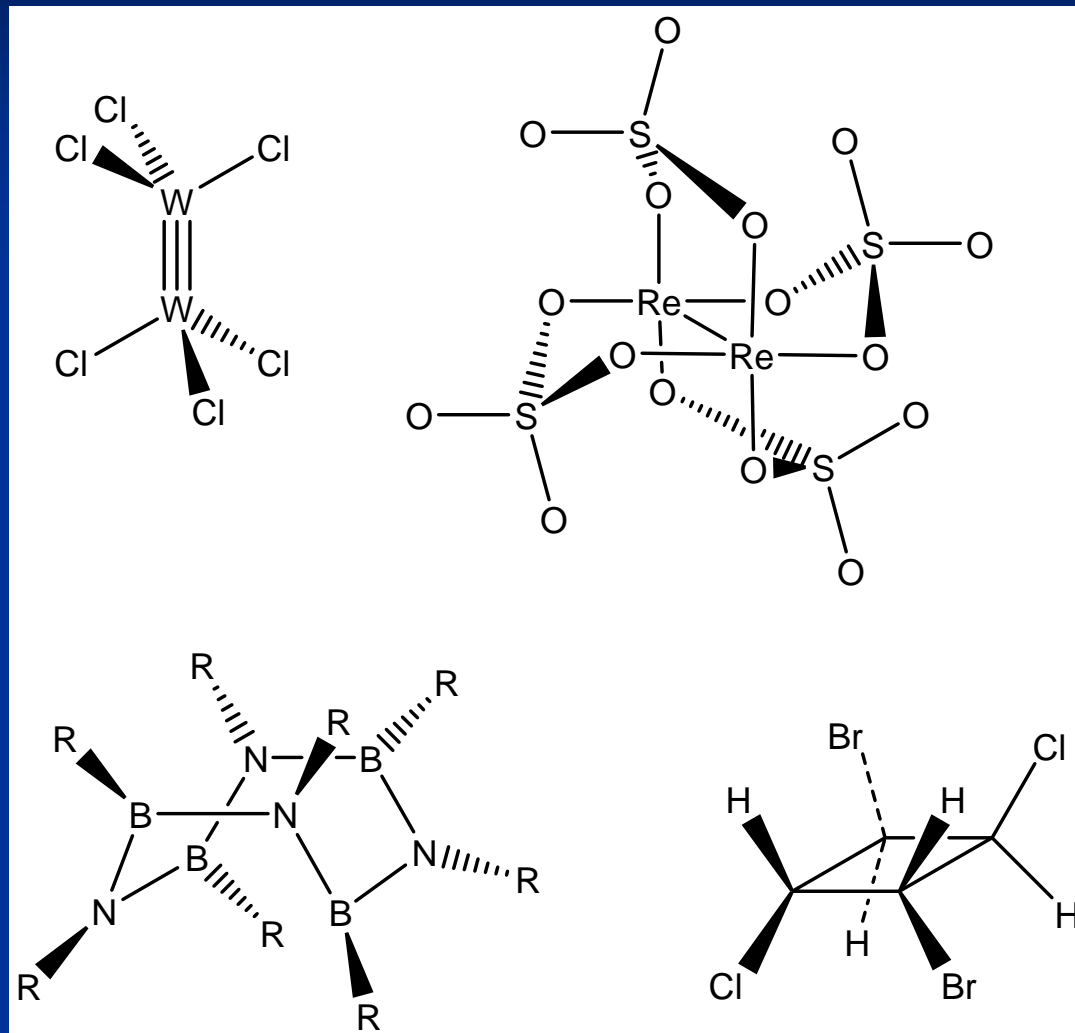
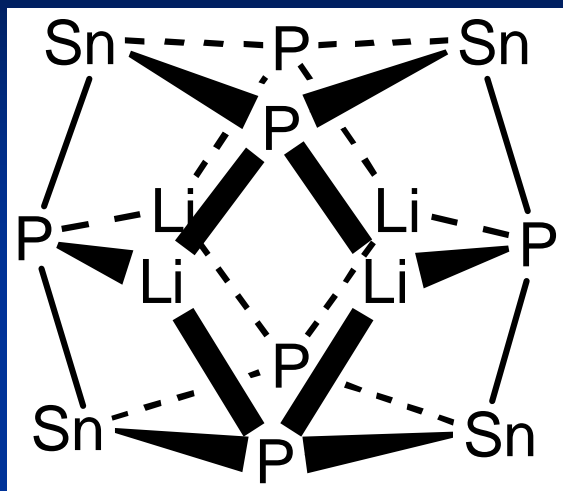
Chemical Shift

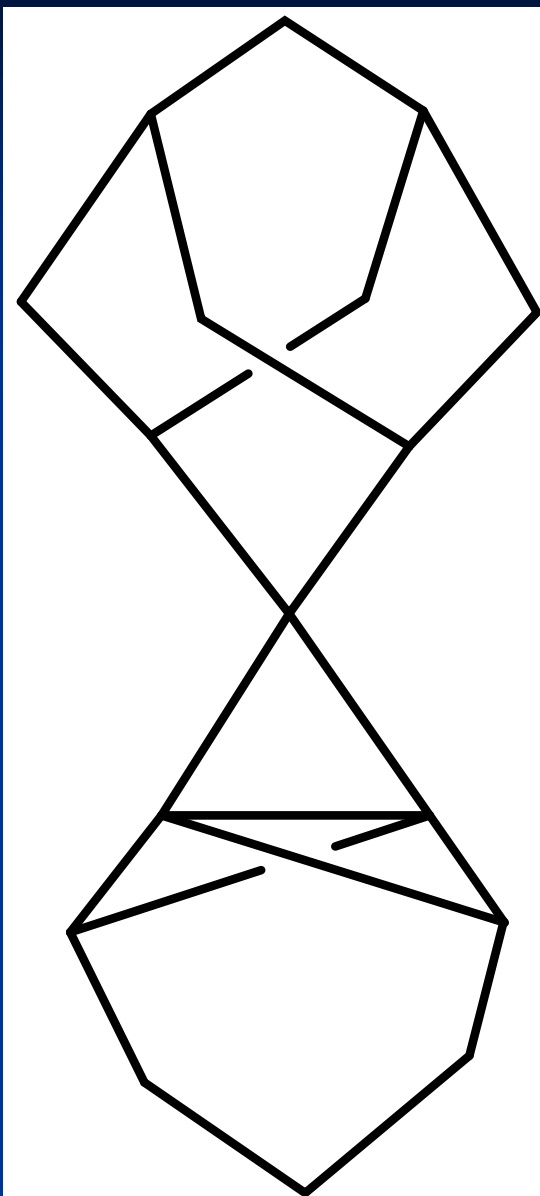


Chemical Shift



Chemical Shift





^1H NMR (600 MHz, CDCl_3 , TMS):

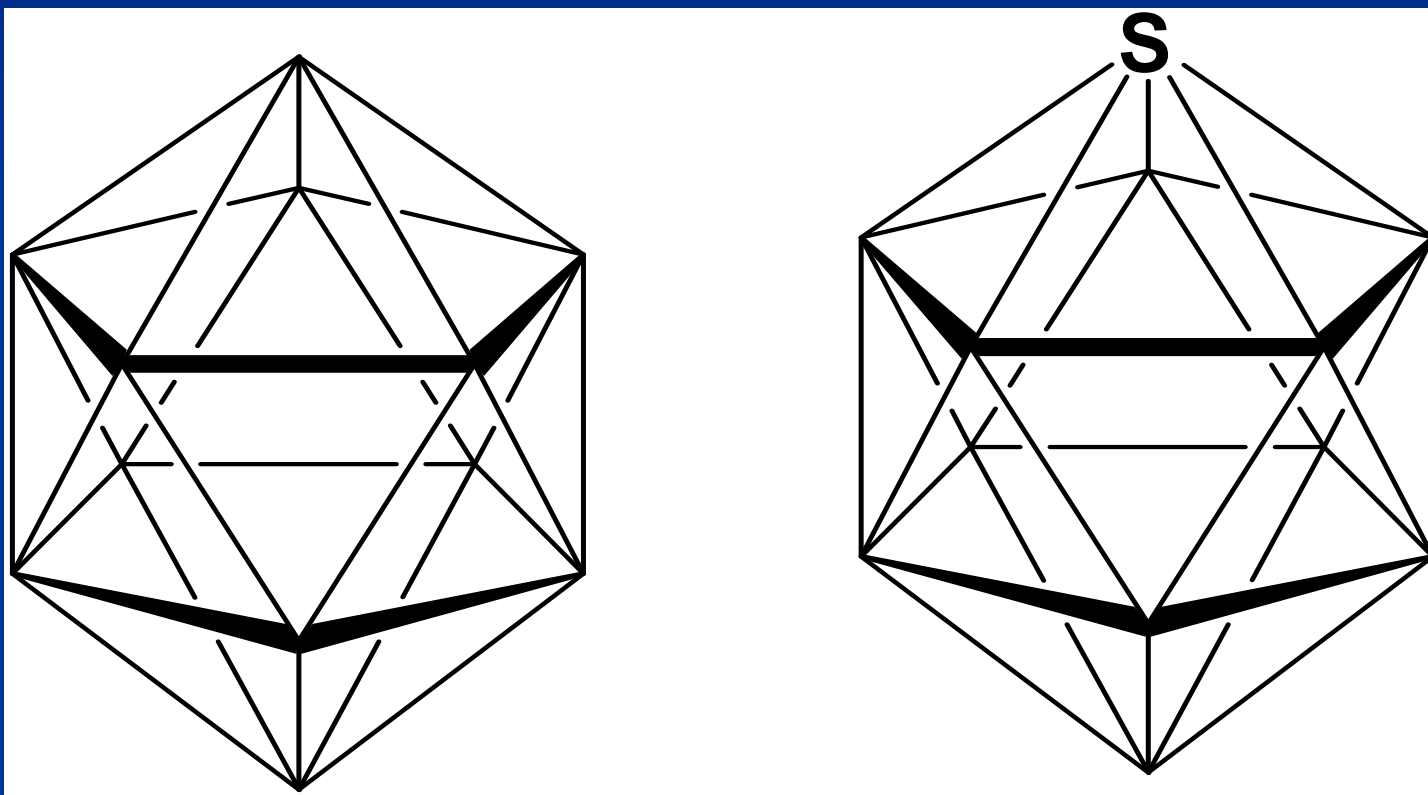
3.25 (s, 2H, H-2' and H-6'),
1.70 (br s, 2H, H-1 and H-3),
1.57 (br s, 2H, H-5 and H-7),
1.55 (br s, 4H, H-4, 8, 9, 10),
1.45 (m, 6H, H-4, 8, 9, 10 and H-6),
1.34 (m, 4H, H-3' and H-5'),
0.96 ppm (m, 2H, H-4')

^{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

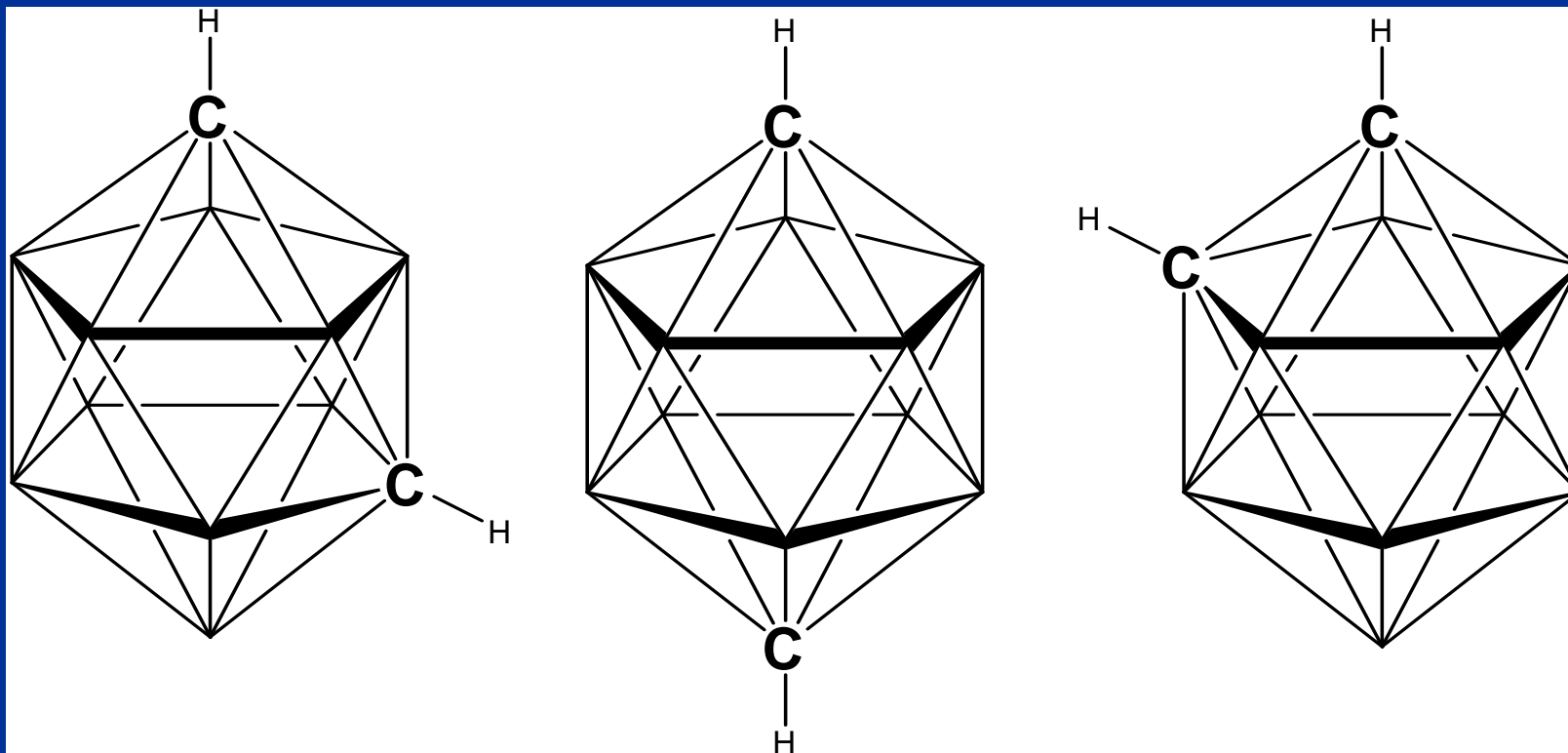
^{11}B NMR



Chemical Shift

^{11}B NMR

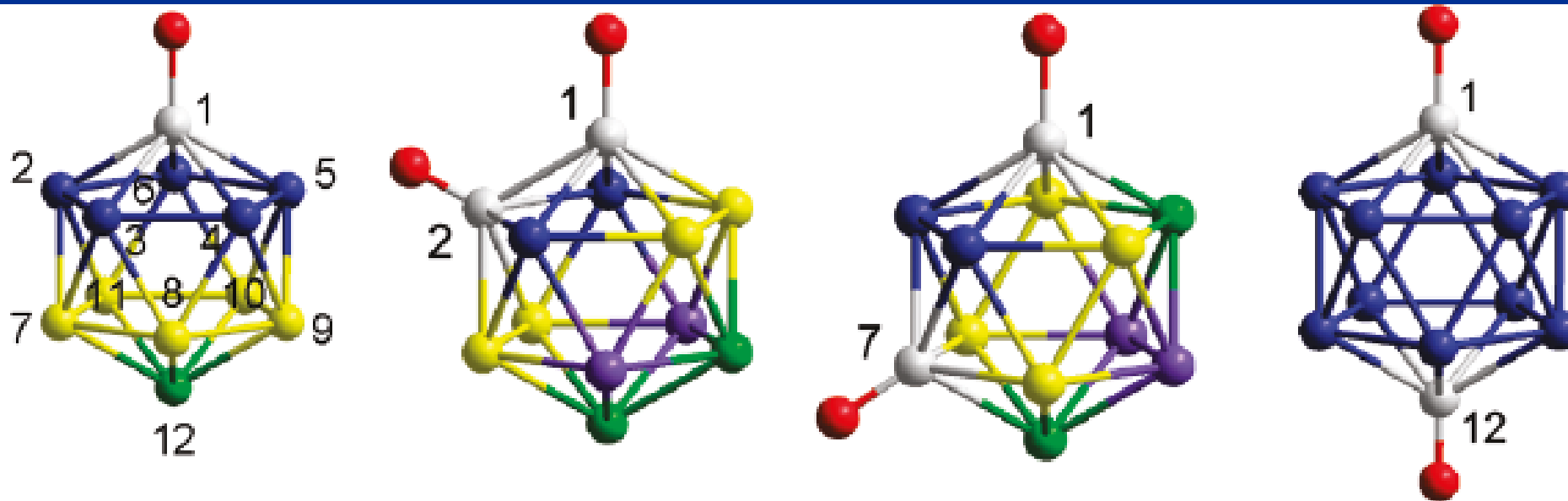
Isomers of $\text{B}_{10}\text{H}_{10}\text{C}_2\text{H}_2$



Chemical Shift

^{11}B NMR

Mono- and Disubstituted $\text{B}_{12}\text{H}_{12}^{2-}$ Molecules with Identical Substituents



C_{5v}

C_{2v}

C_{2v}

D_{5d}

1 : 5 : 5 : 1

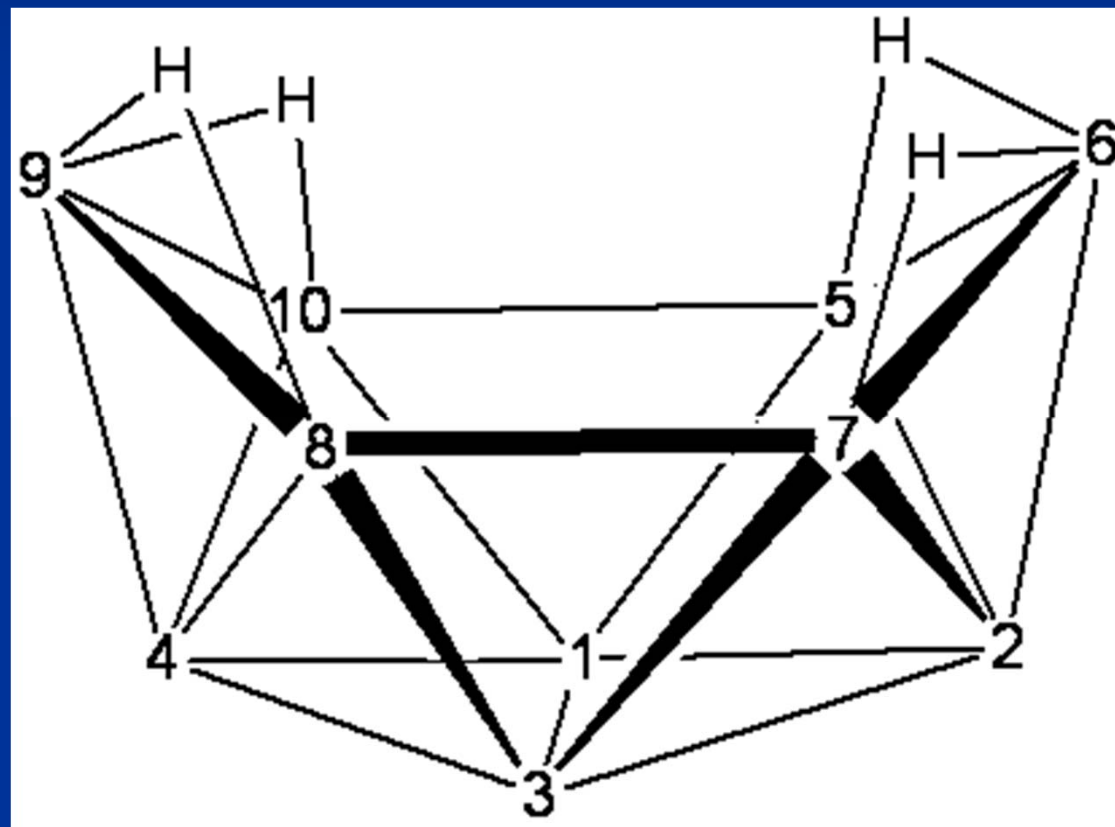
2 : 2 : 4 : 2 : 2

2 : 2 : 4 : 2 : 2

2 : 10

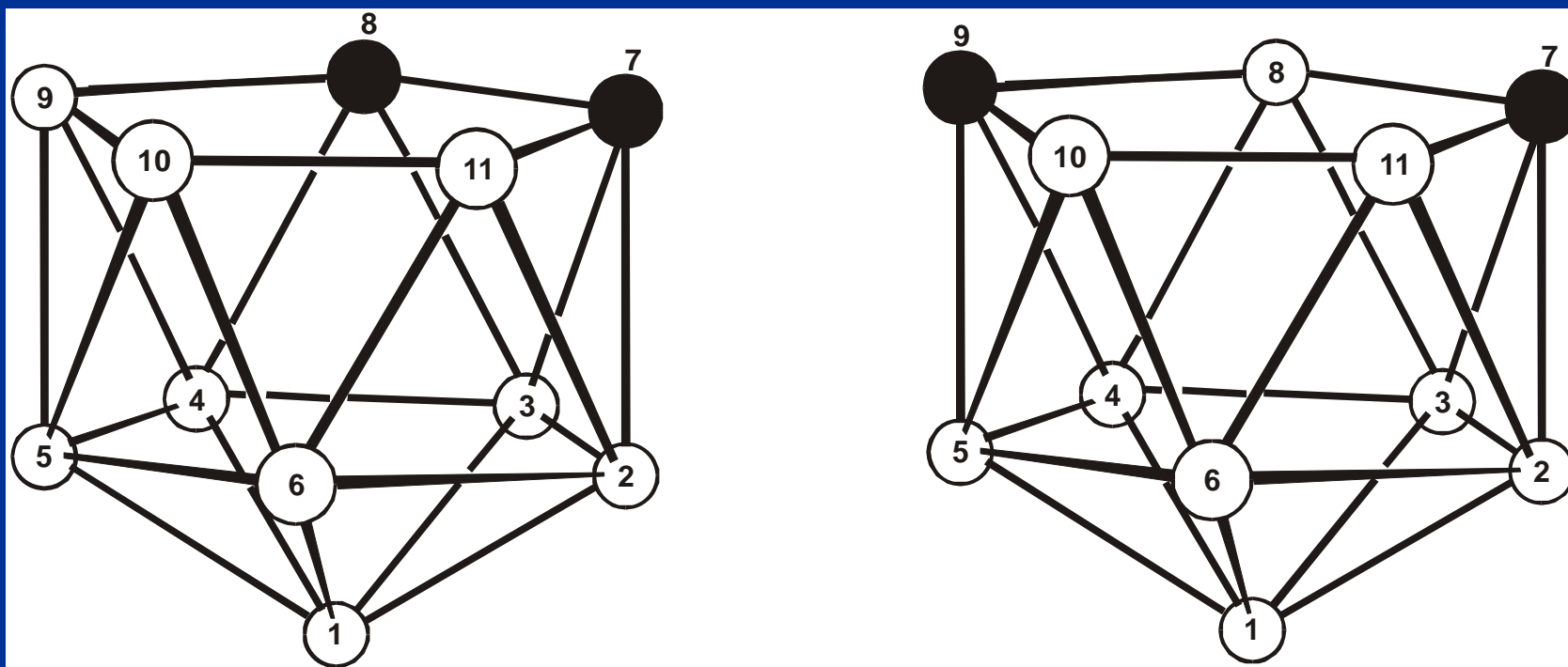
Chemical Shift

^{11}B NMR

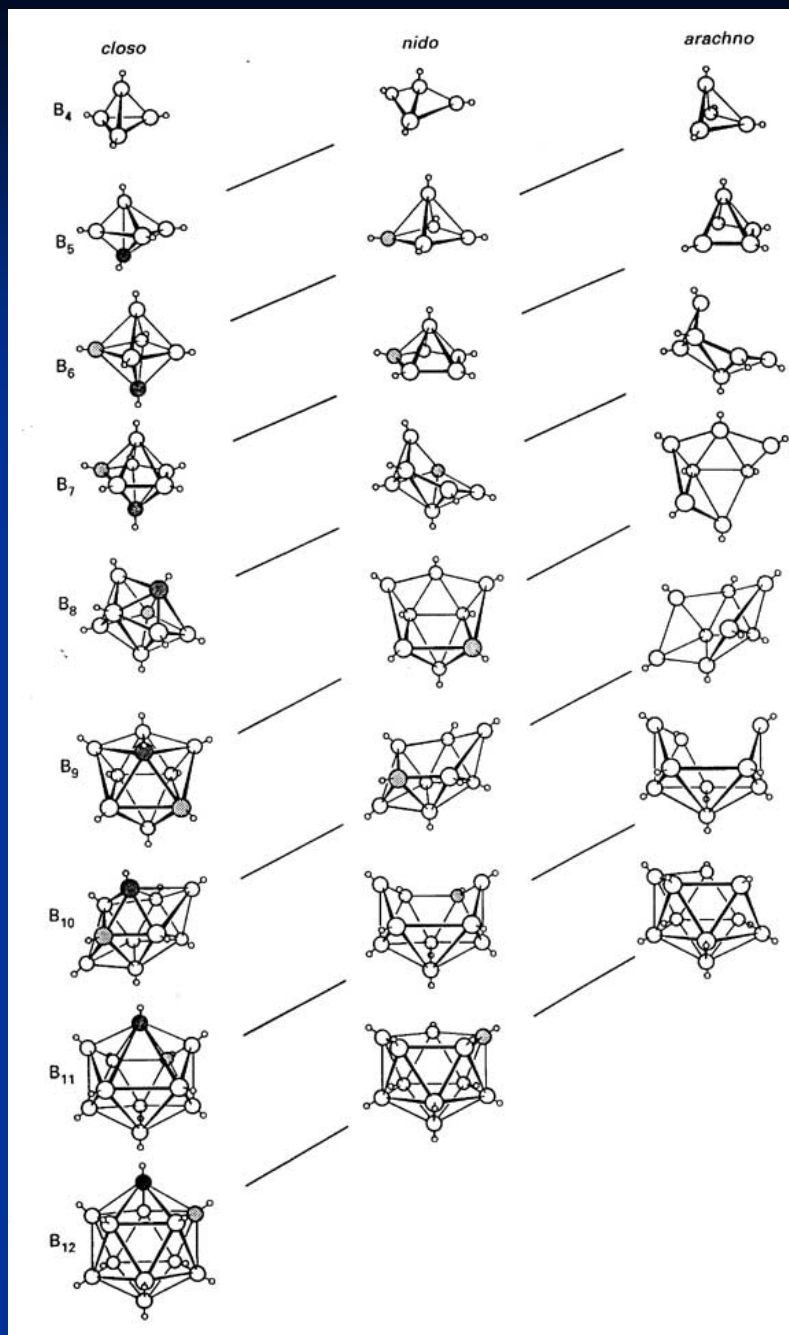


Chemical Shift

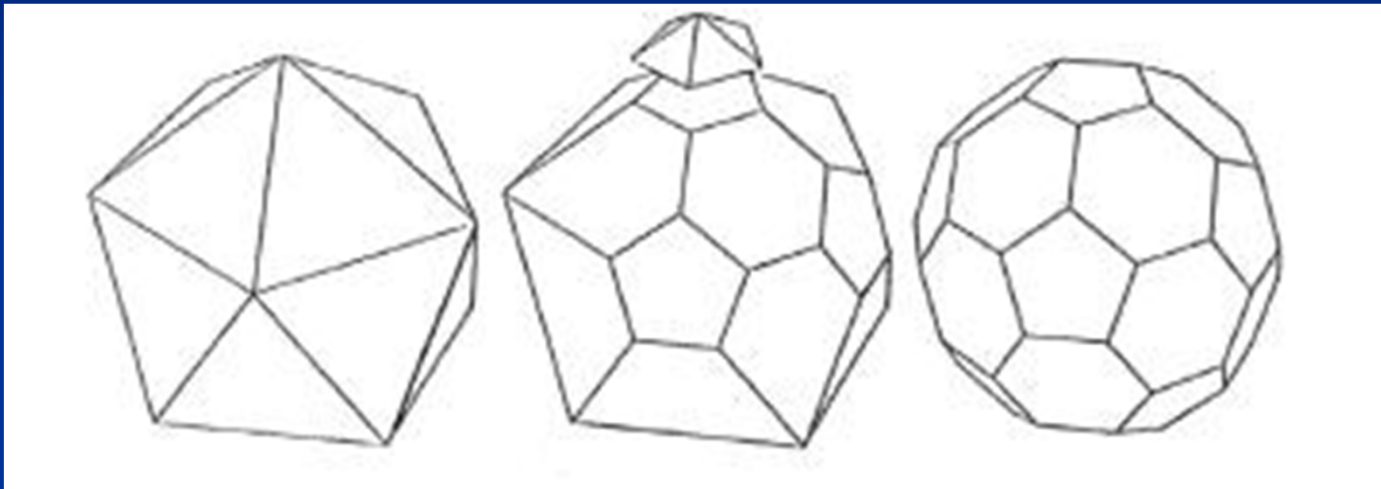
^{11}B NMR



^{11}B NMR



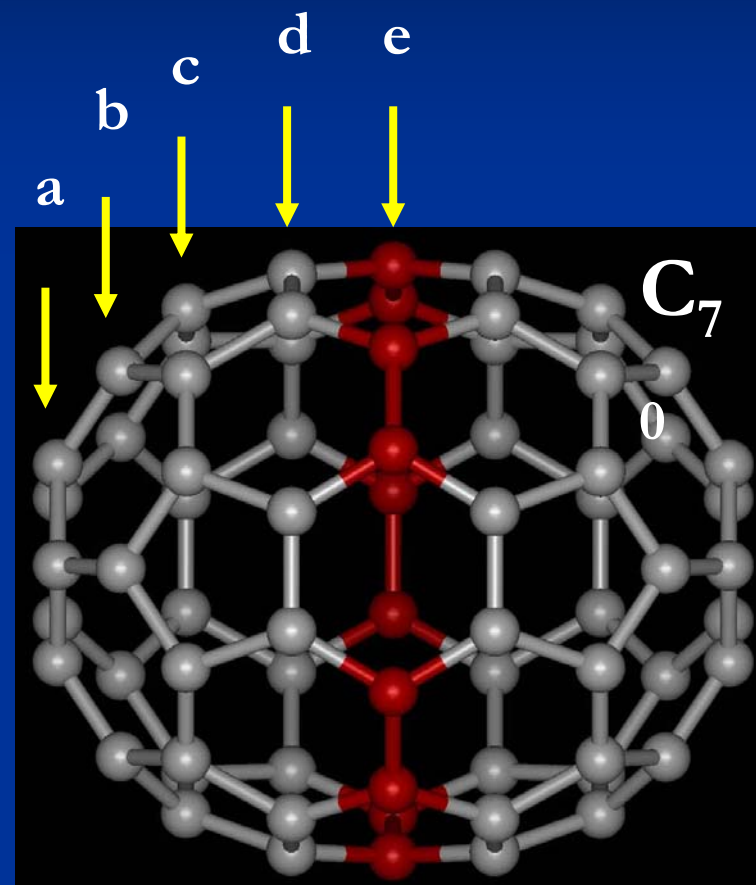
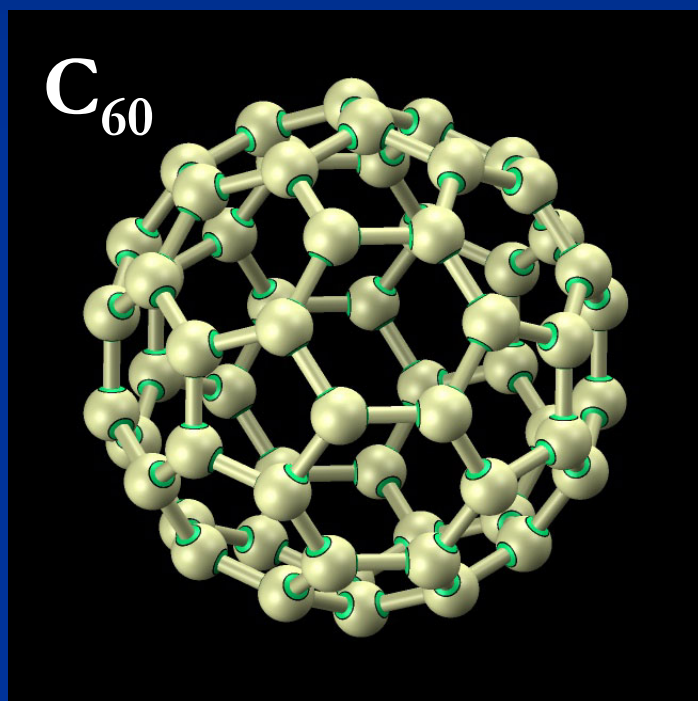
Fullerenes



Icosahedron

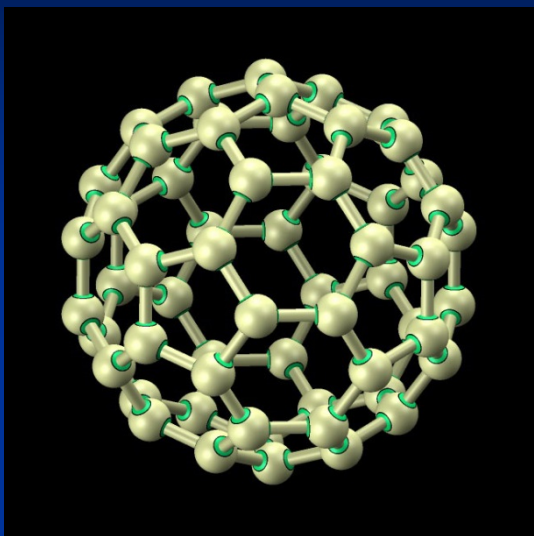
Truncated icosahedron

Chemical Shift

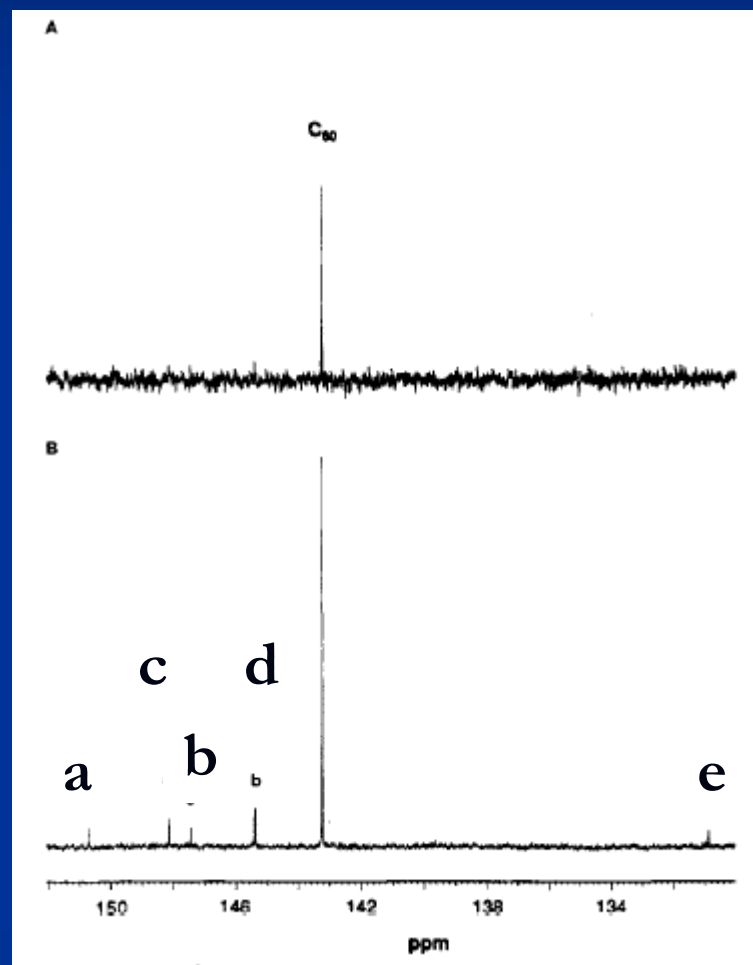


$$\delta (^{13}C) = 143 \text{ ppm}$$

Chemical Shift



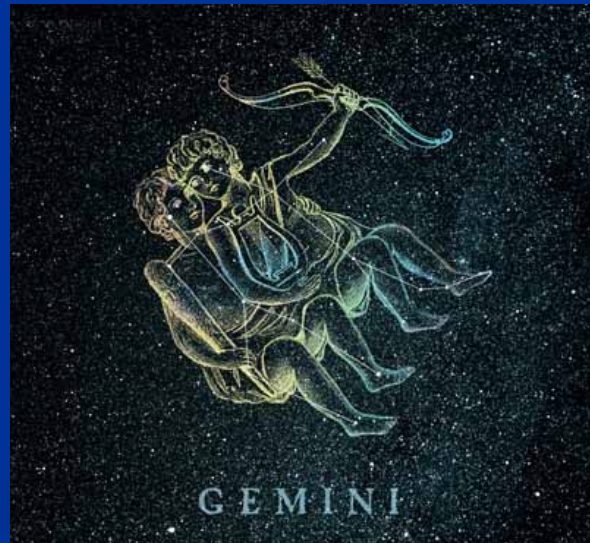
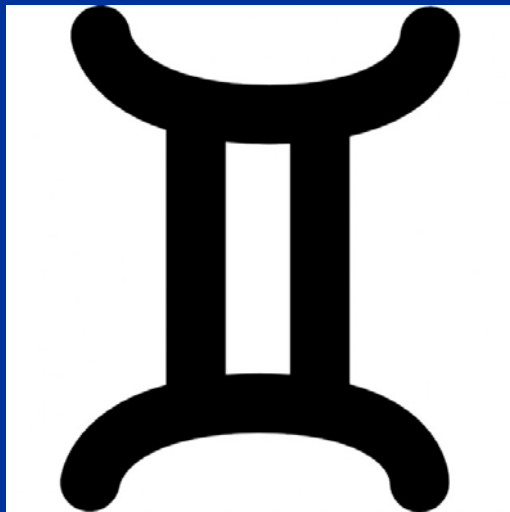
δ (^{13}C)	ppm
a	150.07
c	147.52
b	146.82
d	144.77
e	130.28



Geminal Groups

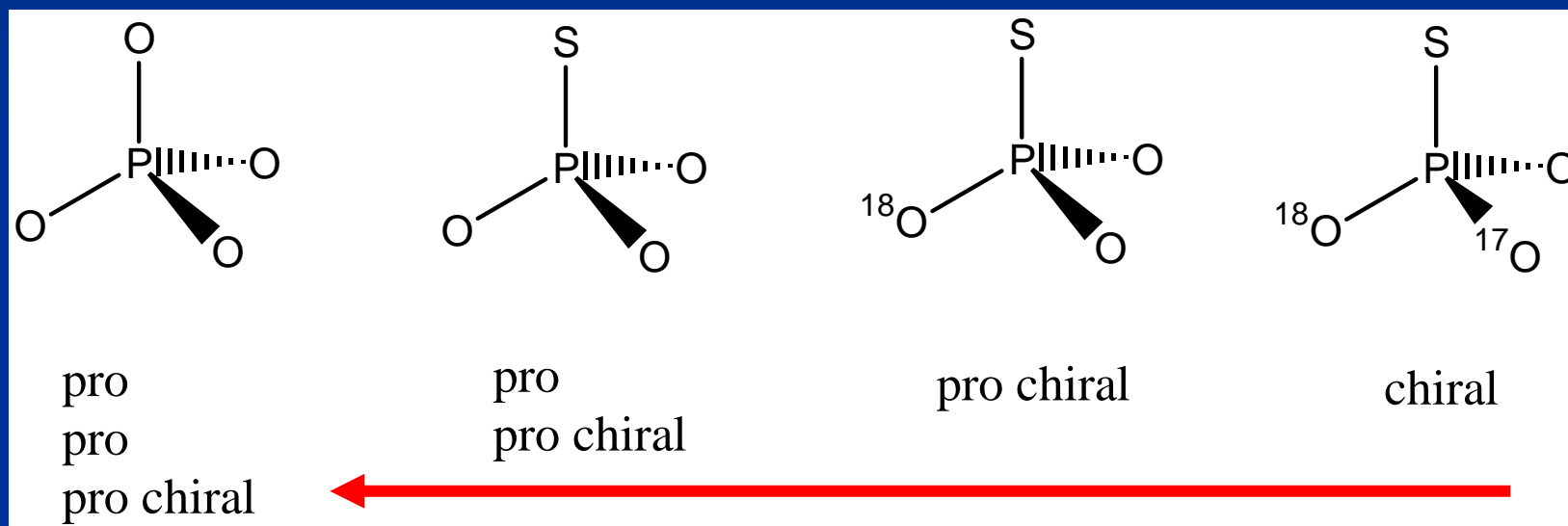
Geminal groups – paired ligands

Y-E-Y: CH_2 , $\text{C}(\text{CH}_3)_2$, CF_2 , SiMe_2 , $\text{P}(\text{CH}_3)_2$, ...



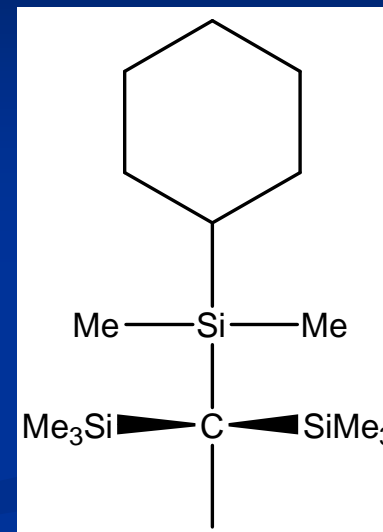
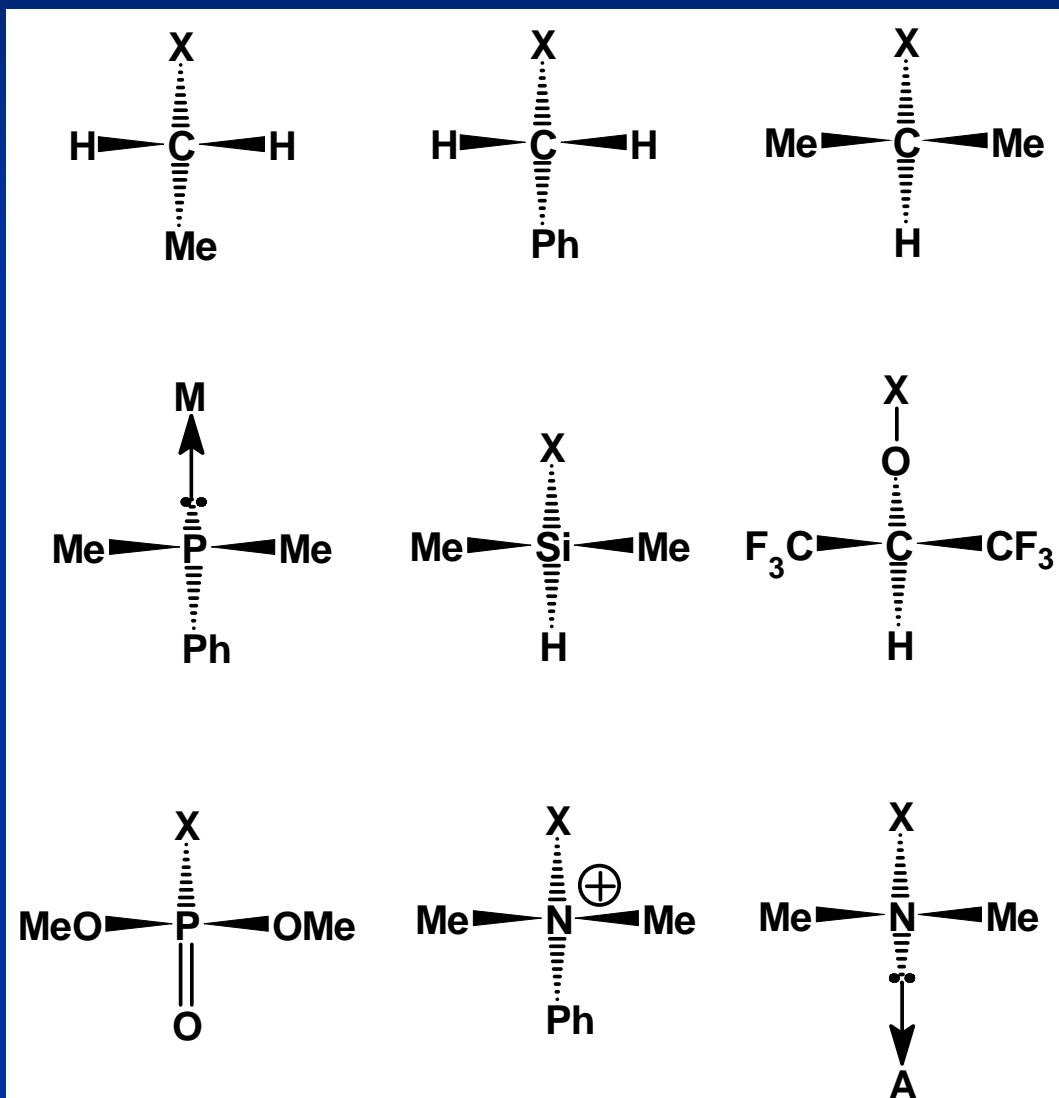
Prochiral Groups

Substitution



Symmetry

Geminal groups in Prochiral Groups

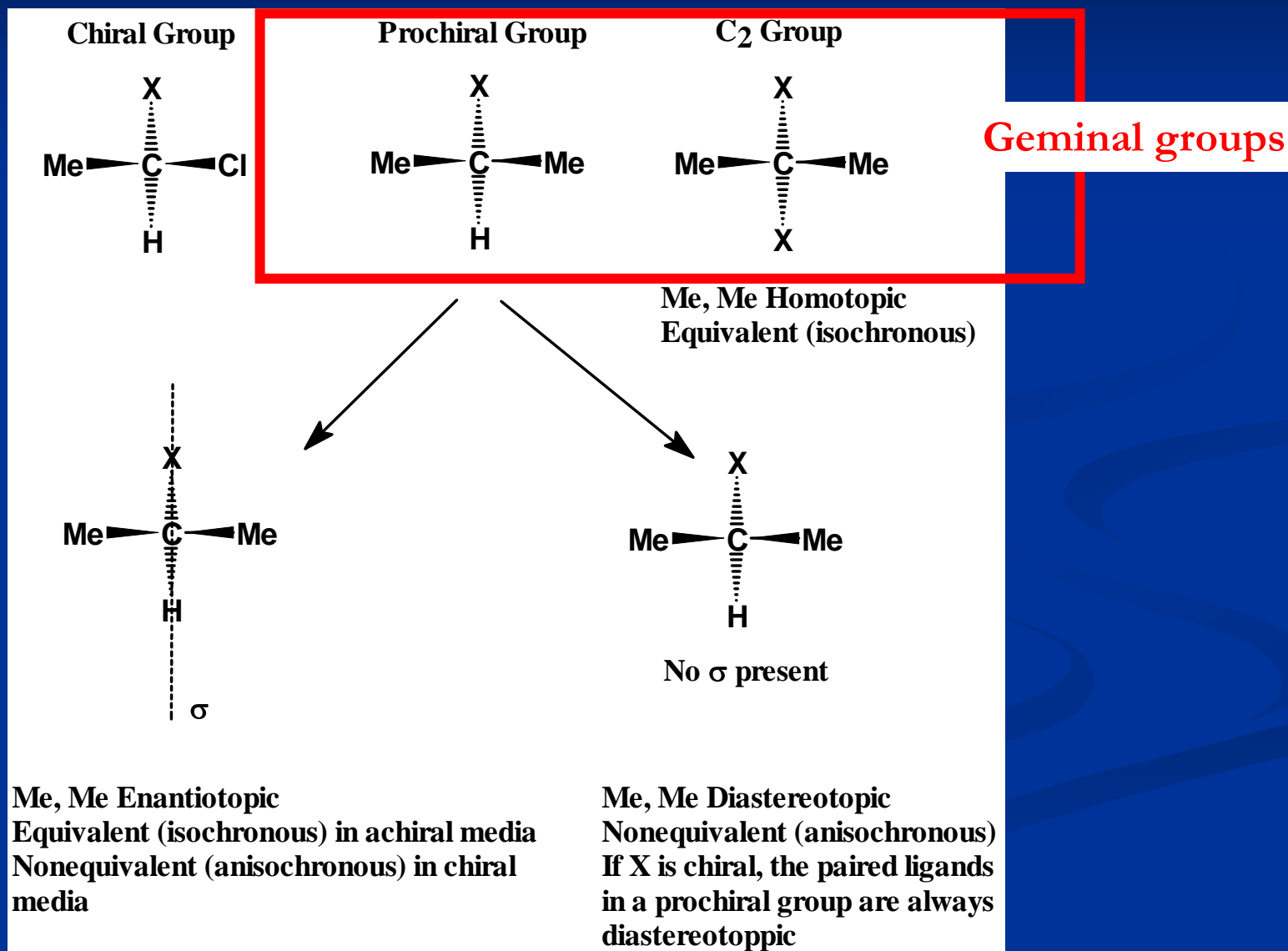


X = rest of the molecule

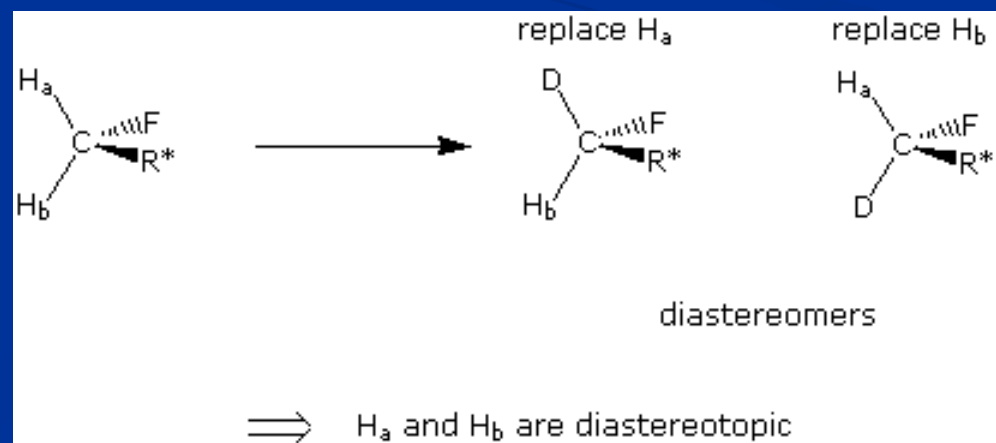
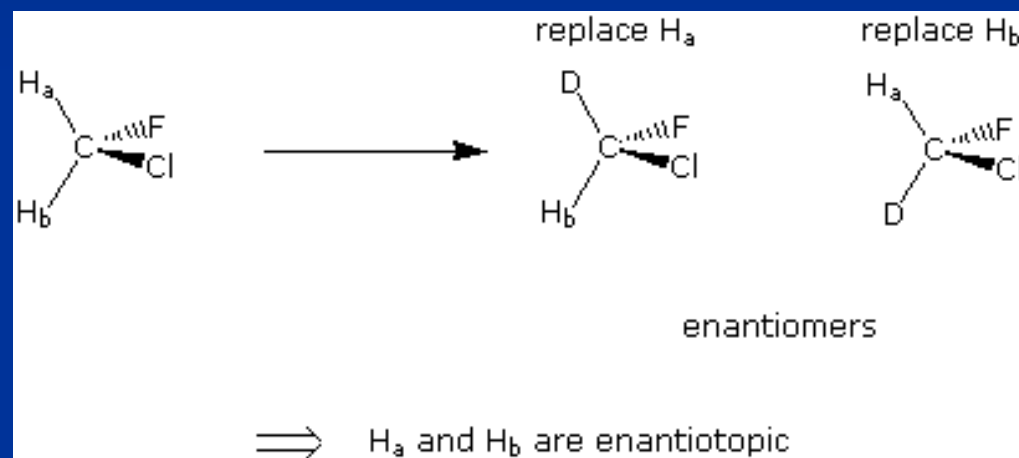
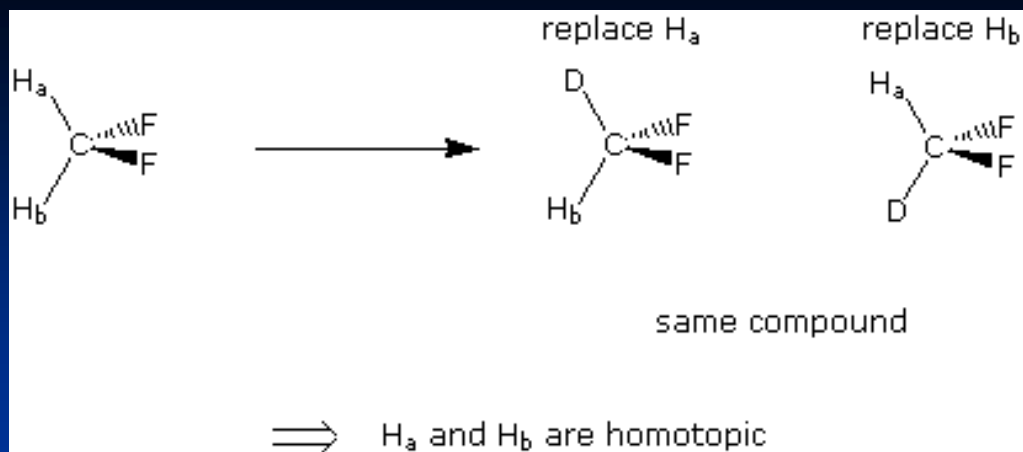
M = transition metal fragment

A = Lewis acid

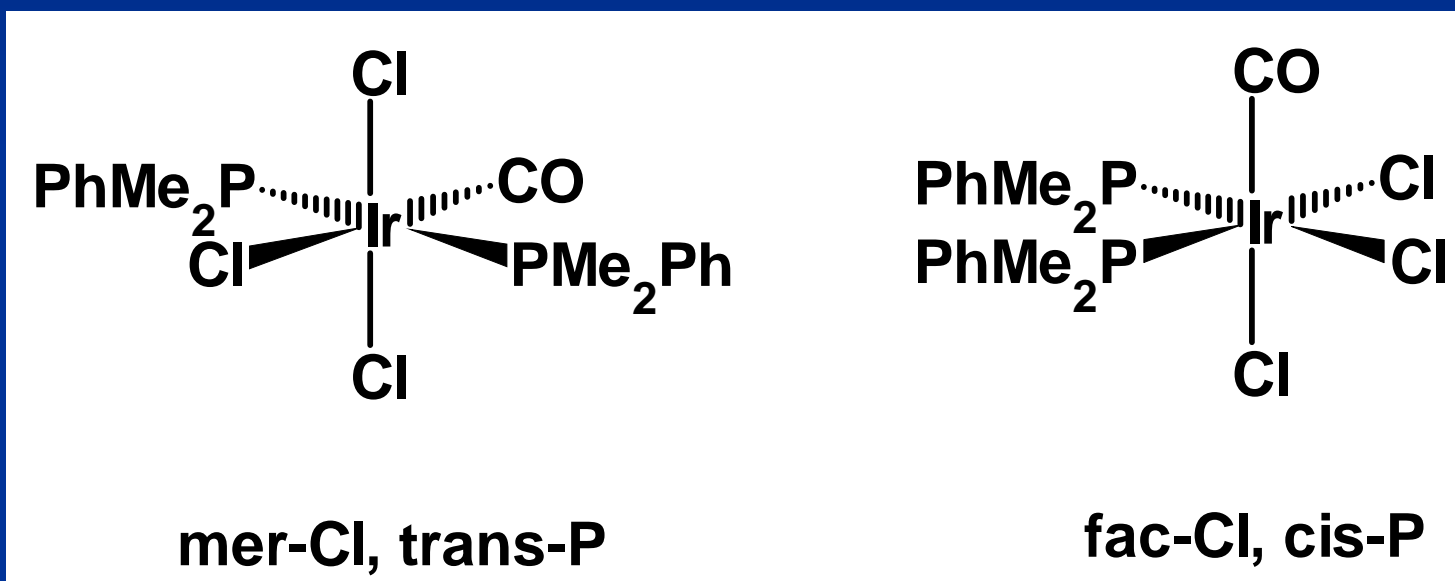
Chemical Shift Nonequivalence of Geminal Ligands in Prochiral Groups



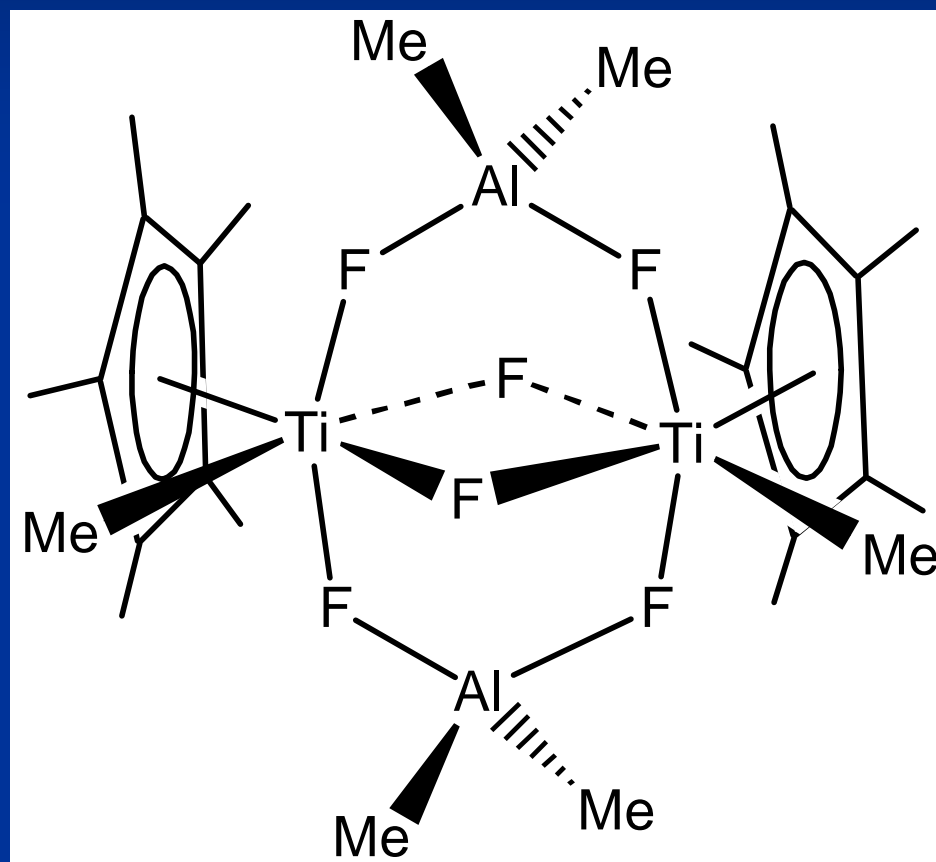
Substitution Test of Geminal Groups



Chemical Shift Nonequivalence in Prochiral Groups



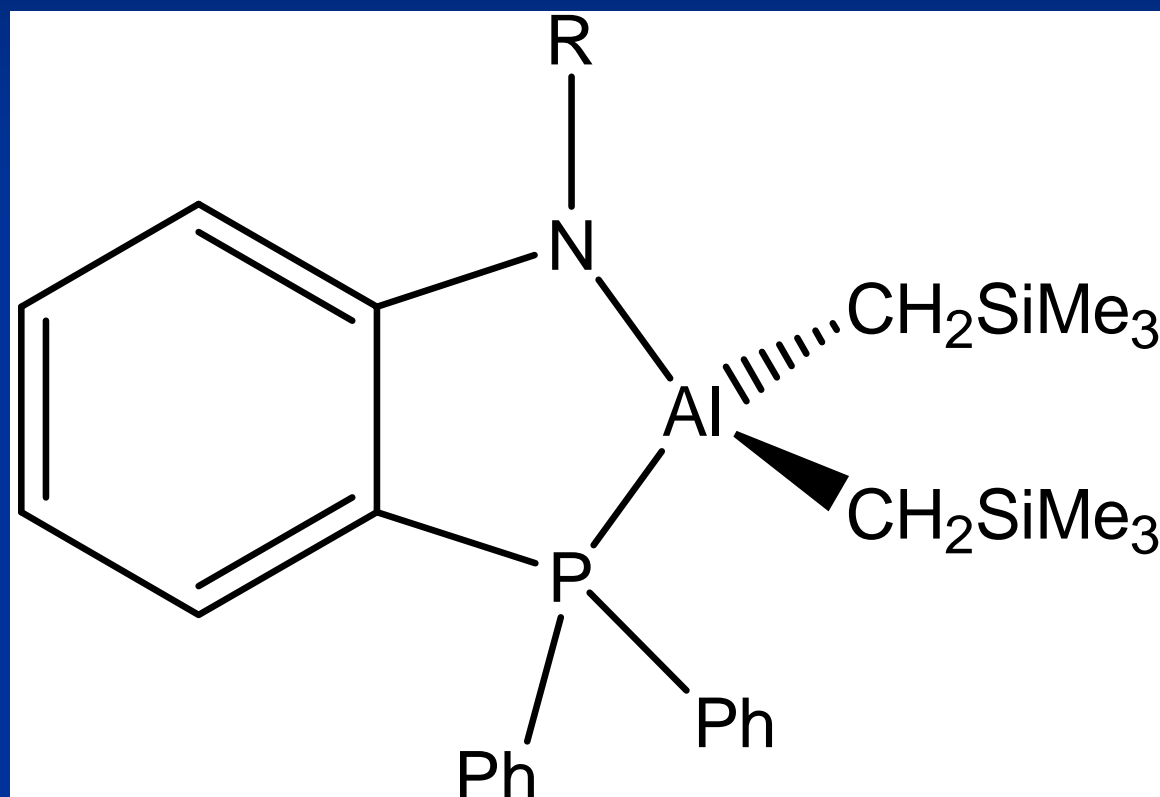
Chemical Shift Nonequivalence in Prochiral Groups



Chemical Shift Nonequivalence in Prochiral Groups

R = Me

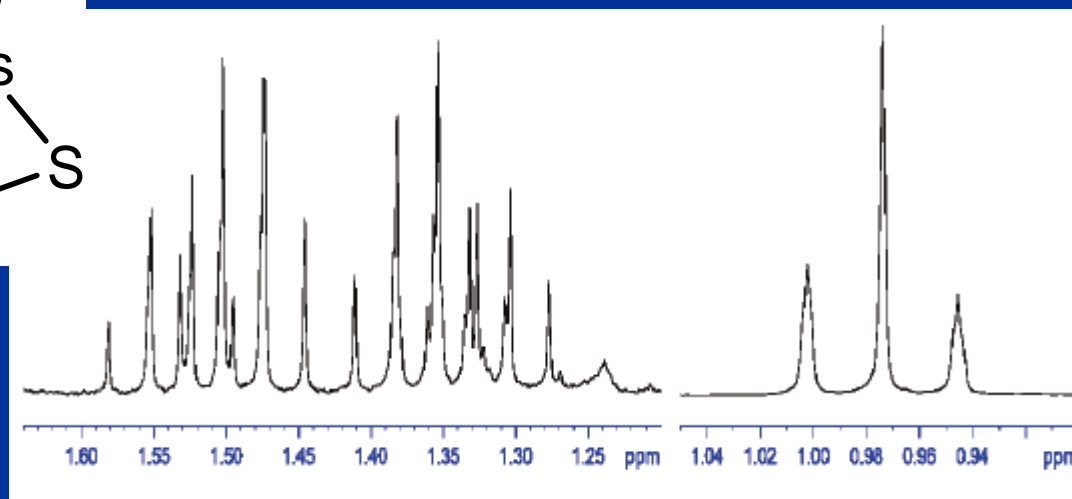
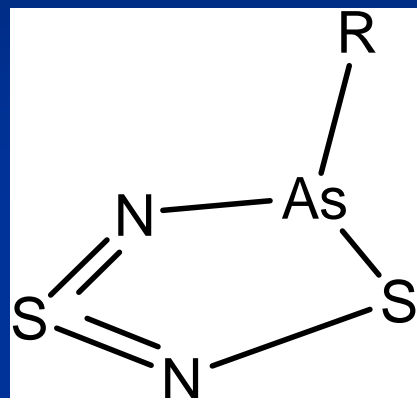
R = 2-butyl



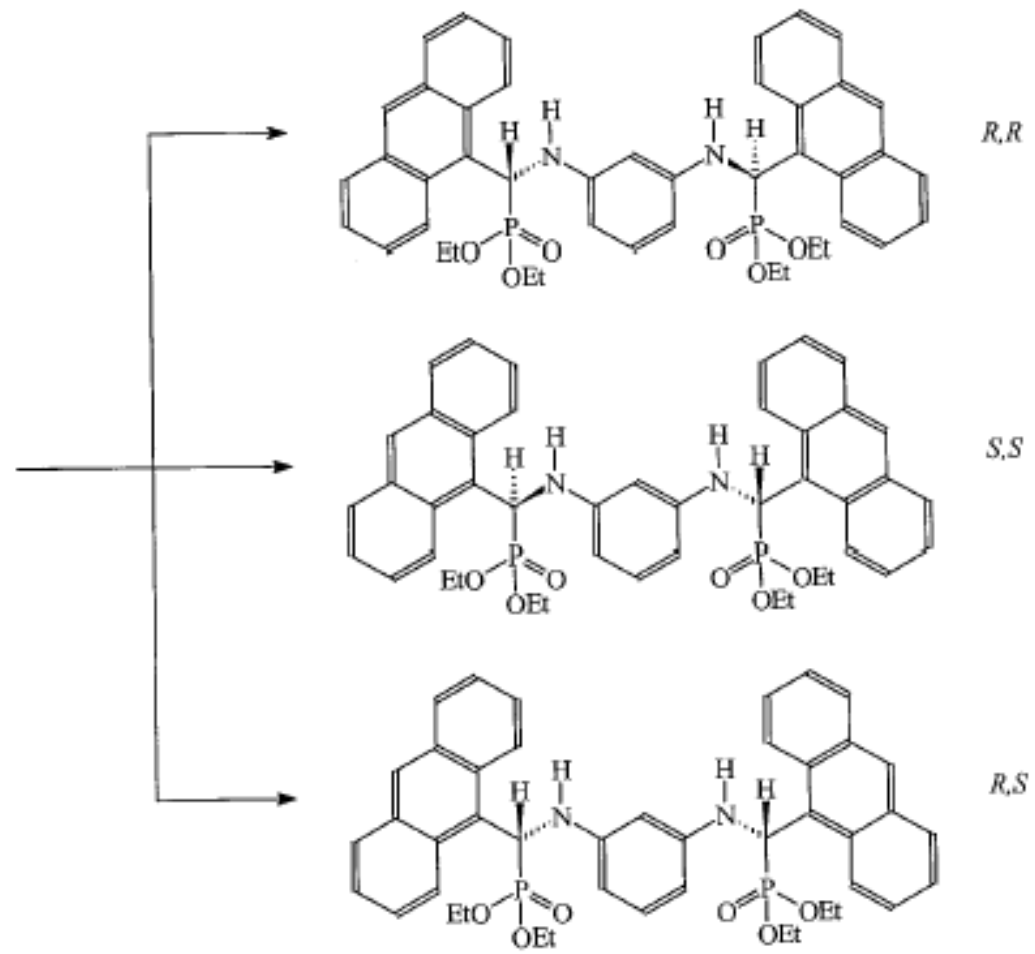
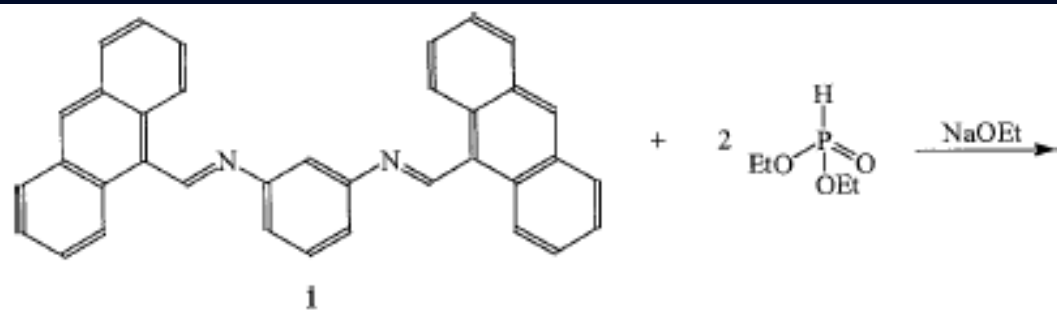
Pyramidal N - Fast inversion on N

Chemical Shift Nonequivalence in Prochiral Groups

R = Et



R = ⁱPr



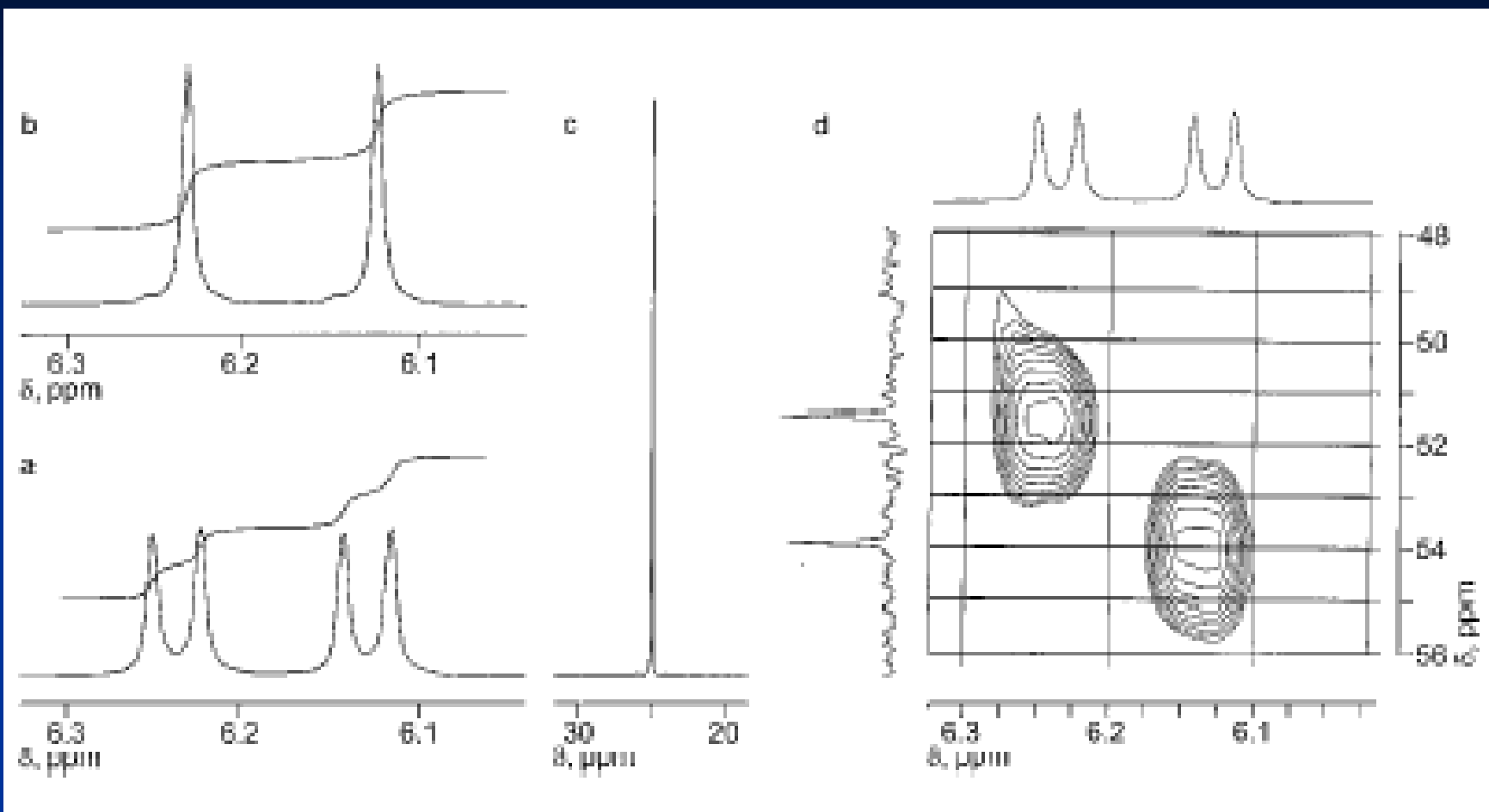
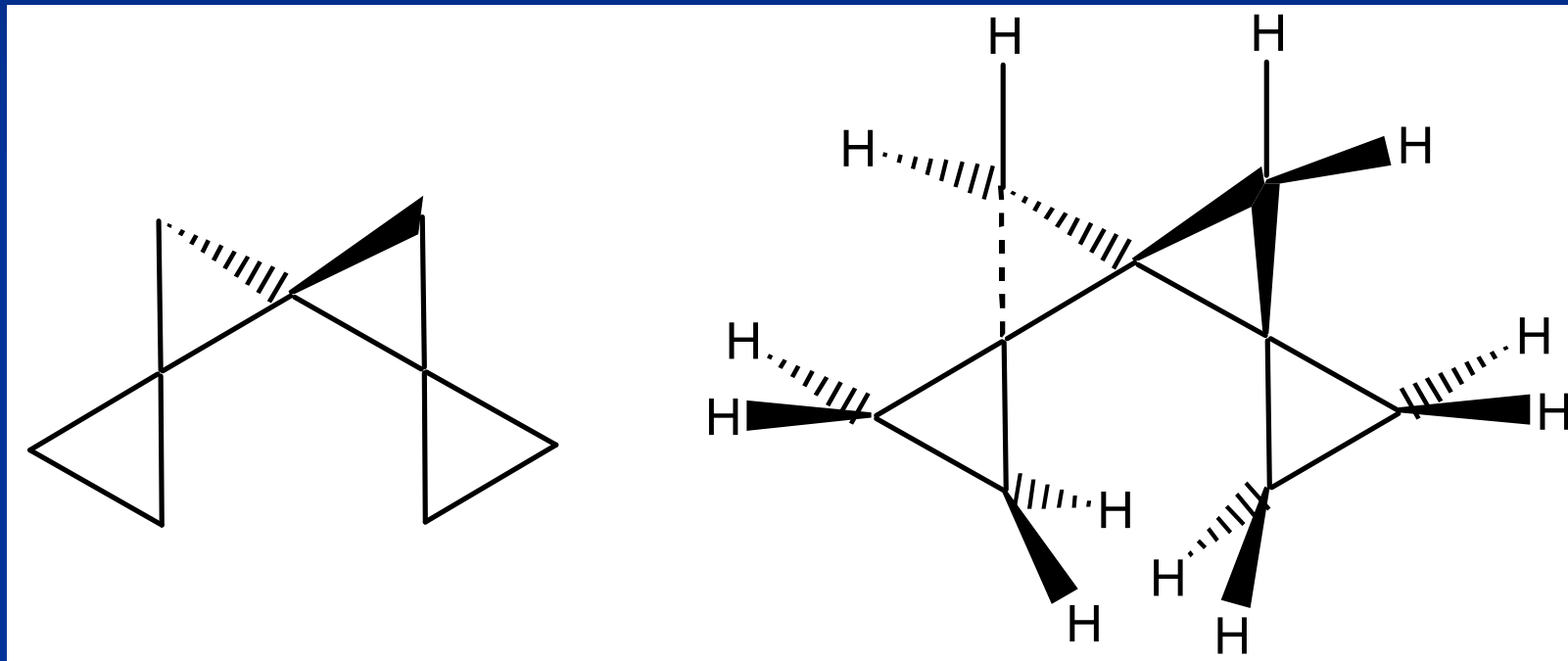
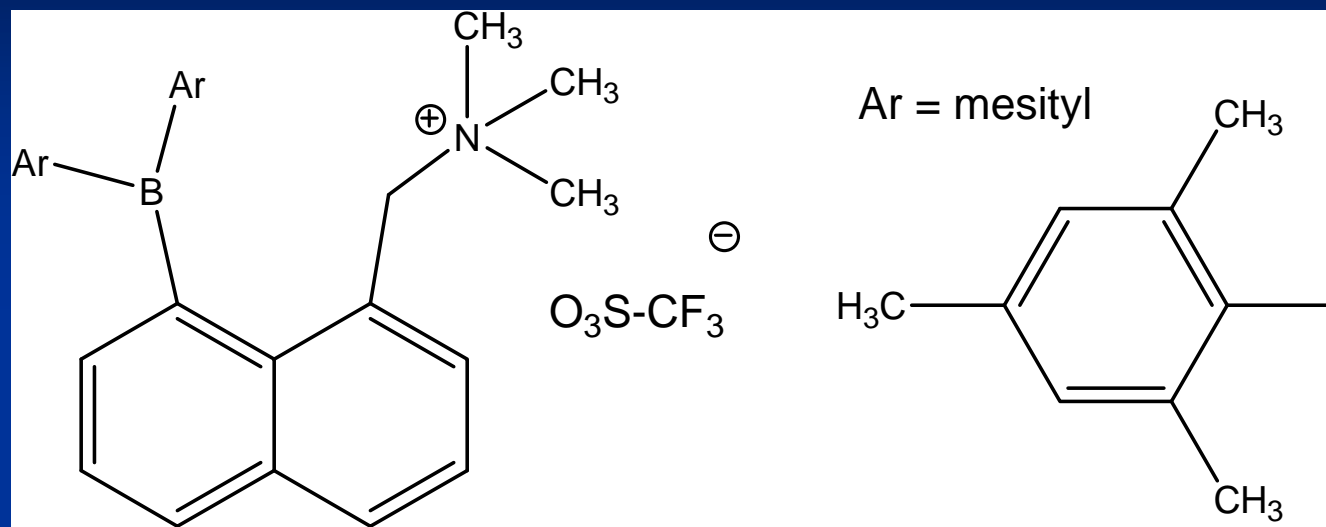


FIGURE 1 NMR spectra of CH(P) moiety of compound 2: a), b) ^1H NMR spectra in CDCl_3 and $\text{CDCl}_2, \text{D}_2\text{O}$ respectively; c) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in CDCl_3 ; d) CH COSY diagram in CDCl_3 .

[4] triangulane



Prochiral Groups



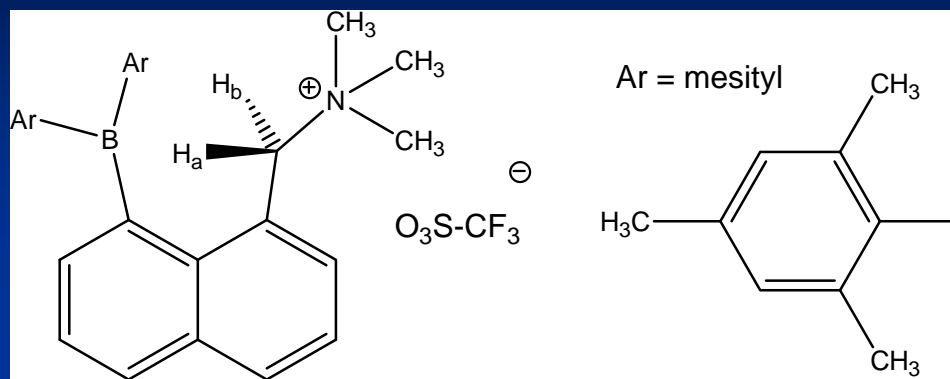
¹H NMR spectrum

6 CH aromatic signals

6 CH₃ mesityl signals

How many CH₂ signals ?

Prochiral Groups



steric congestion

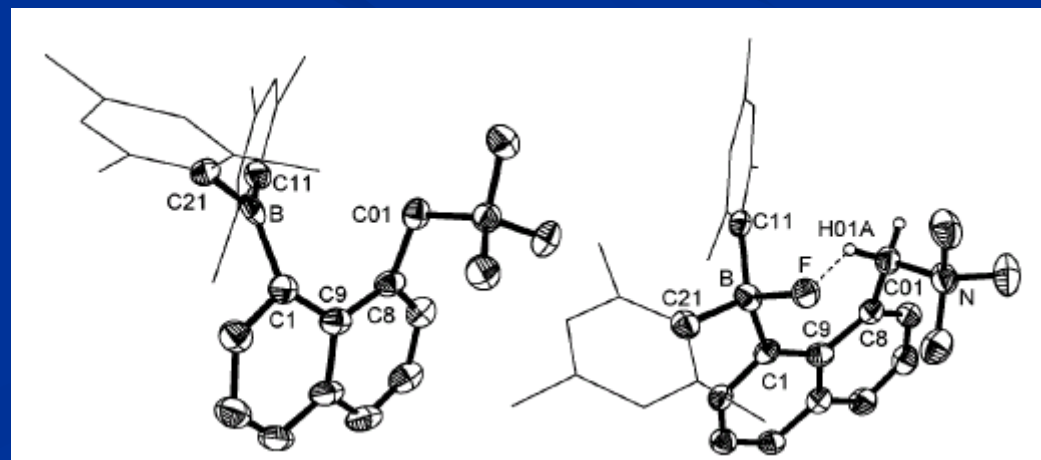
¹H NMR spectrum

The methylene hydrogens are diastereotopic

6 CH aromatic signals

two signals at 3.69 and 4.81 ppm

6 CH₃ mesityl signals



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

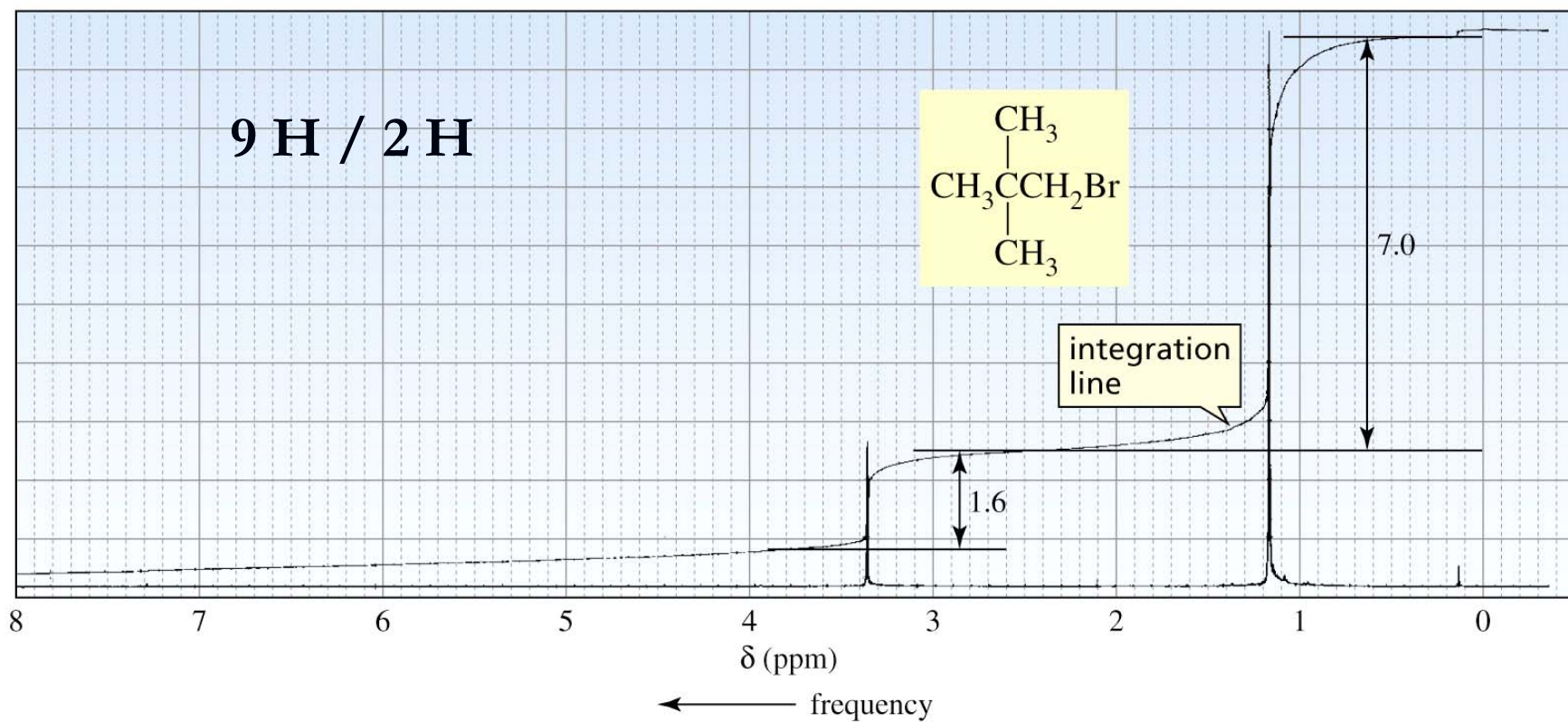
Integration

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

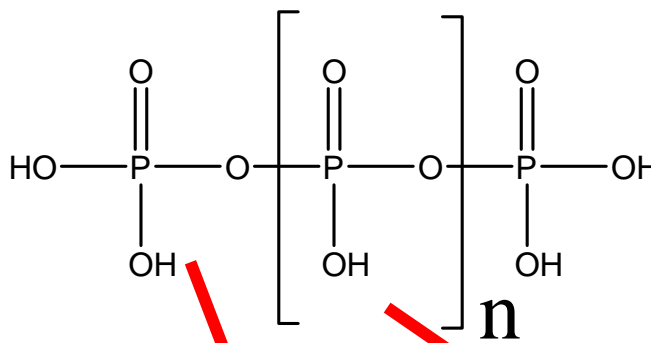
The height of each integration step is proportional to the area under a specific signal

The integration tells us the relative number of protons that give rise to each signal, not absolute number

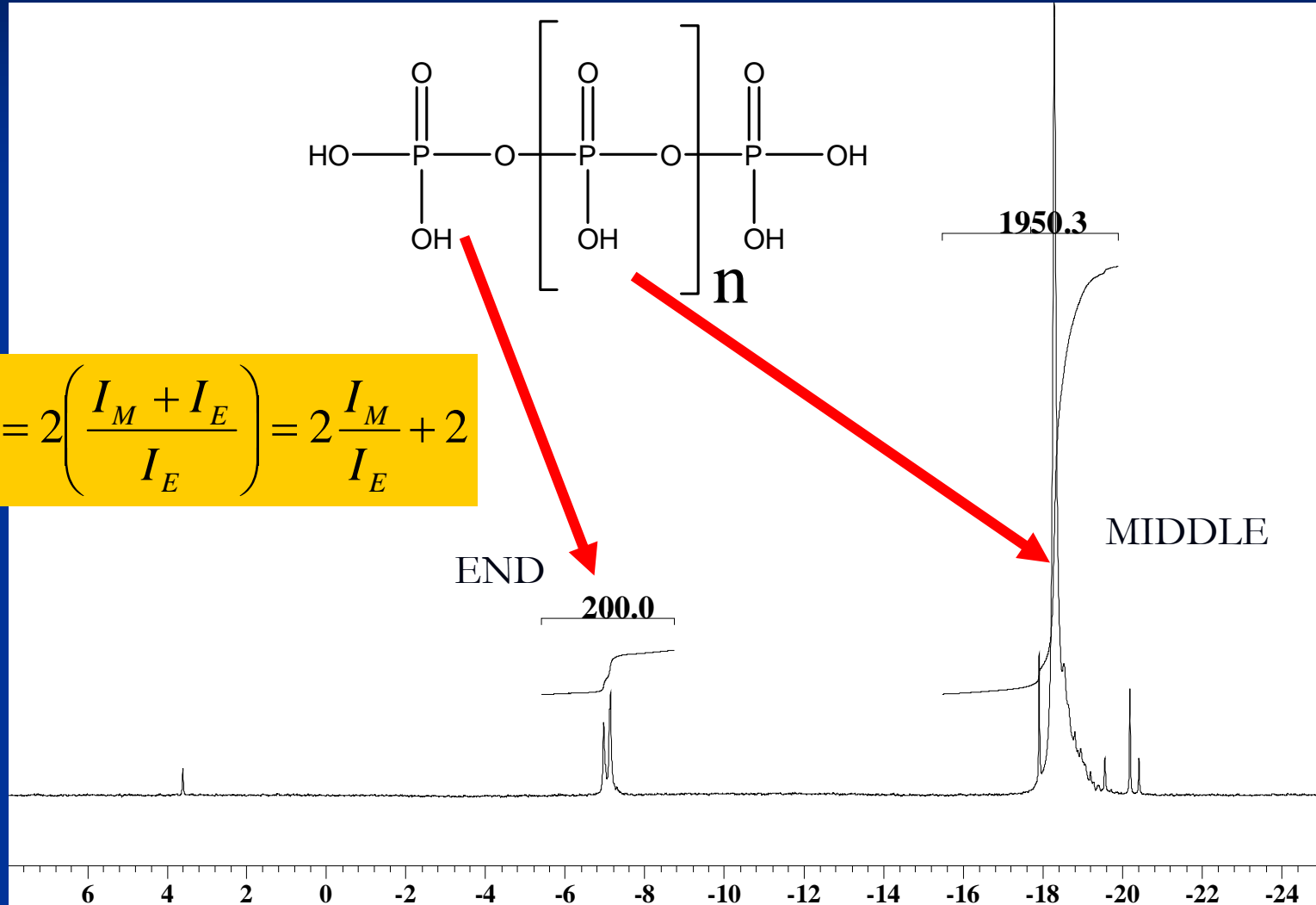
Relative Signal Intensity



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

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

Estimate their ratio

