

## Chapter 17

What is an unknown compd?  $\Rightarrow$  determination of molecular weight (M.W.)  
molecular formula

determination of the presence of certain  
functional groups

spectrometer  $\Leftarrow$  degradation to simpler compds

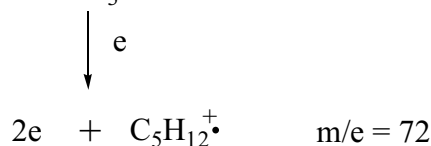
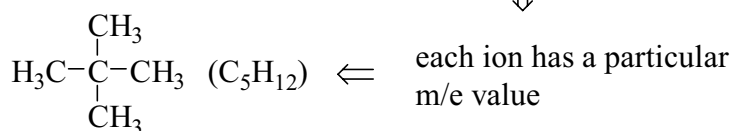
conversion into derivatives

synthesis by an unambiguous route

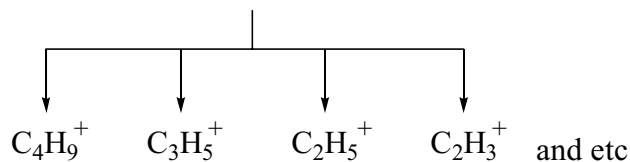
mass spectrometer

molecule  $\xrightarrow{\text{electron beam}}$  many fragments  $\Rightarrow$  some are positive ions  
(+1 for most of them)

$\Downarrow$



molecular ion



$$m/e \quad 57 \quad 41 \quad 29 \quad 27 \quad \Rightarrow \quad \text{mass spectrum}$$

$$\text{relative intensity} \quad 100 \quad 41.5 \quad 38.5 \quad 15.7 \quad \Downarrow$$

$$\uparrow$$
  
base peak

Fig 17.1

$\Downarrow$

all compds have their characteristic mass spectra  
(useful for identification)

give an exact M.W.  $\Rightarrow$  molecular formula

$\Downarrow$

the presence of certain  
structural units

the peak of highest m/e value of a mass spectrum  $\Rightarrow$   $M^+$  (molecular ion) peak ?  $\Rightarrow$  no due to isotopes

isotope peaks are useful to determine the molecular formula

ex) benzene  $M^+ : m/e 78 \rightarrow C_6H_6^+$   $\Leftarrow$  Table 17.1

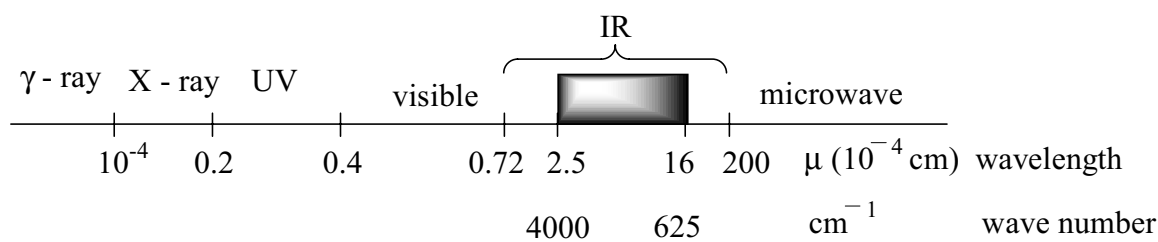
$M+1 : m/e 79 \rightarrow C_5^{13}CH_6^+$  or  $C_6H_5D^+ \rightarrow 6.75\%$

ex) Table 17.2  $M+2 : m/e 80 \rightarrow C_4^{13}C_2H_6^+$ ,  $C_5^{13}CH_5D^+$  or  $C_6H_4D_2 \rightarrow 0.18\%$

from the study of mass spectrum of known compd  $\Rightarrow$  preferential formation of more stable carbocations  
 $\Rightarrow$  elimination of small stable molecules ( $H_2O$ ,  $NH_3$ ,  $CO$  etc)  
 $\Rightarrow$  rearrangement toward more stable ions

$\Downarrow$

the accumulated knowledge is applied to deducing the structure of an unknown compd.



$\Downarrow$  electronic

$\Downarrow$  vibrational  $\left\{ \begin{array}{l} \text{stretching} \\ \text{bending} \end{array} \right.$

$\Downarrow$

each compd has its own specific spectrum  $\Leftarrow$  IR spectrum

(finger-print region :  $1300 \sim 650 \text{ cm}^{-1}$ )

$\Downarrow$

absorbance ( $\log 1/T$ ) or transmittance ( $I/I_0$ )

wavelength or wave number

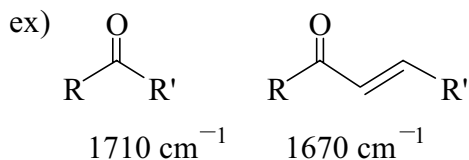
characteristic absorption band :

O-H	stretch	$3200 \sim 3600 \text{ cm}^{-1}$
C=O	stretch	$1710 \text{ cm}^{-1}$ (ketone)
C $\equiv$ N		$2250 \text{ cm}^{-1}$
CH <sub>2</sub> -H	stretch	$2950 \sim 2850 \text{ cm}^{-1}$
	bending	$1450 \sim 1375 \text{ cm}^{-1}$

Fig 17.2

not simple to interpret IR spectrum : overtones, combination tones  
 shifted by various structural features  
 (conjugation, inductive effect, angle strain  
 steric strain, resonance effect etc)

Table 17.3 ←



IR

C-C stretch

aromatic : 1500~1600

sp<sup>2</sup> : 1650 (~1600 by conjugation) } may not appear  
 due to Δμ = 0

sp : 2100

C-H stretch

sp<sup>3</sup> : 2800~3000

sp<sup>2</sup>, aromatic : 3000~3100

sp : 3300

C-H bending

1370 CH<sub>3</sub>

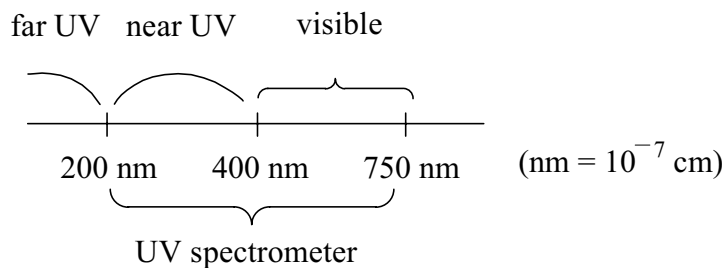
1450 CH<sub>2</sub>, CH<sub>3</sub>

out of plane (stronger) : 1000~650cm<sup>-1</sup>

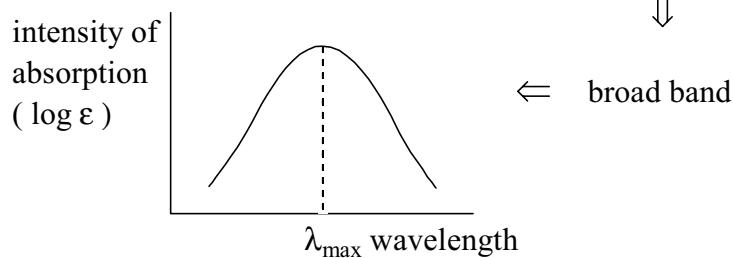
in plane : 1000~1100cm<sup>-1</sup>

	990	970	910	890	700
RCH=CH <sub>2</sub>	✓		✓		
t-RCH=CHR		✓			
R <sub>2</sub> C=CH <sub>2</sub>				✓	
c-RCH=CHR					✓

	830	780	750	700
p-di	✓			
m-di		✓		✓
o-di			✓	
mono			✓	✓

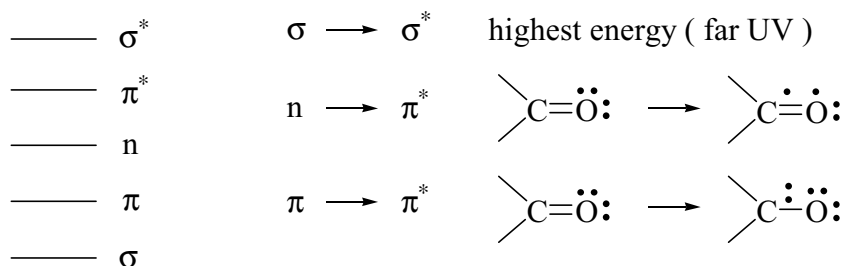


↓  
 electronic excitation  $\Rightarrow$  accompanied by vibrational & rotational excitation



(  $\log I_0/I = A = \epsilon cl$  )

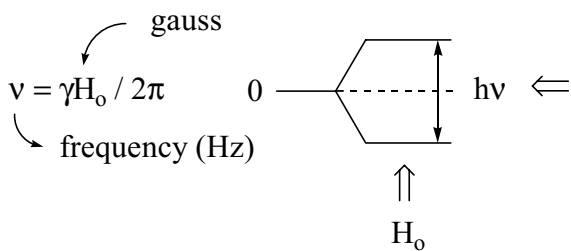
↓    ↓  
 absorbance    molar extinction coefficient



$\pi \rightarrow \pi^*$     ethylene : far UV  
 more conjugation lowers the transition energy

resonance stabilizes the excited state more than the ground state  $\Leftarrow$  absorption moves to longer wavelengths

proton : spinning charged particle  $\Rightarrow$  generate magnetic moment



$\Downarrow$   
 a proton in an external magnetic field  
 has two energy states  
 ( $I = 1/2, 2I + 1$  states)

$H_0 = 14092 \text{ gauss} \longrightarrow \nu = 60 \text{ MHz}$   
 ( $\text{sec}^{-1}$ )

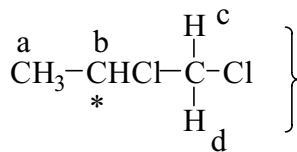
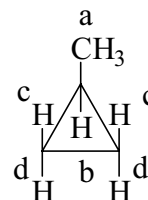
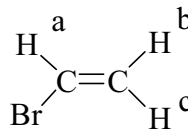
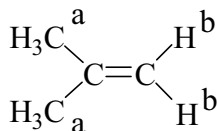
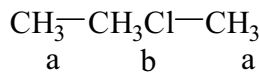
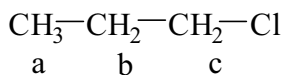
$\Downarrow$   
 NMR (PMR, CMR)

$\Downarrow$   
 protons under the same environment (equivalent protons) : feel the same field strength

protons under different environments : feel different field strength

$\Downarrow$   
 need different frequency for resonance

$\Downarrow$   
 need the same frequency for resonance



c, d are diastereotopic  $\Rightarrow$  different

enantiotopic  $\Rightarrow$  identical

different kinds of protons have  
 different electronic environment  $\Rightarrow$

electrons in a molecule circulate and  
 generate secondary magnetic fields in a  
 magnetic field (induced magnetic field)

circulation of electrons about the proton itself  $\Rightarrow$  generate an induced field opposed to the applied field  $\Rightarrow$  the proton felt a diminished field (the proton is shielded)

$\Downarrow$

it requires a higher applied field strength (or a lower radiofrequency) for resonance  $\Leftarrow$  the proton with more electron density is more shielded

circulation of electrons about nearby nuclei  $\Rightarrow$  generate an induced field which can oppose or reinforce the applied field at the proton  $\Rightarrow$  depends on the proton's location ( Fig 17.9 )

$\Downarrow$

reference point  $\Leftarrow$  chemical shift  $\Leftarrow$  ( upfield shift  $\leftarrow$  shielding  
 Me<sub>4</sub>Si :  $\delta = 0.00\text{ppm}$   $\leftarrow$  downfield shift  $\leftarrow$  deshielding

( induced secondary field  $\propto$  applied field)

for 60 MHz

$$\delta = \text{observed shift (Hz)} \times 10^6 / 60 \times 10^6 \text{ (Hz)}$$

$\Downarrow$

Table 17.4

R-CH <sub>3</sub>	$\delta$ 0.9	CH <sub>3</sub> Cl	$\delta$ 3.0	CH <sub>3</sub> -C-Cl	$\delta$ 1.5
R <sub>2</sub> CH <sub>2</sub>	$\delta$ 1.3	RCH <sub>2</sub> Cl	$\delta$ 3.4	RCH <sub>2</sub> -C-Cl	$\delta$ 1.7
R <sub>3</sub> CH	$\delta$ 1.5	R <sub>2</sub> CHCl	$\delta$ 4.0	R <sub>2</sub> CH-C-Cl	$\delta$ 1.6
Ar-H	$\delta$ 6 ~ 8.5				

$\Downarrow$

Fig 17.10

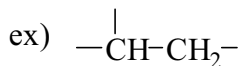
$\Downarrow$

the ratio of the peak areas = the ratio of the proton numbers

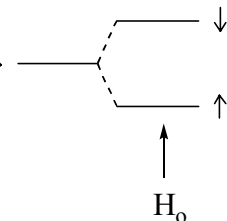
$\Downarrow$

Fig 17.11

Fig 17.13  $\Rightarrow$  splitting of NMR signals (multiplicity)  $\Rightarrow$  caused by spin - spin coupling



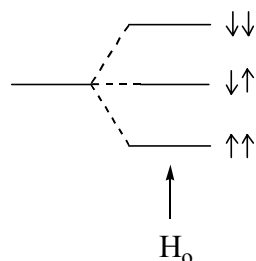
a secondary proton feels slightly increased or decreased magnetic field by the spin of the neighboring tertiary proton.



for half the molecules, absorption is shifted slightly downfield.

for the other half of the molecules, absorption is shifted slightly upfield.

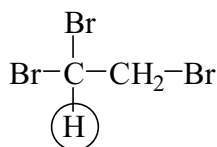
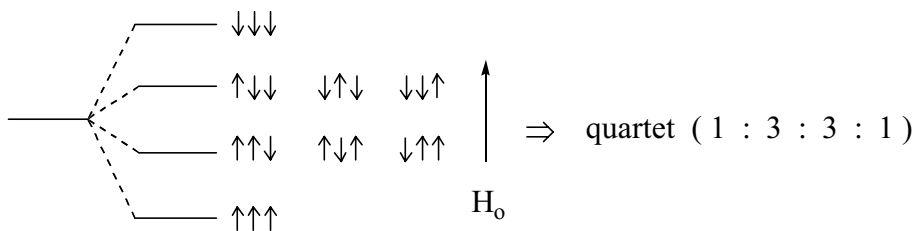
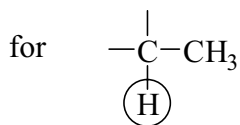
for the tertiary proton  $\Rightarrow$



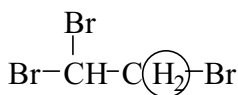
triplet with relative peak intensities 1 : 2 : 1

$\downarrow$   
the signal is split into two peaks with equal peak intensities. (doublet)

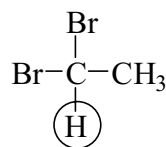
Fig 17.16  
( J = coupling constant)



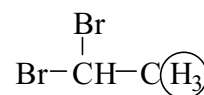
downfield triplet



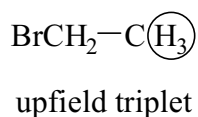
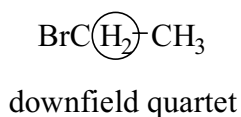
upfield doublet



downfield quartet

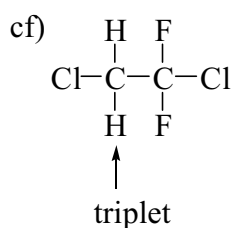
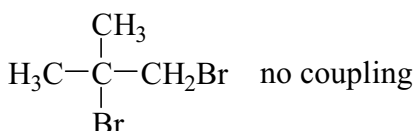
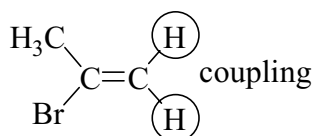
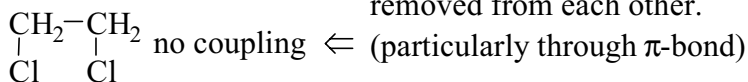
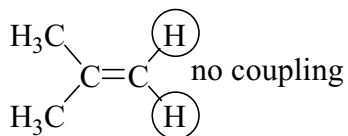


upfield doublet



$\Rightarrow$  Fig on p 616

Which protons in a molecule  $\Rightarrow$  nonequivalent neighboring protons  $\Rightarrow$  most commonly protons on adjacent carbon. sometimes protons further removed from each other. (particularly through  $\pi$ -bond)



p 618, 619

coupling constant  $J$  : the effectiveness of spin-spin coupling  $\Rightarrow$  independent of applied magnetic field

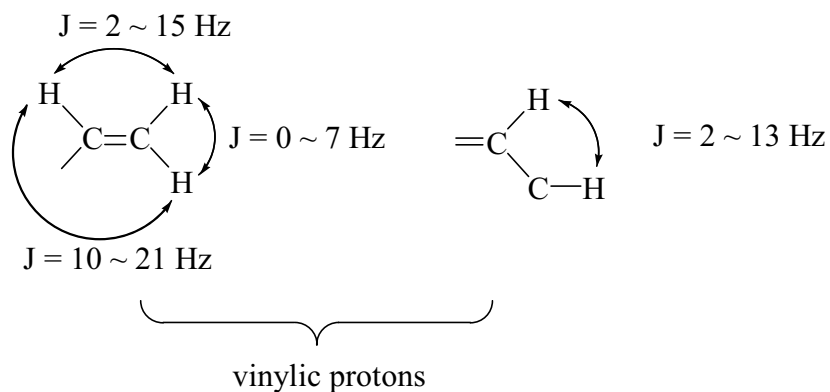
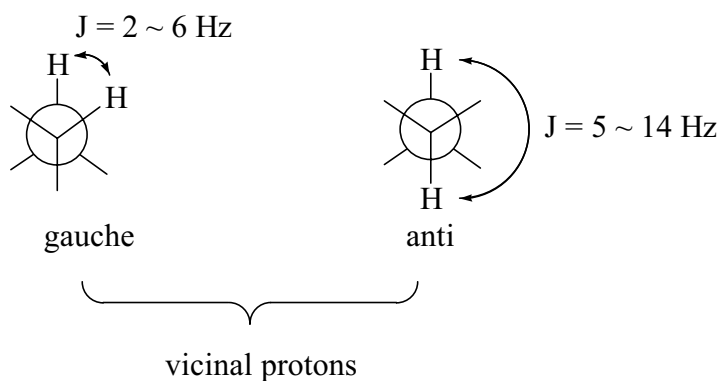
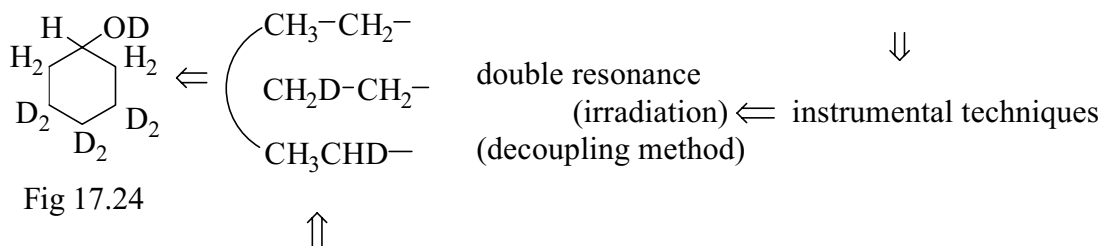
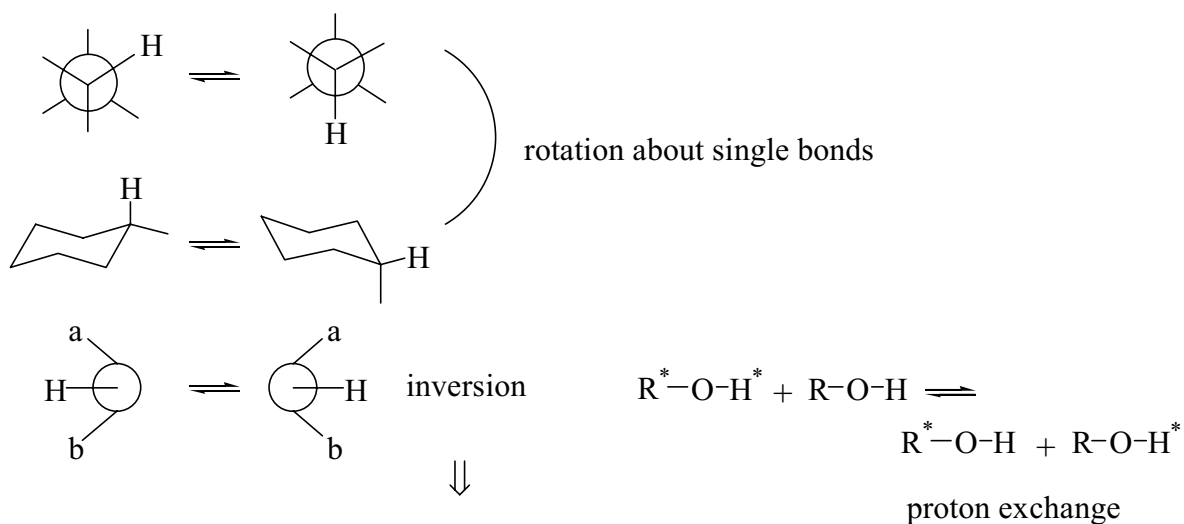


Fig 17. 18-17.22

Fig 17-23 : impossible to do complete analysis  $\Rightarrow$  with other kinds of evidence  
 NMR is useful to determine the right structure.



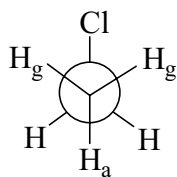
absorb at a much higher field  $\Leftarrow$  ( much smaller magnetic moment  $\Leftarrow$  deuterium  $\Leftarrow$  chemical method weak coupling labeling)



a given proton changes electronic and protonic environment, which can change its chemical shift and its coupling with other protons.

Which does NMR spectrometer see, the proton in each environment or in an average of all of them?

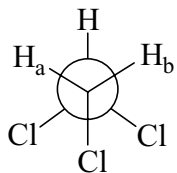
depending on the temperature



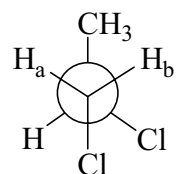
two gauche protons  
one anti protons )  $\Rightarrow$  not equivalent  $\Rightarrow$  single NMR signal



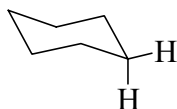
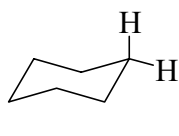
NMR spectrometer sees an average environment by rotation about the single bond.



$H_a$  and  $H_b$  have an identical average environment.



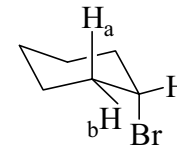
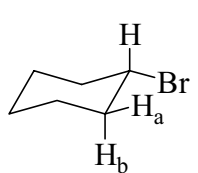
$H_a$  and  $H_b$  are not identical.



two kinds of protons { 6-equatorial  
6-axial



a single NMR signal : in an identical average environment



$H_a$  and  $H_b$  have different environments  
the stabilities of the two conformations are different



their populations are different

lowering temperature slows down rotation about single bonds



$\longrightarrow$  lower T

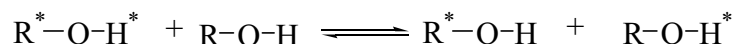
R-O-H : shifted downfield by hydrogen bonding



chemical shift depends on the degree of hydrogen bonding (1~5ppm)



concn, temp, solvents



proton exchange is so fast  $\Rightarrow$  cannot see nearby protons in their various combinations of spin alignments.



sees a single average alignment

$^{13}\text{C}$  : 1.1% natural abundance  $\Rightarrow$  can couple with nearby  $^{13}\text{C}$   $\Rightarrow$   $^{13}\text{C} - ^{13}\text{C}$  0.01%

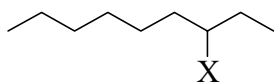
with protons



no coupling



decoupled by instrument



1 BS = 7.5 ppm

$\text{sp}^3$  :  $(\alpha + \beta) \times 7.5$  ppm

X :  $\alpha$ -effect  $\beta$ -effect  $\Rightarrow$  downfield

$\gamma$ -effect  $\Rightarrow$  upfield

$\alpha$ -effect

premium method

C-X

F : + 8 BS

O : + 5 BS

Cl, N : + 3 BS

Br : + 2 ~ 3 BS

C=C : + 1/2 BS

SN method

C- $\frac{3}{2}$ -X

NO<sub>2</sub> : + 8.5 BS

C=O : + 4 BS

COOR : + 2.6 BS

C $\equiv$ C : + 2/3 BS

C $\equiv$ N : 0 BS



( ~ 120 ppm)

$\beta$ -effect

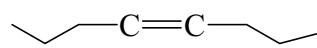
1 ~ 0 BS

← electronegative

$\gamma$ -effect ( steric effect )

O  $sp^3$  : -1 BS      O  $sp^2$  : -2/3 BS      CH<sub>3</sub>: -1/3 BS  
Cl


$sp^2$

 reference point : 121.5ppm

$$\delta = 121.5 + 7.5 [(\alpha + \beta) - \alpha']$$

cis :  $\gamma$ -effect = -2/3 BS

$sp$       reference point : 72.5ppm

 : 125~130 ppm

$$\delta = 72.5 + 7.5 [ (\alpha) + 2/3(\beta) - 2/3(\alpha') ]$$

ESR (electron spin resonance)