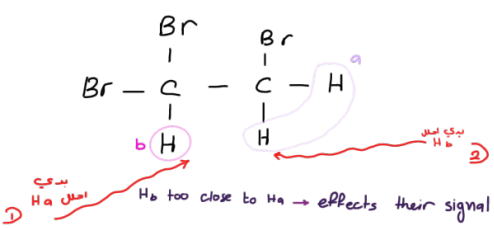
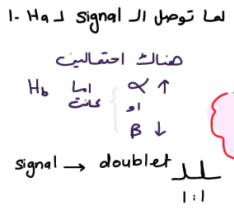
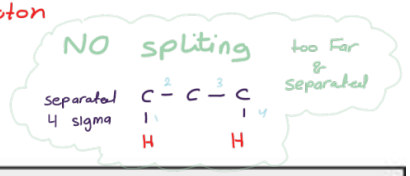


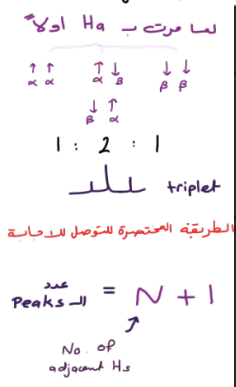
The *N* + 1 Rule



If a signal is split by *N* equivalent protons, it is split into *N* + 1 peaks.

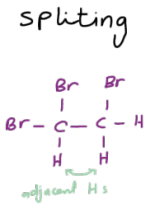
a proton will split its neighboring proton when they're on adjacent carbons & separated by 3 sigma bond





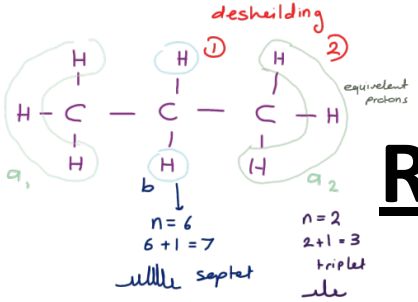
Relative Peak Intensities of Symmetric Multiplets

Number of Equivalent Protons Causing Splitting	*Number of Peaks (multiplicity)*	*Area Ratios (Pascal's triangle)*
0	1 (singlet)	1
1	2(doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

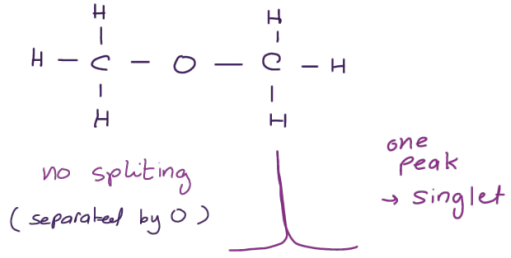


ارتفاع الـ Peak يتناسب مع الاحتمال

1 : 2 : 1
triplet



Range of Magnetic Coupling



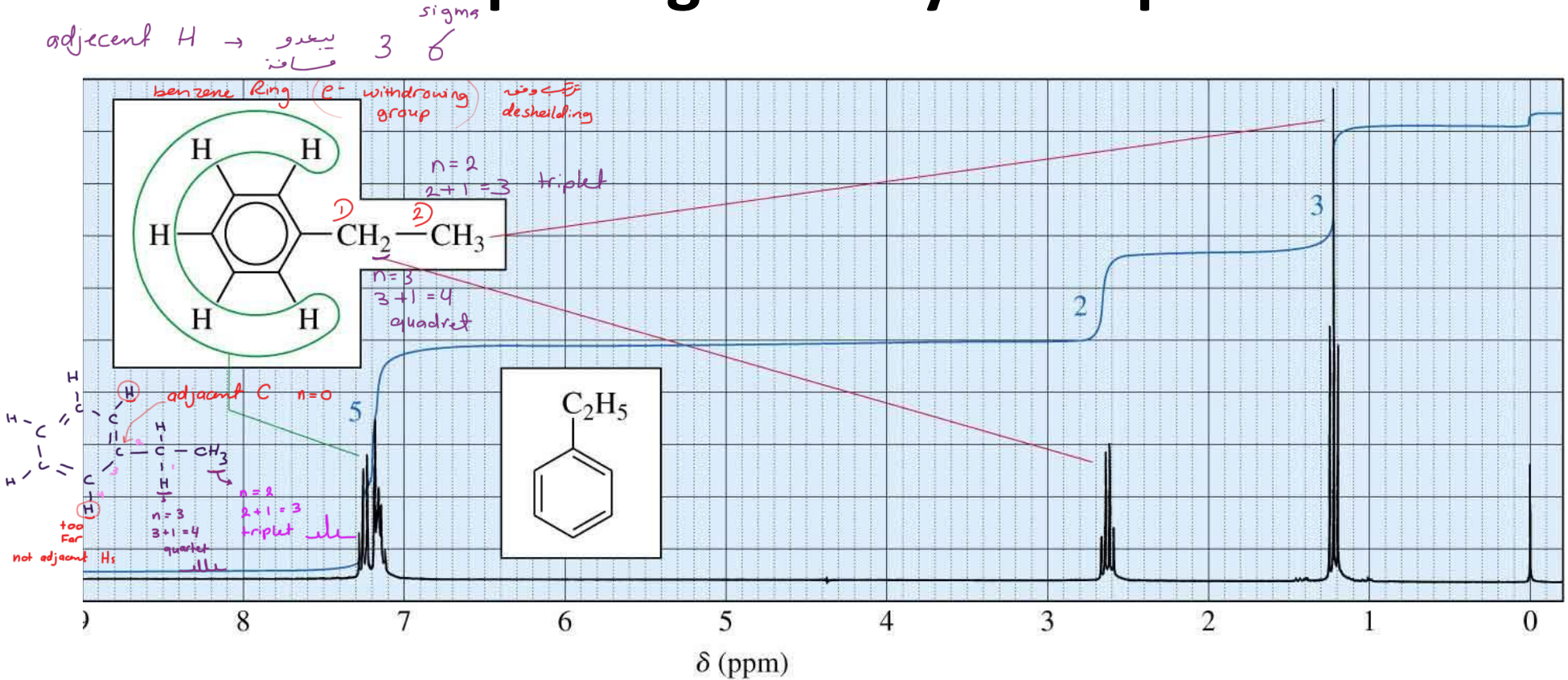
- Equivalent protons do not split each other.

- Protons bonded to the same carbon will split each other only if they are not equivalent.

- Protons on adjacent carbons normally will couple.

- Protons separated by four or more bonds will not couple.

Splitting for Ethyl Groups

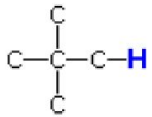


n=0

no Hs on adjacent Cs

no spliting / coupleing

No Coupled Hydrogens



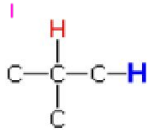
A Singlet

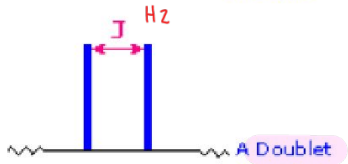
n=1

1+1=2

doublet

One Coupled Hydrogen



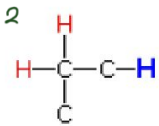


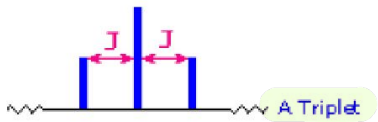
n=2

2+1=3

triplet

Two Coupled Hydrogens



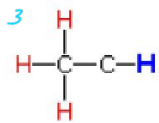


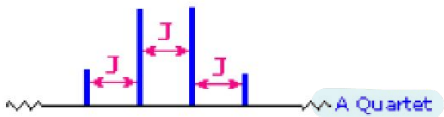
n=3

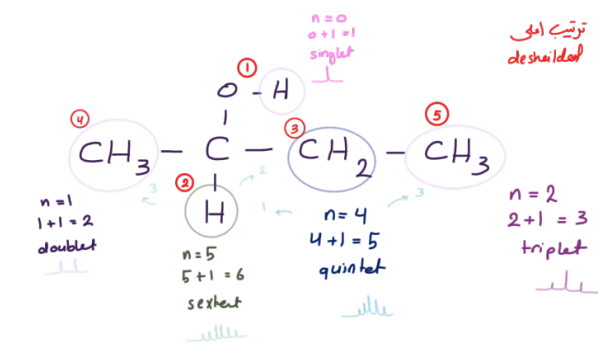
3+1=4

quartet

Three Coupled Hydrogens

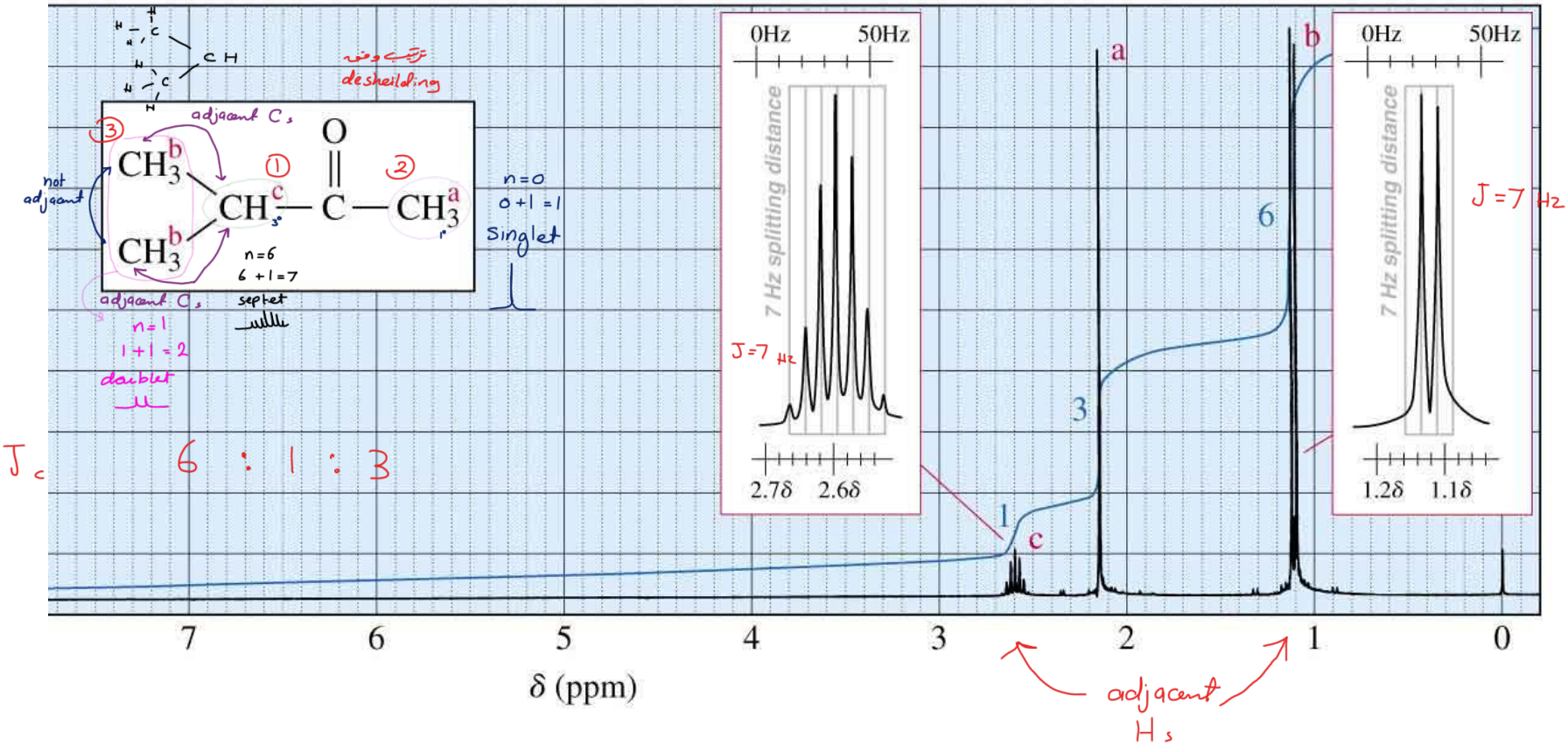






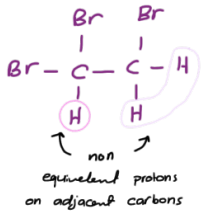
J splitting constant → distance between split peaks

Splitting for Isopropyl Groups



$J_b = J_c$

6 : 1 : 3



B_o → external magnetic Feild

Spin-Spin Splitting

nuclear spin ← كل نواة عدد وتولد حقل مغناطيسي

↑ α aligned reinforces B_o

↓ β opposed يعاكس B_o

- Nonequivalent protons on adjacent carbons have magnetic fields that may align with or oppose the external field.

قرب الـ H nuclei على بعض

- This magnetic coupling causes the proton to absorb slightly downfield when the external field is reinforced and slightly upfield when the external field is opposed.

$B_{induced}$ تأثير

a magnetic Feild other than B_o

↑B_o ↑ مع reinforce

↑ B_o ↓ عكس oppose

↑ B_o effective

↑ ν to Flip

↓ B_o الموثر على الذرة

↓ ν needed to Flip

الحل ← down Feild

to Flip a constant ν والعين تأثيره

deshielded

→ up Feild

Sheilded

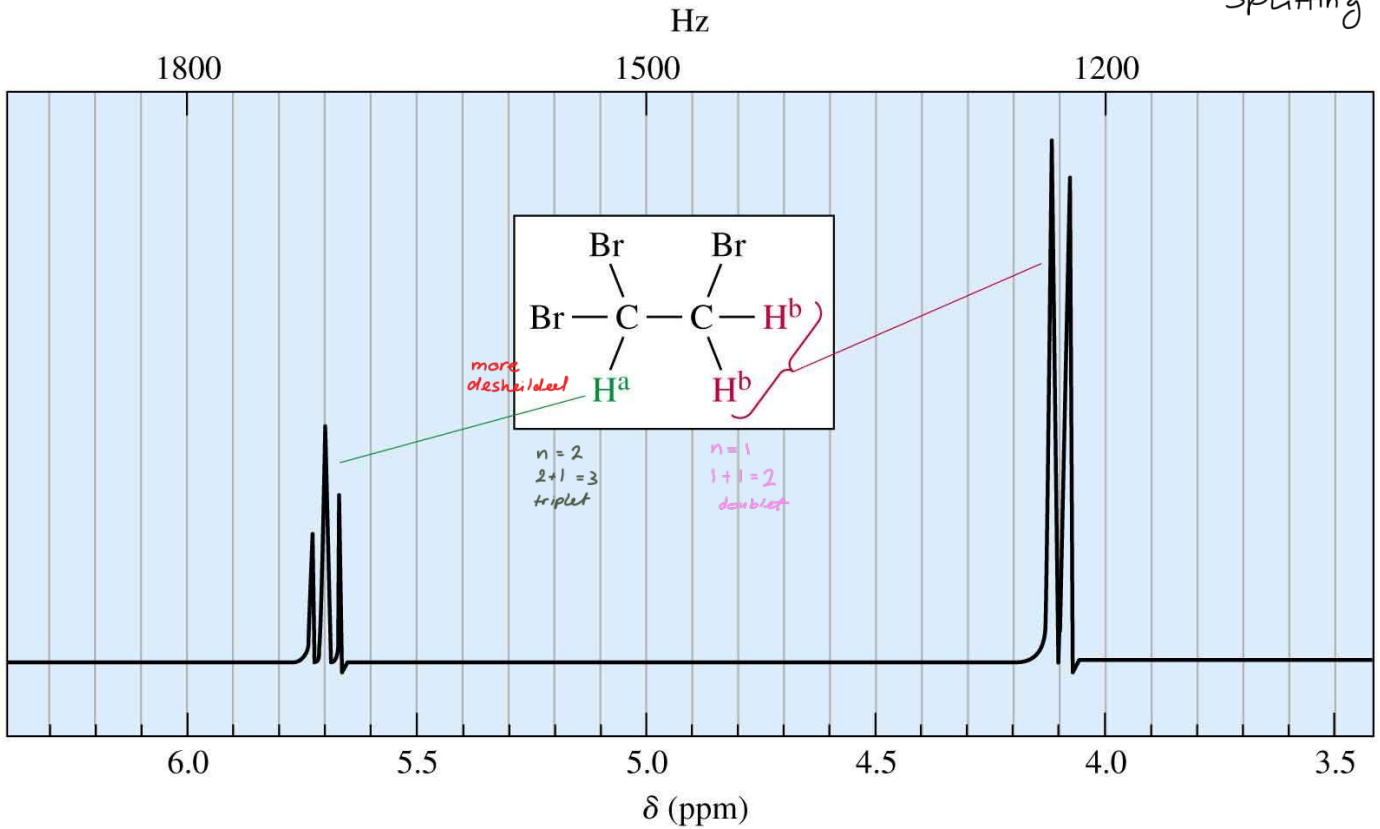
- All possibilities exist, so signal is split.

ارتفاع الـ peak يدل على

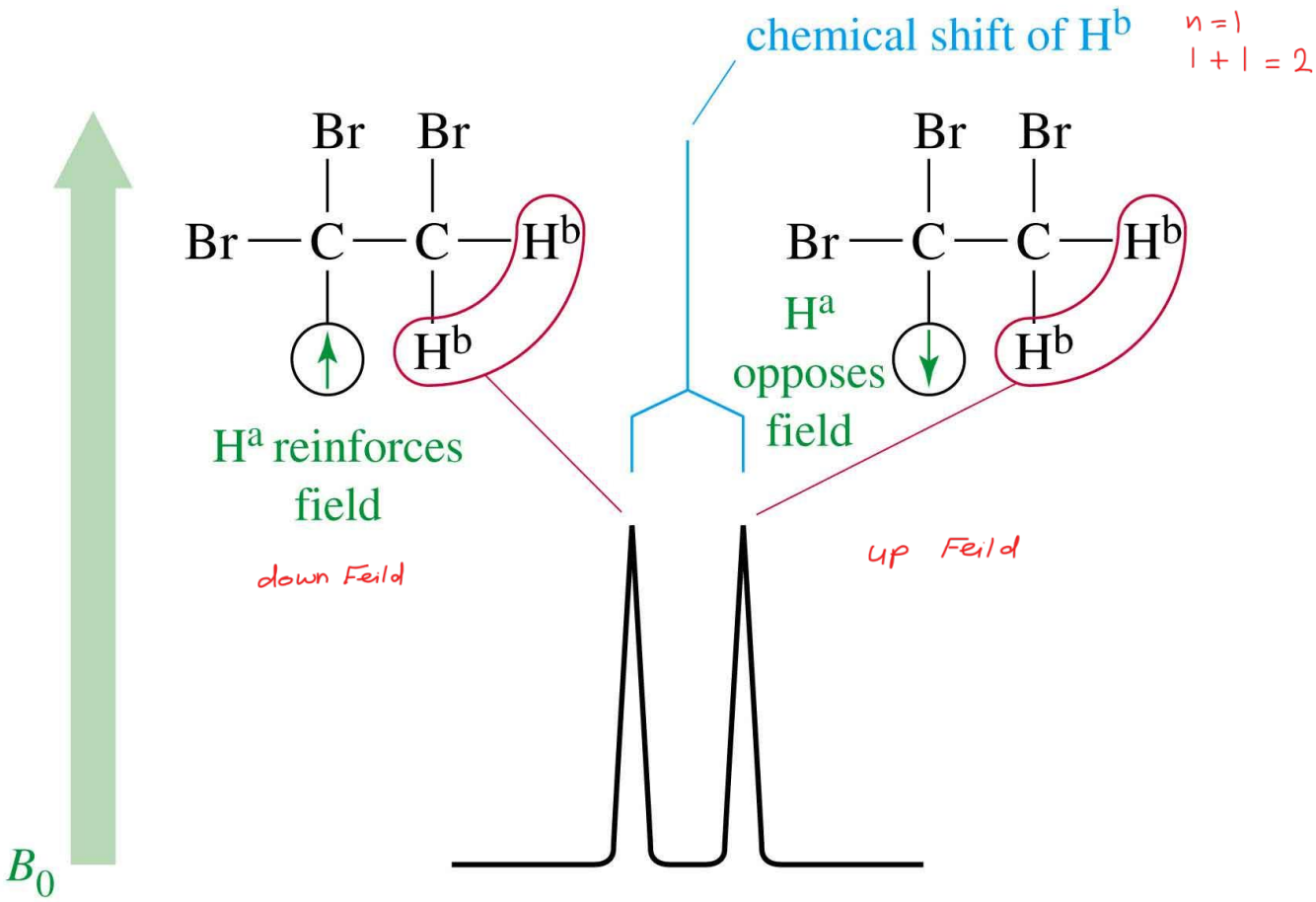
1,1,2-Tribromoethane

Nonequivalent protons on adjacent C

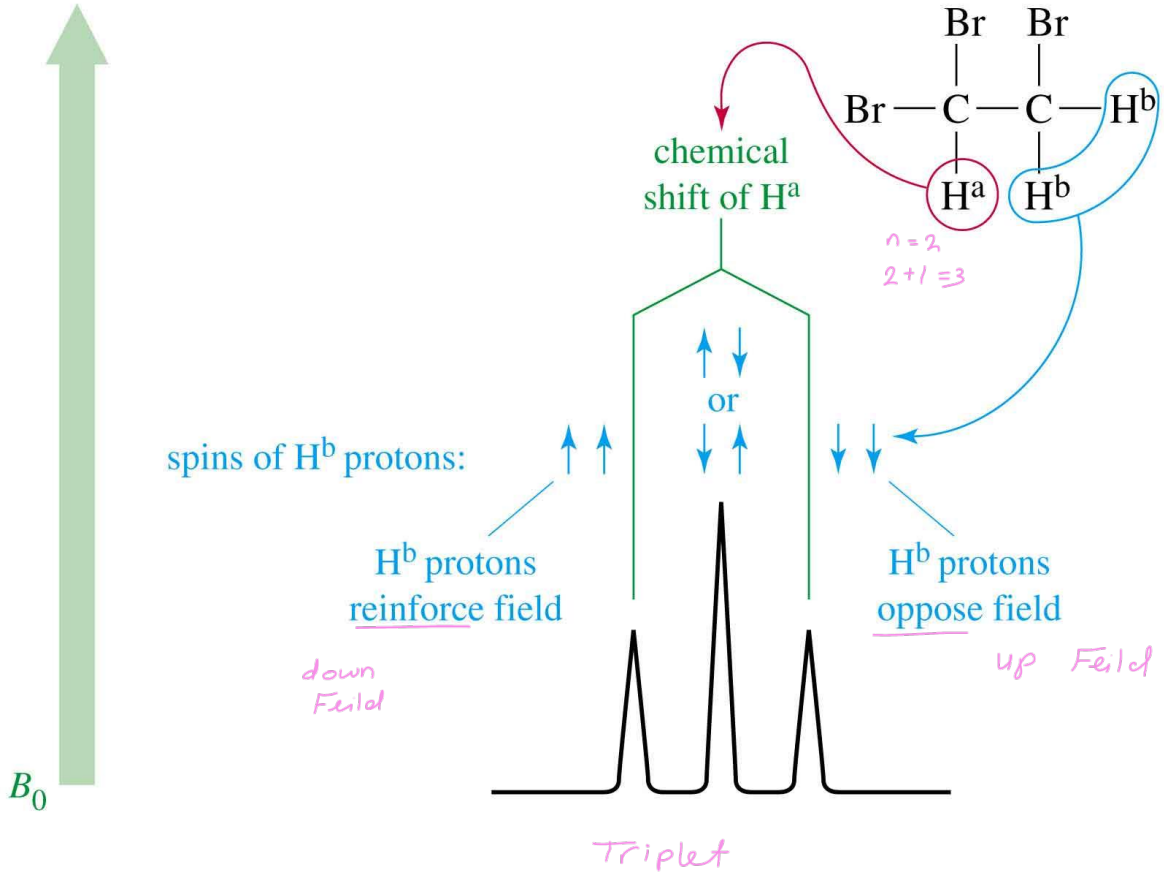
cause coupling & splitting to each other

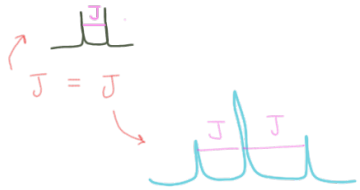


Doublet: 1 Adjacent Proton



Triplet: 2 Adjacent Protons





Hs that these peaks belong to are adjacent

J Coupling Constants

= or ring chiral

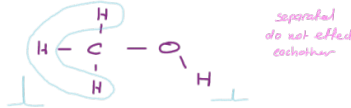
proton NMR

- Distance between the peaks of multiplet
- Measured in Hz
- Not dependent on strength of the external field

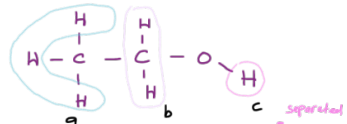
Bo

- Multiplets with the same coupling constants may come from adjacent groups of protons that split each other.

1) equivalent protons



2) adjacent carbon



splitting coupling n+1

3) non equivalent protons

complex splitting

chiral = cycle

2 Hs one same C

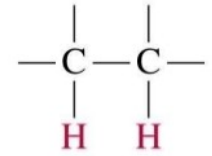
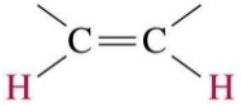
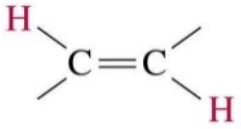
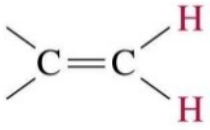
adjacent non equivalent Hs كلما الـ

يقربو على بعض

J (Hz) تقل

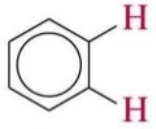
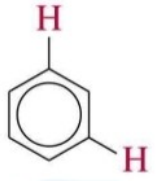
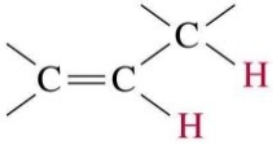
Values for Coupling Constants

- geminal (اقرب اشي)
- meta
- allylic
- Free rotation
- ortho
- cis
- trans

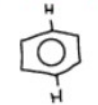
		Approx. J
	(free rotation)	7 Hz[a]
	(cis)	10 Hz
	(trans)	15 Hz
	(geminal)	2 Hz

ابعد شي عن بعض

اقرب شي

		Approx. J
	(ortho)	8 Hz
	(meta)	2 Hz
	(allylic)	6 Hz

meta → اقرب Hs على بعض (3D shape) J اصغر < ortho Hs ابعد عن بعض < para



ابعد اشي اكبر J

[a]The value of 7 Hz in an alkyl group is averaged for rapid rotation about the carbon–carbon bond. If rotation is hindered by a ring or bulky groups, other splitting constants may be observed.

moving closer to H

العراد تمليلها

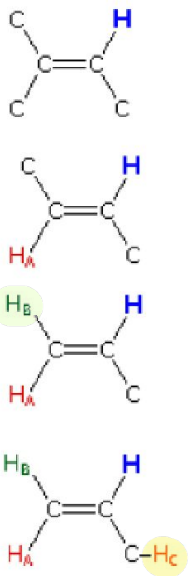
J تقل

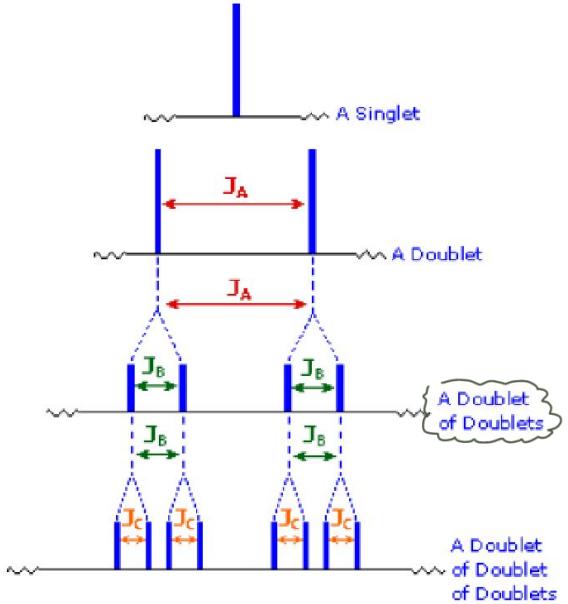
Trans — One Coupled Hydrogen

معزوم ما نطبق على القاعدة n+1 مع π — n=1, 1+1=2

cis — Two Coupled Hydrogens

allylic — Three Coupled Hydrogens





1 peak

2 peaks

4 peaks

8 peaks

cis

allylic

Farther

closer than

J <

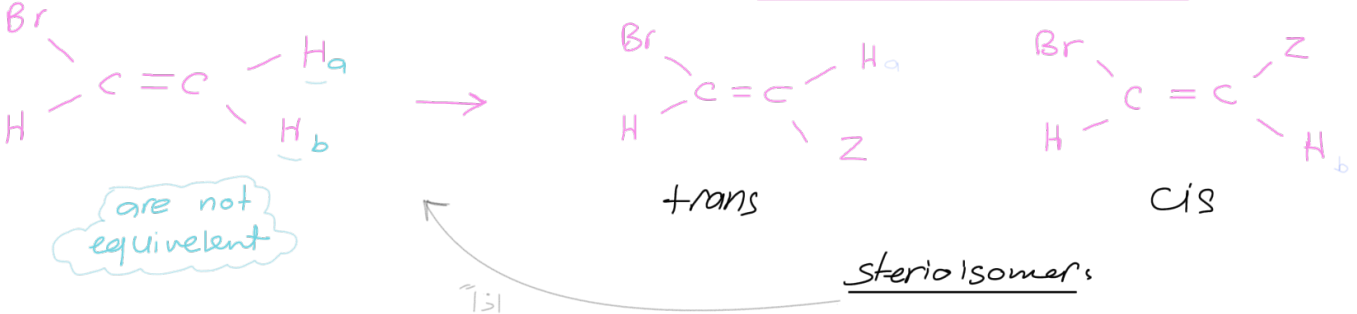
J

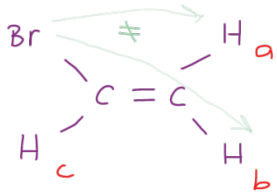
due to tetrahedral 3D shape

Stereochemical Nonequivalence

- Usually, two protons on the same C are equivalent and do not split each other.

- If the replacement of each of the protons of a -CH_2 group with an imaginary "Z" gives stereoisomers, then the protons are non-equivalent and will split each other.





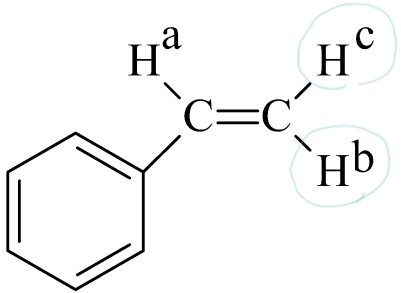
$H_a \neq H_b$

non equivalent

Some Nonequivalent Protons

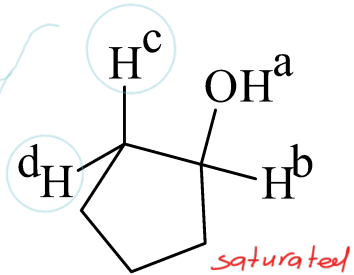
2 Hs on the same C but are not equivalent

(=)



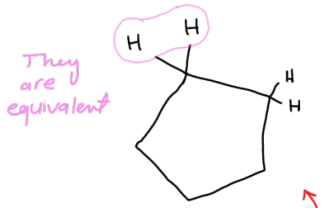
are non equivalent

cycle



saturated ring

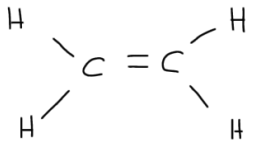
عشان اقرر بشوف الـ C المحاورة شو عليها



They are equivalent

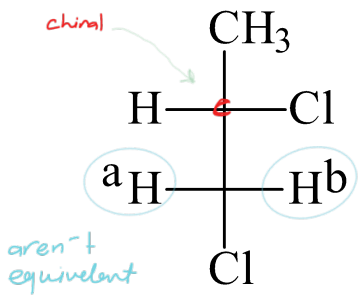
ما في مجاميع مختلفة

no coupleing



They are equivalent

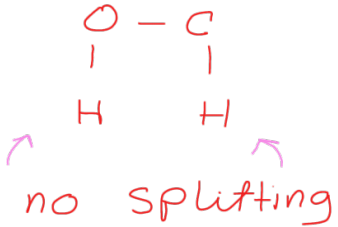
chiral



aren't equivelent

Time Dependence

- Molecules are tumbling relative to the magnetic field, so NMR is an averaged spectrum of all the orientations.
- Axial and equatorial protons on cyclohexane interconvert so rapidly that they give a single signal.
- Proton transfers for OH and NH may occur so quickly that the proton is not split by adjacent protons in the molecule.



حالة استثنائية *

Hydroxyl Proton

100%

تتصرف كأنها C adjacent

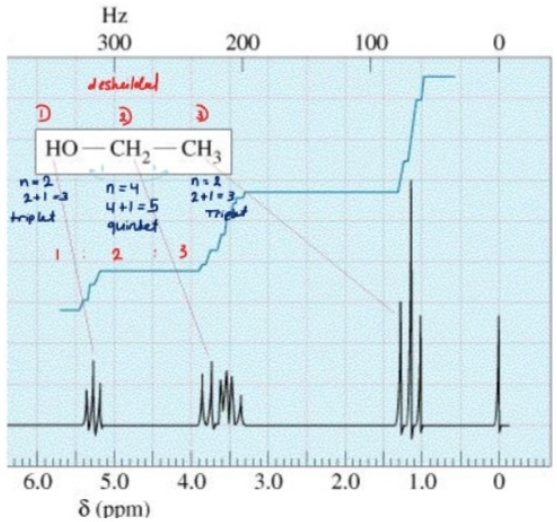
- Ultrapure samples of ethanol show splitting.

- Ethanol with a small amount of acidic or basic impurities will not show splitting.

95% ethanol

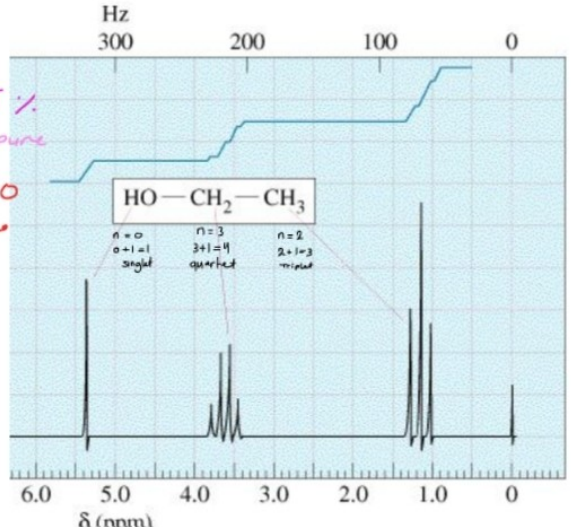
pure 100%

تعاملت مع الـ O كأنها C



95% no pure

O تفصل الـ H من الباقي و O-H تشارك في الـ splitting



N-H Proton

- Moderate rate of exchange.
- Peak may be broad.

H - bonding → broudness of peak

$X - H \cdots H - X$ (H bonding)

X = F, Cl, Br, I, O, or N

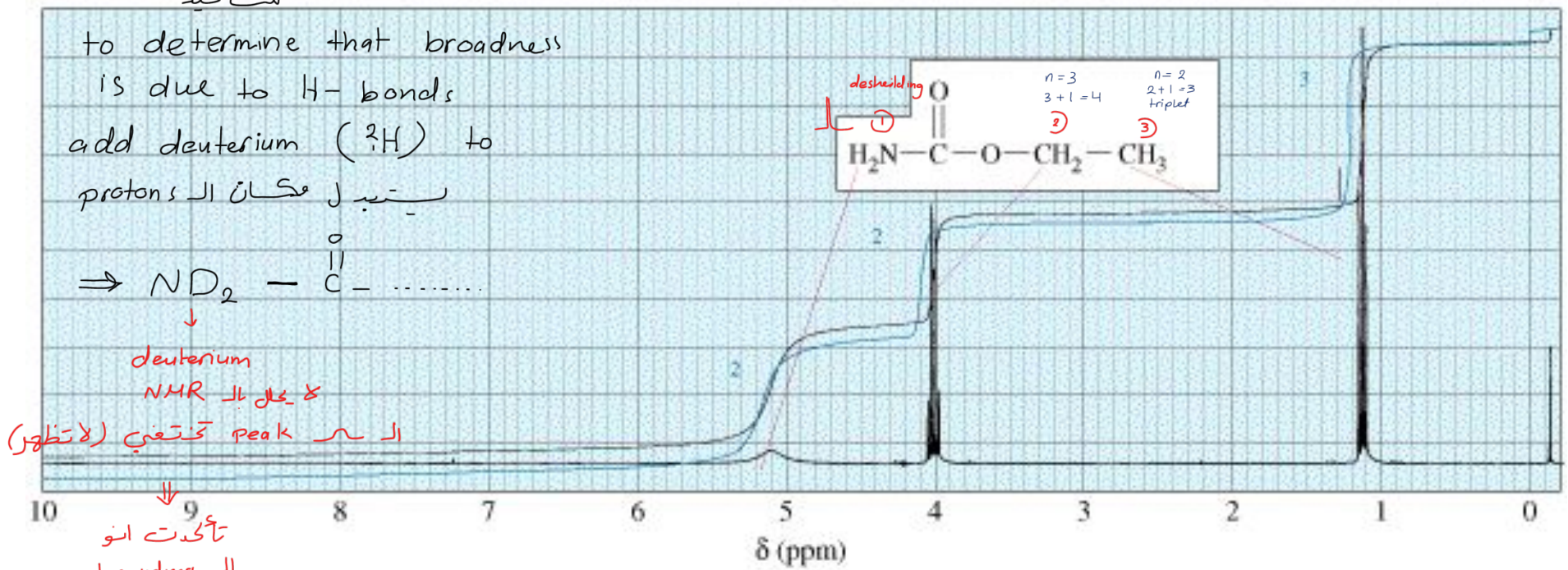
لتأكيد

to determine that broadness is due to H- bonds add deuterium (^2H) to protons

يستبدل مكان الـ

$\Rightarrow ND_2 - \overset{O}{\overset{\|}{C}} - \cdots\cdots$

deuterium NMR يظل بال & الـ peak تختفي (لا تظهر)



تأكدت انو broudness الـ H bond كانت بسبب

Identifying the O-H or N-H Peak

↑ concentration
↑ H bonding
↑ desheilding
↑ broadness of peak

δ

- Chemical shift will depend on concentration and solvent.

+ B induced

- To verify that a particular peak is due to O-H or N-H, shake the sample with D_2O deuterium (^2_1H)

- كل محلهم

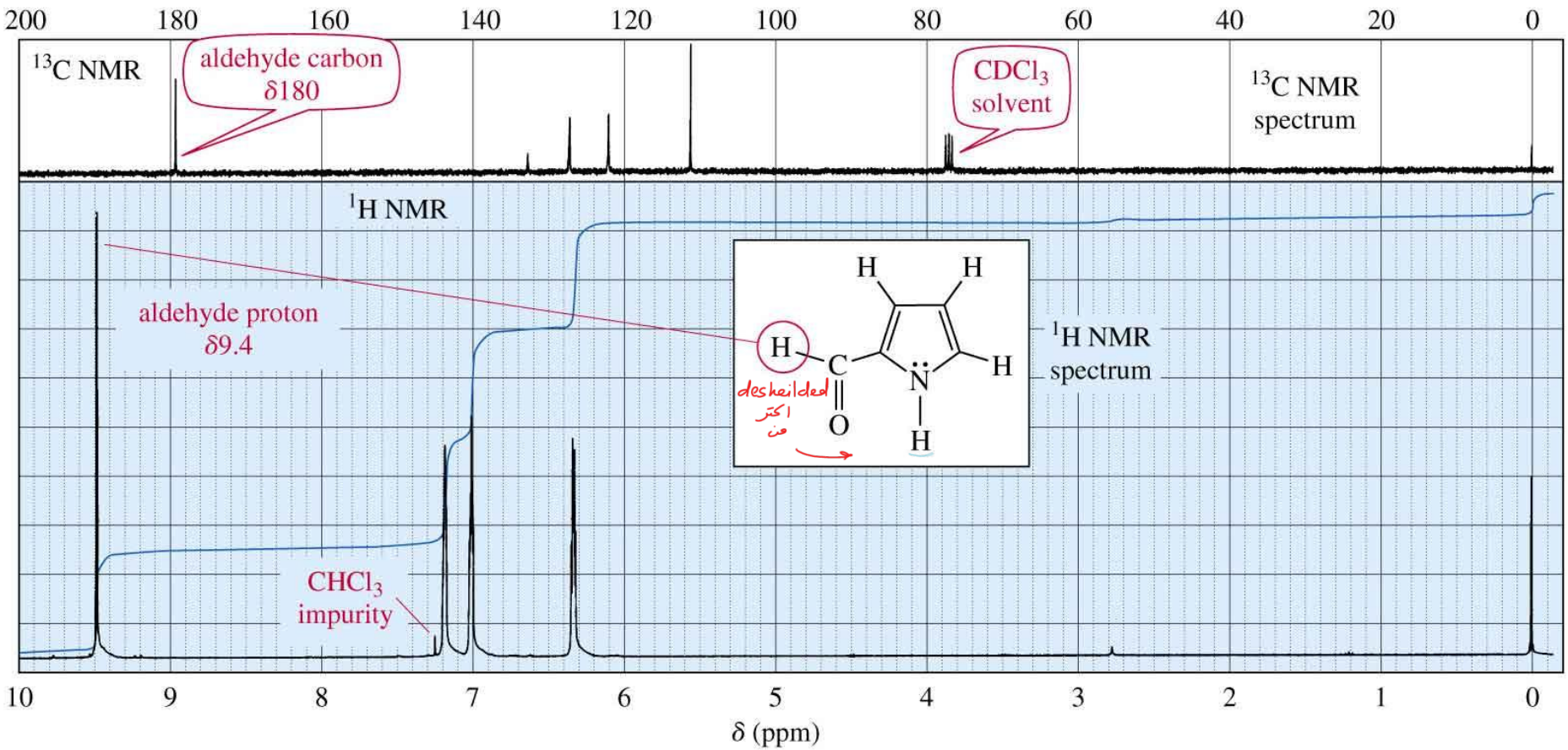
- Deuterium will exchange with the O-H or N-H protons.

- On a second NMR spectrum the peak will be absent, or much less intense.

مش موجودة

يقل ↓ N-H, O-H present استبدلتم ب N-D, O-D

Combined ^{13}C and ^{1}H Spectra



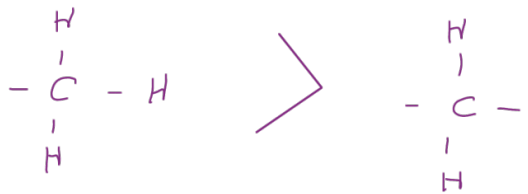
60 MHz ν to Flip ^1H nuclei
اربع اضعاف

Differences in ^{13}C Technique

15 MHz ν to Flip ^{13}C nuclei

ν

- Resonance frequency is ~~one-fourth~~, 15.1 MHz instead of 60 MHz.
- Peak areas are not proportional to number of carbons.
- Carbon atoms with more hydrogens absorb more strongly.



Spin-Spin Splitting

^{13}C 1.1 %

- It is unlikely that a ^{13}C would be adjacent to another ^{13}C, so splitting by carbon is negligible.
- ^{13}C will magnetically couple with attached protons and adjacent protons.
- These complex splitting patterns are difficult to interpret.

Proton Spin Decoupling

- To simplify the spectrum, protons are continuously irradiated with “noise,” so they are rapidly flipping.
- The carbon nuclei see an average of all the possible proton spin states.
- Thus, each different kind of carbon gives a single, unsplit peak.

Off-Resonance Decoupling

- ^{13}C nuclei are split only by the protons attached directly to them.

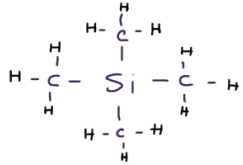
- The $N + 1$ rule applies: a carbon with N number of protons gives a signal with $N + 1$ peaks.

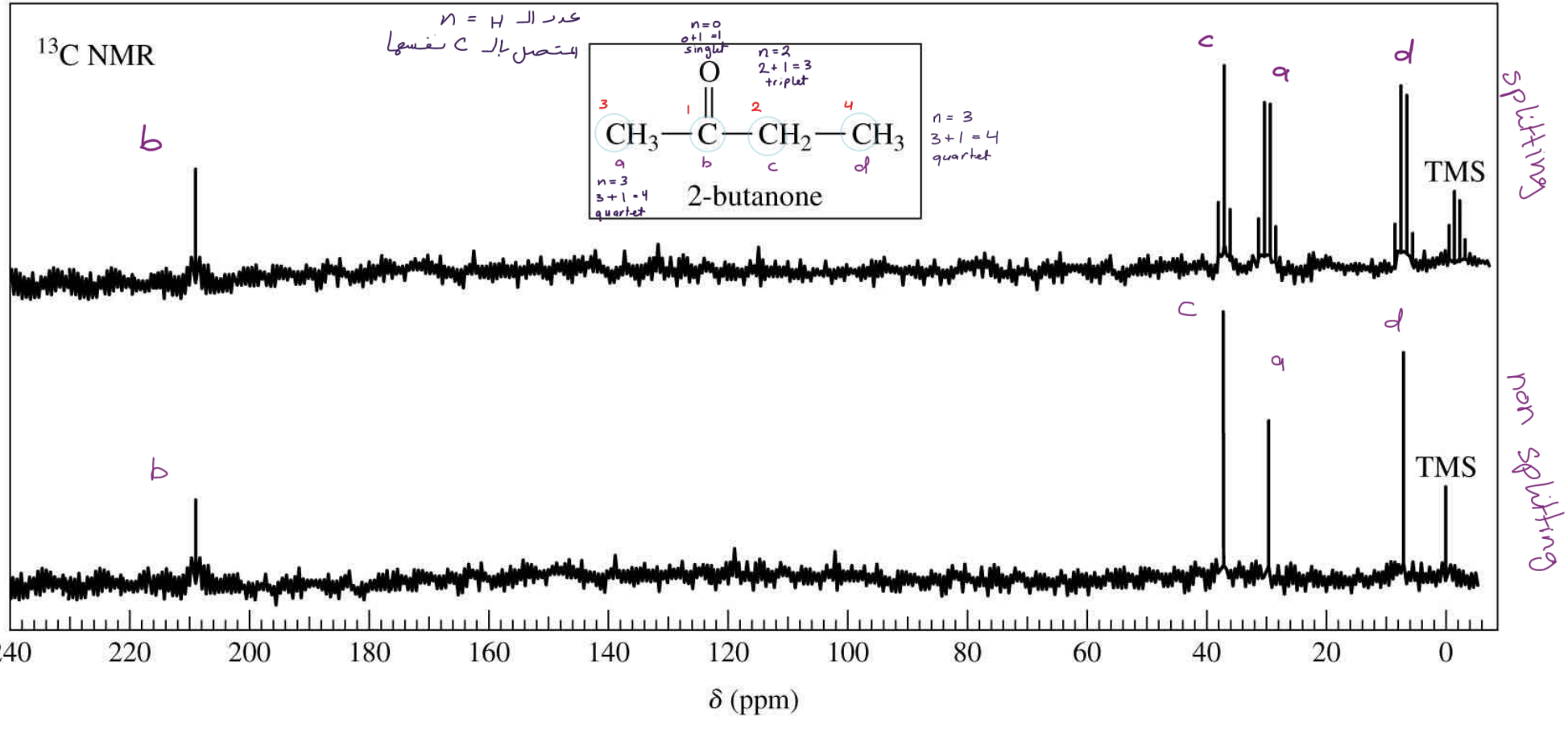
attached
directly

Interpreting ^{13}C NMR

- The number of different signals indicates the number of different kinds of carbon.
- The location (chemical shift) indicates the type of functional group.
- The peak area indicates the numbers of carbons (if integrated).
- The splitting pattern of off-resonance decoupled spectrum indicates the number of protons attached to the carbon.

Two ^{13}C NMR Spectra





Hydrogen and Carbon Chemical Shifts