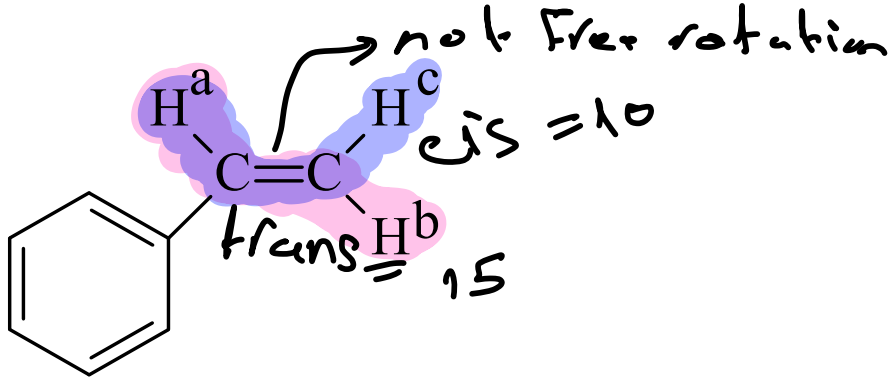
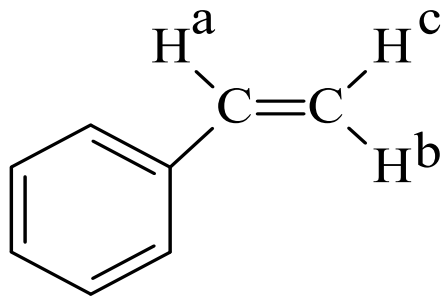
Complex Splitting

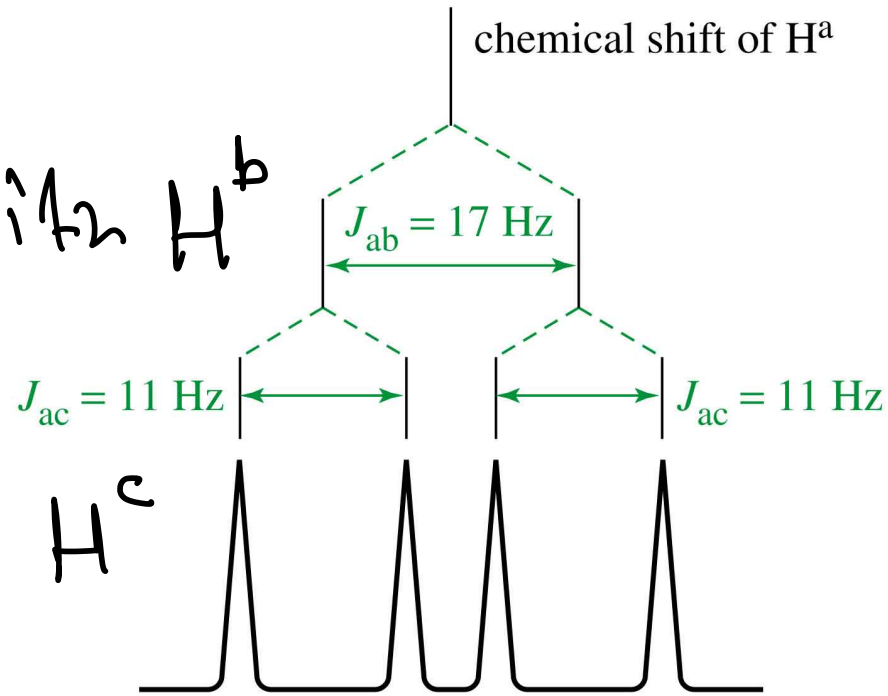


- Signals may be split by adjacent protons, different from each other, with different coupling constants.

- Example: Ha of styrene which is split by an adjacent H *trans* to it (J = 17 Hz) and an adjacent H *cis* to it (J = 11 Hz).

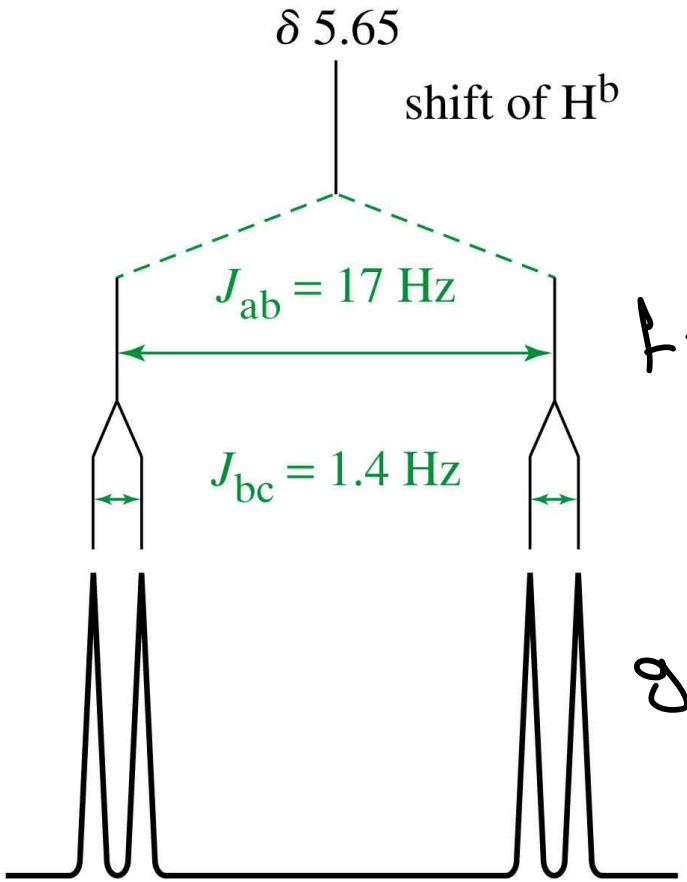
Splitting Tree





trans with H^b

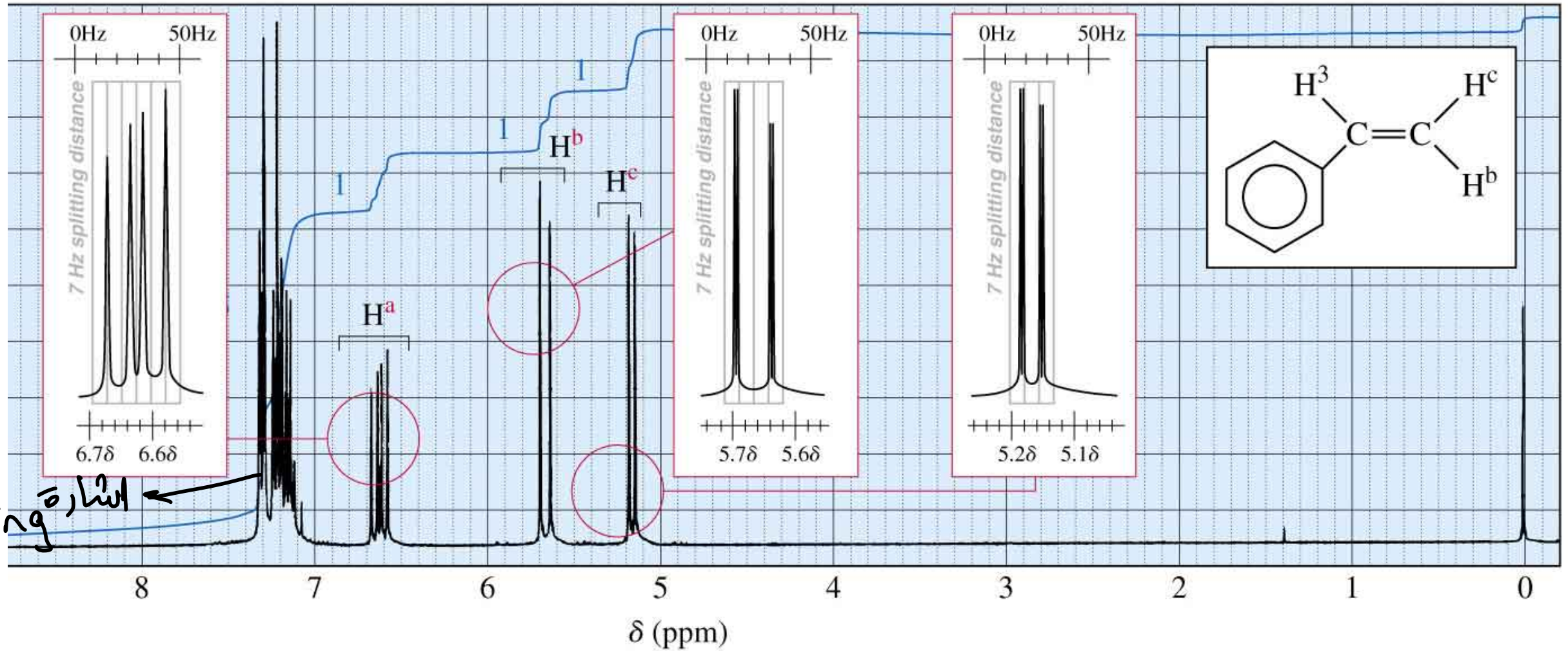
cis with H^c



trans with H^a

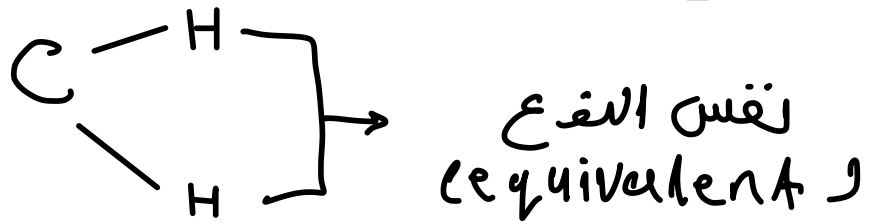
geminal with H^c

Spectrum for Styrene



Stereochemical Nonequivalence

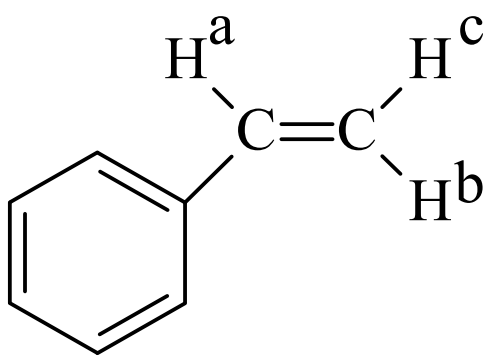
- Usually, two protons on the same C are equivalent and do not split each other.

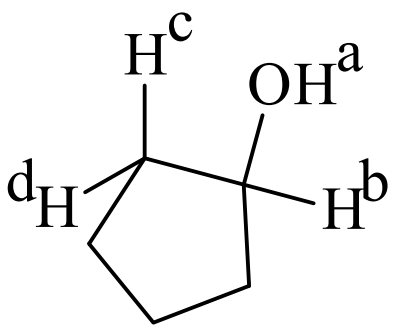


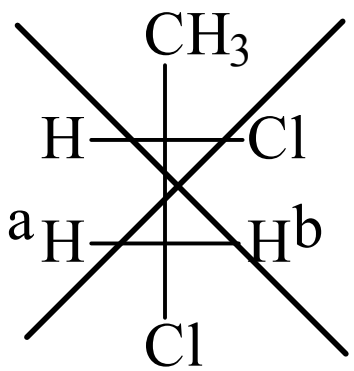
- If the replacement of each of the protons of a -CH2 group with an imaginary "Z" gives stereoisomers, then the protons are non-equivalent and will split each other.

stereoisomer ← مركب يتكون من نفس عدد C ونفس عدد الأشياء المرتبطة مع الكربون ونفس عدد الروابط لكن توزيعهم مختلف فيعطي isomer وأنواع مختلفة.

Some Nonequivalent Protons







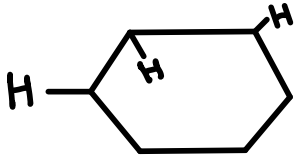
بكونوا بلفوا و بتأرجحوا

Time Dependence

Magnetic Field بال

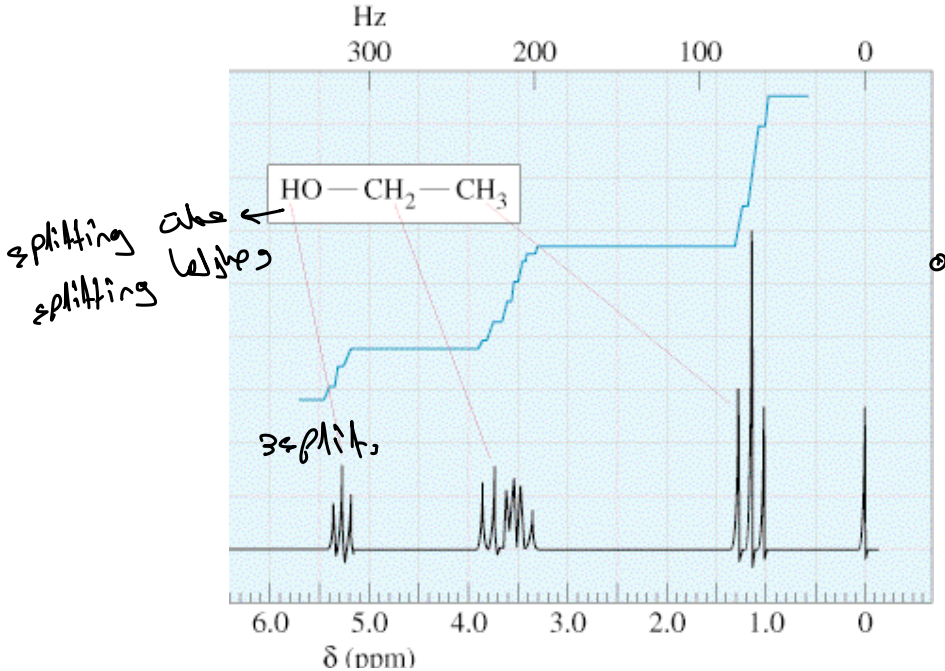
- Molecules are tumbling relative to the magnetic field, so NMR is an averaged spectrum of all the orientations.

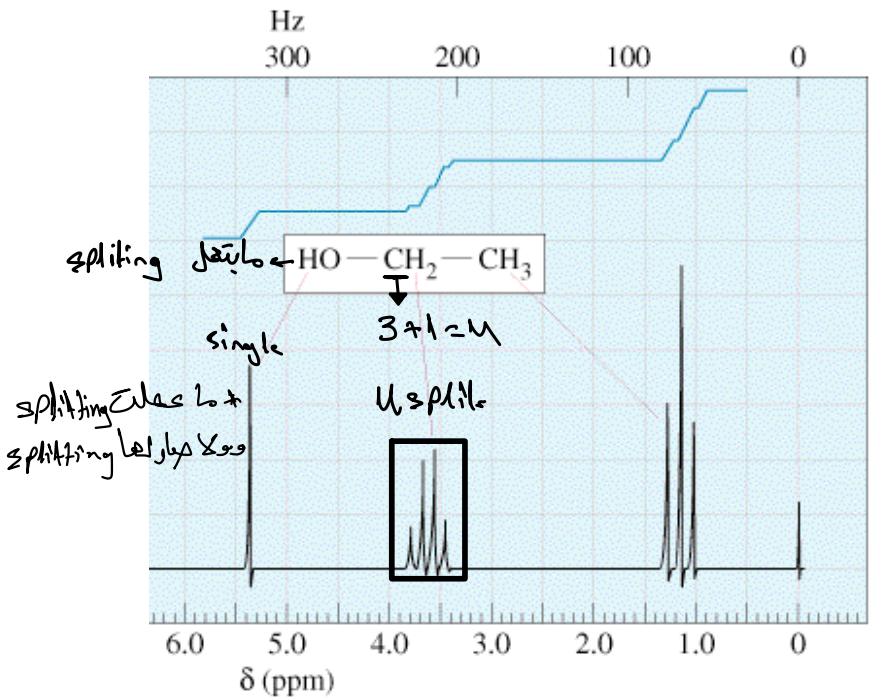
- Axial and equatorial protons on cyclohexane interconvert so rapidly that they give a single signal.



- Proton transfers for OH and NH may occur so quickly that the proton is not split by adjacent protons in the molecule.

* البروتونات الموجودة على OH او NH مابعملوا splitting



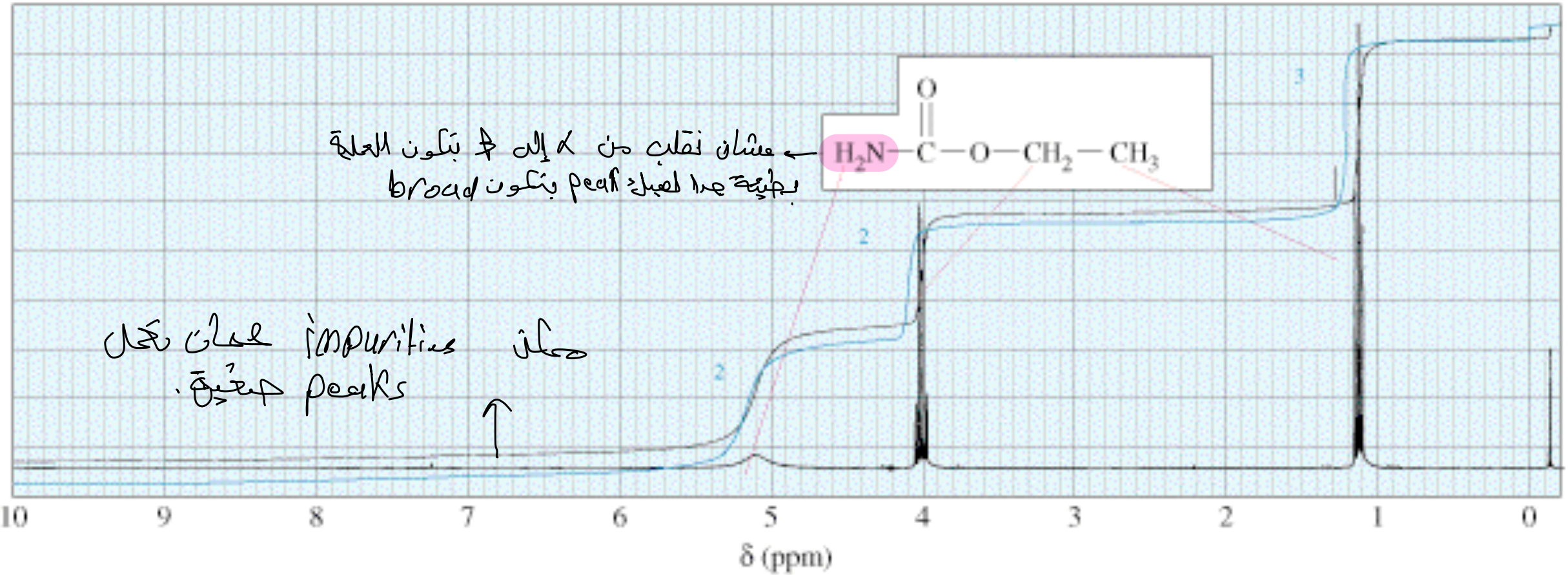


Hydroxyl Proton

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

N-H Proton

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



Identifying the O-H or N-H Peak

- Chemical shift will depend on concentration and solvent.

- To verify that a particular peak is due to O-H or N-H, shake the sample with D2O

* بنجيب العينة إللي عملت عندك peak محيرة بعد ما طلعناها بنحط عليها D_2O
D_2 رح ترتبط مع N بدل H إللي كانت مرتبطة معها وبروح بحطها فالجهاز مرة ثانية و D_2N وفي
nmr inactive فبشوف التحليل الثاني إذا ظهرت peak بتكون للـ impurities وإذا اختفت بتكون للـ H-bonding.

واحد من نظائر الهيدروجين ←
nmr inactive ← ^2_1H

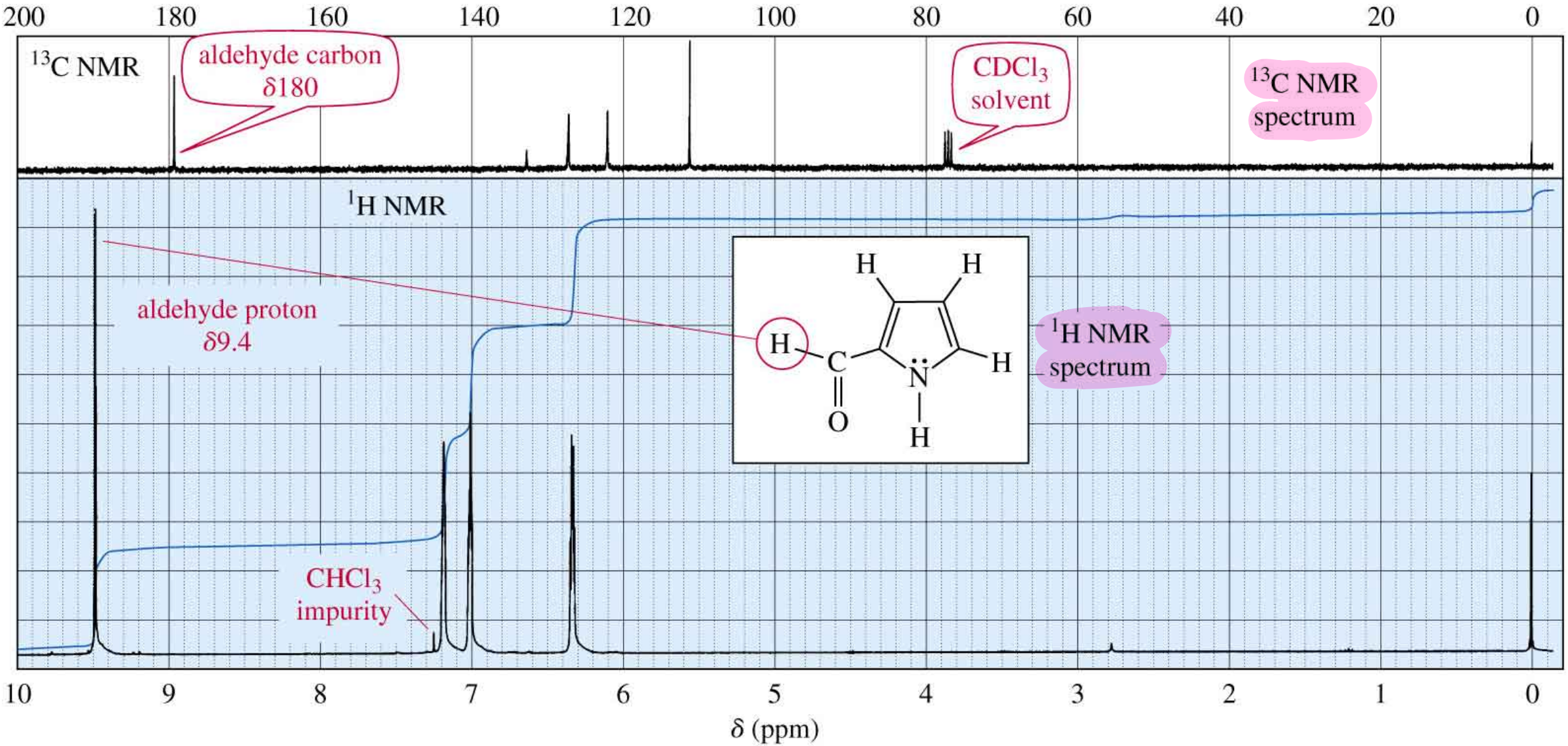
- Deuterium will exchange with the O-H or N-H protons.

← بستعمله عشان الكشف عن الـ peak هل هي لـ H bonding أو للـ impurities

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

اذا كانت peak للـ H-bonding , واذا ضلت تكون للشوائب

Combined 13C and 1H Spectra



* الطاقة المحتاجة او الجهاز اللي رح استخدمه في الهيدروجينات كان يحتاج مقدار طاقة كبير جوصل لـ 60 MHz عشان اقدر اقلب الدوران من Beta الى alpha لكن بالـ ^{13}C ما يحتاج مقدار هالطاقة الكبير يحتاج طاقة اقل من اللي بستخدمه مع البروتونات او H. بس 15.1 MHz وبستخدم جهاز

Differences in 13C Technique

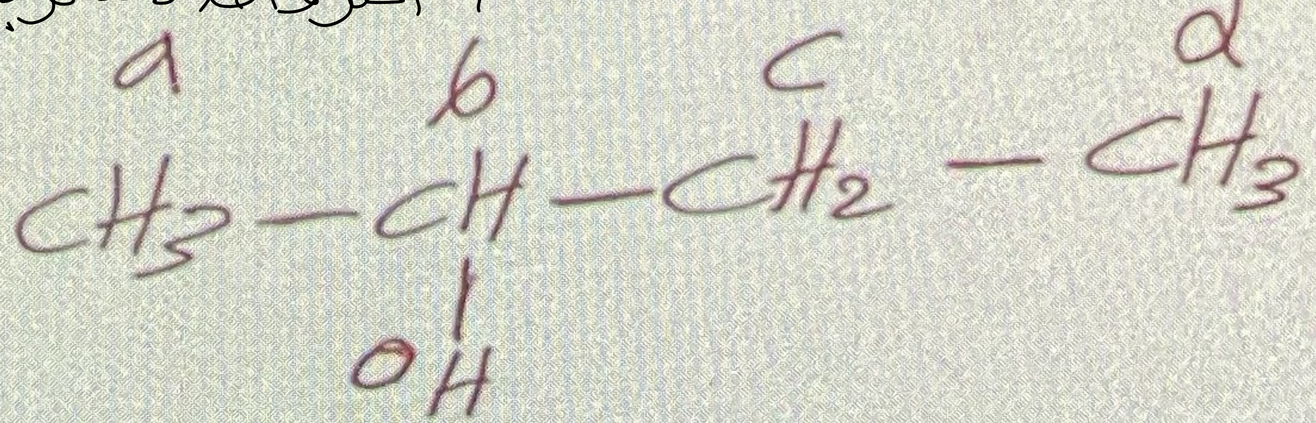
- Resonance frequency is ~ one-fourth, 15.1 MHz instead of 60 MHz.
- Peak areas are not proportional to number of carbons.

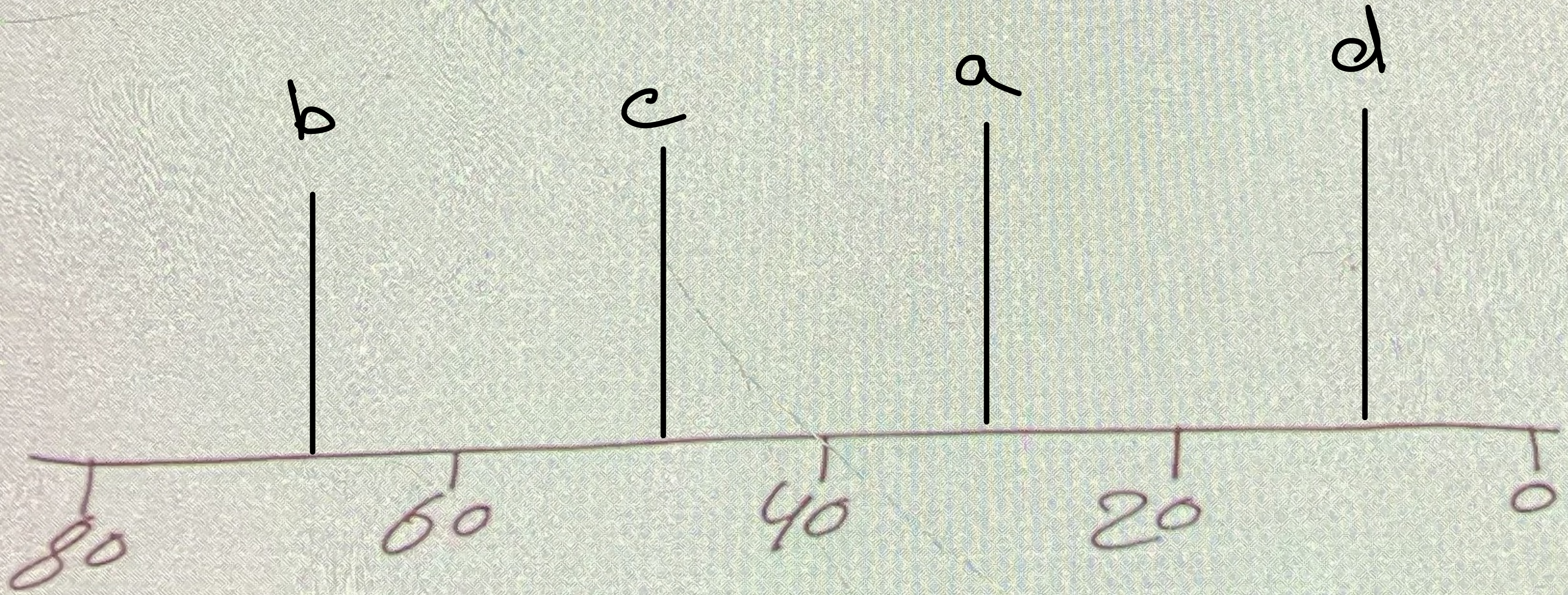
ارتفاع الـ peak مالو دخل بعدد الذريات اللي من نفس النوع.

- Carbon atoms with more hydrogens absorb more strongly.

كل ما زادت عدد الهيدروجينات الموجودة على الكربون رح تمتص بشكل اكبر.

٢ اكثر واحد متأثر بال OH





Spin-Spin Splitting

- It is unlikely that a 13C would be adjacent to another 13C, so splitting by carbon is negligible.
- 13C 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.

. splitting to each other الكربونات ما يحلوا

Off-Resonance Decoupling

- 13C nuclei are split only by the protons attached directly to them. الهيدروجينات المرتبطين مع 13C
هم فقط اللي بقدروا يعملوا splitting

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

Interpreting 13C NMR

- The number of different signals indicates the number of different kinds of carbon.

- The location (chemical shift) indicates the type of functional group.

  Electronegativity حسب

- The peak area indicates the numbers of carbons (if integrated).

  لو إذا C كان إلهم نفس البيئة تبعت سحب e منهم وبيجوا فوق بعض بالطيف
  هذا الشيء بخلي انه السيجنال تكون أكبر.

- The splitting pattern of off-resonance decoupled spectrum indicates the number of protons attached to the carbon.

13C Chemical Shifts

are measured in ppm (δ) from the carbons of TMS

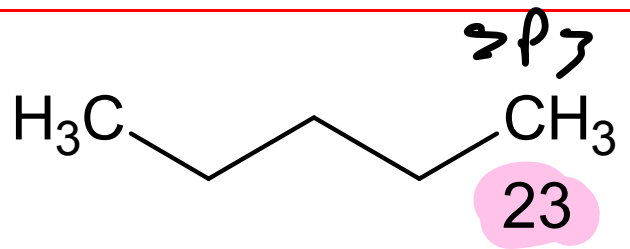
13C Chemical shifts are most affected by:

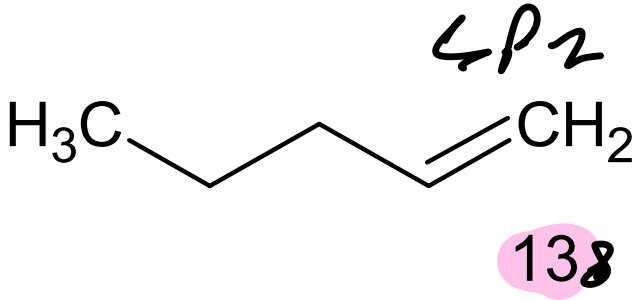
- hybridization state of carbon → sp, sp^2, sp^3 هل هو
- electronegativity of groups attached to carbon

$sp^2 > sp > sp^3$

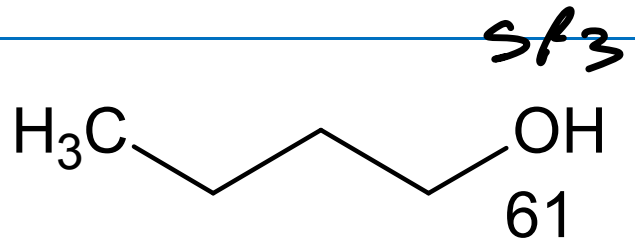
C= C≡ C–

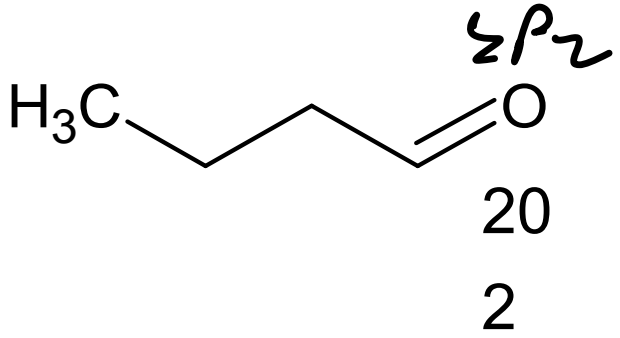
Examples (chemical shifts in ppm from TMS)



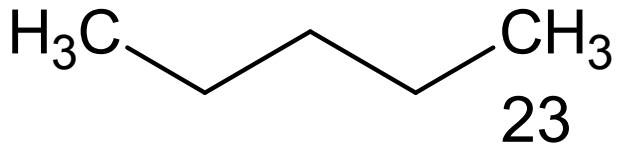


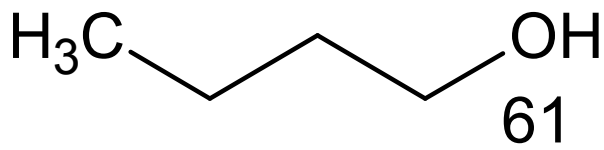
sp3 hybridized carbon is more shielded than sp2





sp3 hybridized carbon is more shielded than sp2





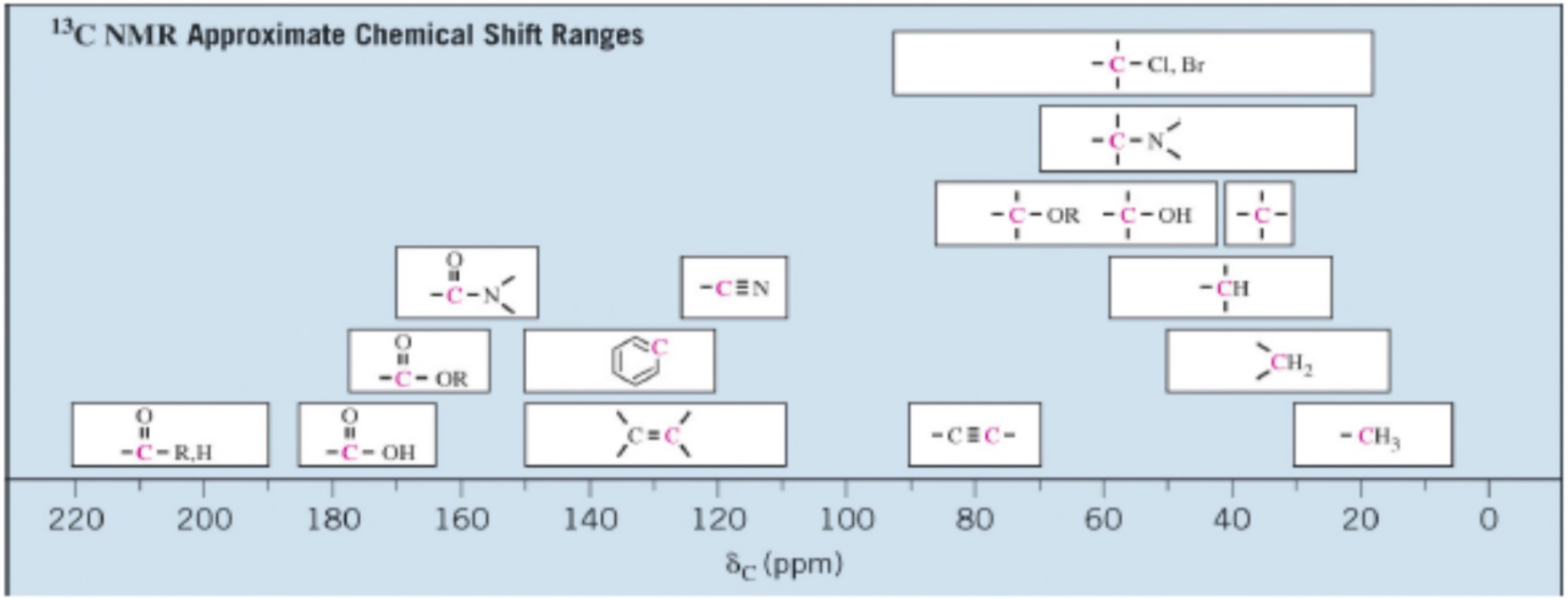
an electronegative atom deshields the carbon to which it is attached

مش حفظ بس افهم المبدأ

Type of carbon	Chemical shift (δ) ppm	Type of carbon	Chemical shift (δ) ppm
RCH_3	0-35	$RC{\equiv}CR$	65-90
R_2CH_2	15-40	$R_2C{=}CR_2$	100-150
R_3CH	25-50		110-175
R_4C	30-40		

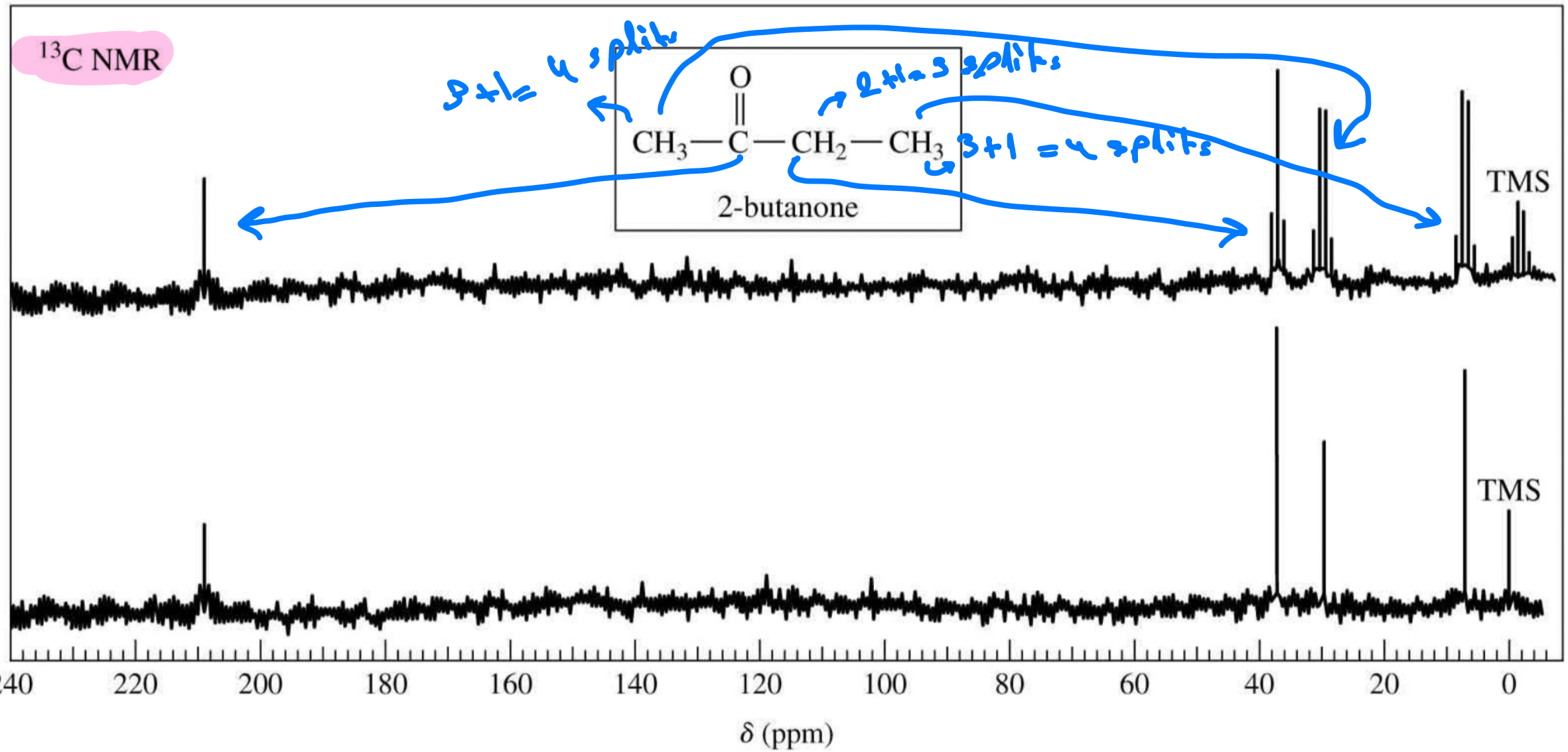
Type of carbon	Chemical shift (δ) ppm	Type of carbon	Chemical shift (δ) ppm
RCH_2Br	20-40		160-185
RCH_2Cl	25-50		
RCH_2NH_2	35-50		190-220
RCH_2OH	50-65		
RCH_2OR	50-65		

- **^{13}C Chemical Shifts**
  - ➔ Just as in ^{1}H NMR spectroscopy, chemical shifts in ^{13}C NMR depend on the electron density around the carbon nucleus
    - Decreased electron density causes the signal to move downfield (*desheilding*)
    - Increased electron density causes the signal to move upfield (*sheilding*)



  - ➔ Because of the wide range of chemical shifts, it is rare to have two ^{13}C peaks coincidentally overlap
  - ➔ A group of 3 peaks at δ 77 comes from the common NMR solvent deuteriochloroform and can be ignored

Two ^{13}C NMR Spectra



Hydrogen and Carbon Chemical Shifts