# $^{13}C$ NMR Spectroscopy

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## *$^1H$ and $^{13}C$ NMR compared:*

both give us information about the number of chemically nonequivalent nuclei (nonequivalent hydrogens or nonequivalent carbons)

both give us information about the environment of the nuclei (hybridization state, attached atoms, etc.)

FT-NMR techniques are standard practice for $^{13}C$ NMR

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## *$^1H$ and $^{13}C$ NMR compared:*

$^{13}C$ requires FT-NMR because the signal for a carbon atom is $10^{-4}$ times weaker than the signal for a hydrogen atom

a signal for a $^{13}C$ nucleus is only about 1% as intense as that for $^1H$ because of the magnetic properties of the nuclei, and

at the "natural abundance" level only 1.1% of all the C atoms in a sample are $^{13}C$ (most are $^{12}C$)

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## *$^1H$ and $^{13}C$ NMR compared:*

$^{13}C$ signals are spread over a much wider range than $^1H$ signals making it easier to identify and count individual nuclei

Figure #1 shows the $^1H$ NMR spectrum of 1-chloropentane; Figure #2 shows the $^{13}C$ spectrum. It is much easier to identify the compound as 1-chloropentane by its $^{13}C$ spectrum than by its $^1H$ spectrum.

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*Figure #1*

$^1H$

$ClCH_2CH_2CH_2CH_2CH_3$

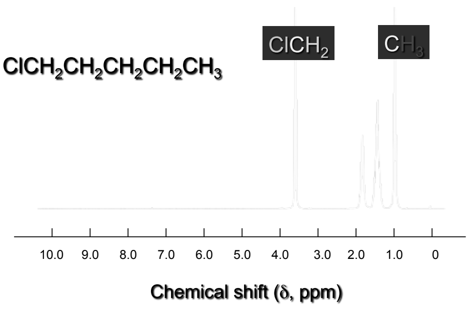

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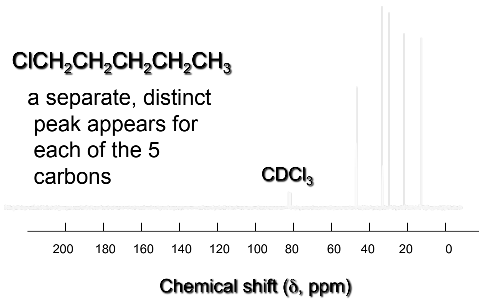
*Figure #2*

$^{13}C$

$ClCH_2CH_2CH_2CH_2CH_3$

a separate, distinct peak appears for each of the 5 carbons

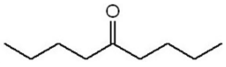


## Question

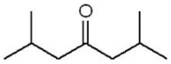
- How many signals would you expect to see in the $^{13}$C-NMR spectrum of *m*-chloroanisole?
- A) 4
- B) 5
- C) 6
- D) 7

## Question

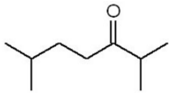
- Which compound has the most signals in its $^{13}$C-NMR spectrum?
- A)



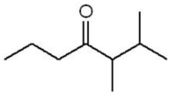
B)



- C)



D)

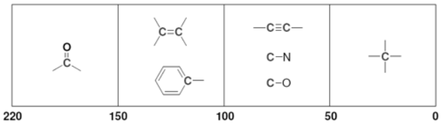


## $^{13}$C Chemical Shifts

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

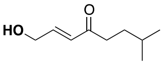
## *$^{13}$C Chemical shifts are most affected by:*

- hybridization state of carbon
- electronegativity of groups attached to carbon
- electronegativity has an even greater effect on $^{13}$C chemical shifts than it does on $^{1}$H chemical shifts.



## Question

Predict the number of signals and location of each signal in 13C NMR for the following.



A: Number of signals __________
B: Number of signals below 50 ppm __________
C: Number of signals between 50 and 100 ppm ________
D: Number of signals between 100 and 150 ppm _______
E: Number of signals above 150 ppm __________

A. A = 7; B = 3; C = 1; D = 1; E = 3
B. A = 7; B = 4; C = 0; D = 3; E = 2
C. A = 7; B = 3; C = 1; D = 2; E = 2
D. A = 8; B = 4; C = 0; D = 1; E = 3
E. A = 8; B = 4; C = 1; D = 2; E = 1

## *Types of Carbons*

|  | Classification | Chemical shift, δ<br>$^{1}$H | <br>$^{13}$C |
|---|---|---|---|
| $CH_4$ |  | 0.2 | -2 |
| $CH_3CH_3$ | primary | 0.9 | 8 |
| $CH_3CH_2CH_3$ | secondary | 1.3 | 16 |
| $(CH_3)_3CH$ | tertiary | 1.7 | 25 |
| $(CH_3)_4C$ | quaternary |  | 28 |

Replacing H with C (more electronegative) deshields C to which it is attached.

## *Electronegativity Effects on $CH_3$*

| | Chemical shift, δ $^1H$ | $^{13}C$ |
|---|---|---|
| $CH_4$ | 0.2 | -2 |
| $CH_3NH_2$ | 2.5 | 27 |
| $CH_3OH$ | 3.4 | 50 |
| $CH_3F$ | 4.3 | 75 |

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## *Electronegativity Effects and Chain Length*

| | Cl— | $CH_2$— | $CH_2$— | $CH_2$— | $CH_2$— | $CH_3$ |
|---|---|---|---|---|---|---|
| Chemical shift, δ | | 45 | 33 | 29 | 22 | 14 |

Deshielding effect of Cl decreases as number of bonds between Cl and C increases.

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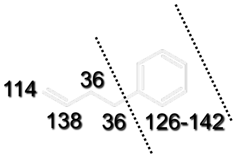
## *Hybridization Effects*

*sp*$^3$ hybridized carbon is more shielded than *sp*$^2$.



*sp* hybridized carbon is more shielded than *sp*$^2$, but less shielded than *sp*$^3$.

$H—C{\equiv}C—CH_2—CH_2—CH_3$

68 84 22 20 13

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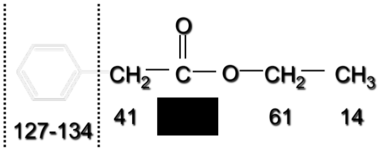
## *Carbonyl Carbons are Especially Deshielded*



$C_6H_5—CH_2—\overset{O}{\overset{\|}{C}}—O—CH_2—CH_3$

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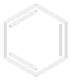
## *Table*

| 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 | | |

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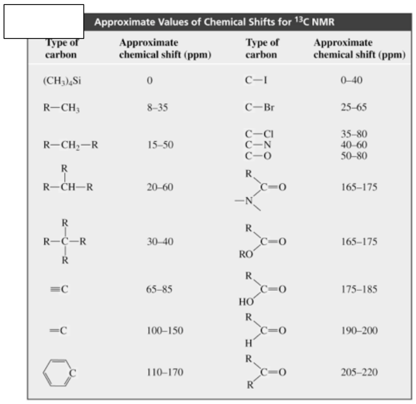
## *Table*

| Type of carbon | Chemical shift (δ), ppm | Type of carbon | Chemical shift (δ), ppm |
|---|---|---|---|
| $RCH_2Br$ | 20-40 | $RC{\equiv}N$ | 110-125 |
| $RCH_2Cl$ | 25-50 |  $R\overset{O}{\overset{\|}{C}}OR$ | 160-185 |
| $RCH_2NH_2$ | 35-50 | | |
| $RCH_2OH$ | 50-65 | | |
| $RCH_2OR$ | 50-65 |  $R\overset{O}{\overset{\|}{C}}R$ | 190-220 |



Approximate Values of Chemical Shifts for $^{13}$C NMR

| Type of carbon | Approximate chemical shift (ppm) | Type of carbon | Approximate chemical shift (ppm) |
|---|---|---|---|
| $(CH_3)_4Si$ | 0 | $C{-}I$ | 0–40 |
| $R{-}CH_3$ | 8–35 | $C{-}Br$ | 25–65 |
| $R{-}CH_2{-}R$ | 15–50 | $C{-}Cl$<br>$C{-}N$<br>$C{-}O$ | 35–80<br>40–60<br>50–80 |
| $R{-}CH(R){-}R$ | 20–60 | $R(N{<})C{=}O$ | 165–175 |
| $R{-}C(R)(R){-}R$ | 30–40 | $R(RO)C{=}O$ | 165–175 |
| $\equiv C$ | 65–85 | $R(HO)C{=}O$ | 175–185 |
| $=C$ | 100–150 | $R(H)C{=}O$ | 190–200 |
| ⌬C | 110–170 | $R(R)C{=}O$ | 205–220 |

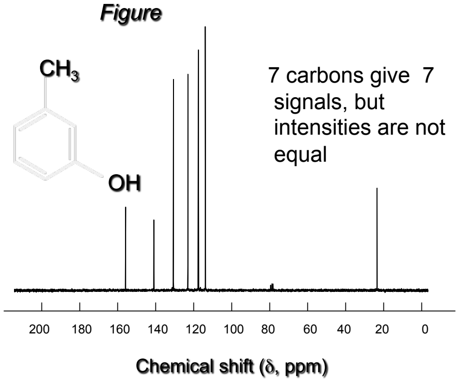
# Question

- In the $^{13}$C-NMR spectrum 1,2,3,5 -tetramethylbenzene, how many peaks are **more shielded** than δ 80 ppm?
- A) 1
- B) 2
- C) 3
- D) 4

## $^{13}$C NMR and Peak Intensities

Pulse-FT NMR distorts intensities of signals. Therefore, peak heights and areas can be deceptive.

## *Figure*



7 carbons give 7 signals, but intensities are not equal

## $^{13}$C—H Coupling

## *Peaks in a $^{13}$C NMR spectrum are typically singlets*

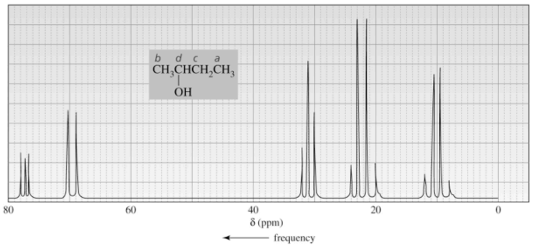
$^{13}$C—$^{13}$C splitting is not seen because the probability of two $^{13}$C nuclei being in the same molecule is very small.

$^{13}$C—$^{1}$H splitting is not seen because spectrum is measured under conditions that suppress this splitting (*broadband decoupling*).

# *DEPT $^{13}C$ NMR Spectra*

- DISTORTIONLESS ENHANCEMENT BY POLARIZATION TRANSFER (DEPT) $^{13}C$ NMR provides information the number of hydrogen atoms attached to each carbon.
- Full decoupled $^{13}C$ spectrum shows all carbon peaks.
- In a DEPT-90, only CH signals appear.
- In a DEPT-135, $CH_3$ and CH give (+) signals, and $CH_2$ give (–) signals.

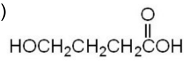
# *Proton-Coupled $^{13}C$ NMR of 2-Butanol*



# Question

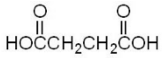
- Which compound has four signals in its $^{13}C$-NMR spectrum: a singlet, a doublet, a triplet,
- and a quartet.

- A)



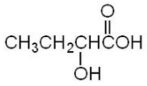
$HOCH_2CH_2CH_2\overset{\overset{O}{\|}}{C}OH$

B)



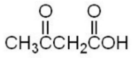
$HO\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{C}OH$

- C)



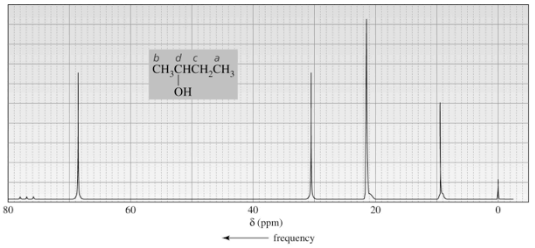
$CH_3CH_2\underset{\underset{OH}{|}}{C}H\overset{\overset{O}{\|}}{C}OH$

D)



$CH_3\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}OH$

# *Proton-Decoupled $^{13}C$ NMR of 2-Butanol*



**Using DEPT to Count the Hydrogens Attached to $^{13}C$**

Distortionless Enhancement of
Polarization Transfer
(De-coupling)

***Measuring a $^{13}C$ NMR spectrum involves***

1. **Equilibration of the nuclei between the lower and higher spin states under the influence of a magnetic field**
2. **Application of a radiofrequency pulse to give an excess of nuclei in the higher spin state**
3. **Acquisition of free-induction decay data during the time interval in which the equilibrium distribution of nuclear spins is restored**
4. **Mathematical manipulation (Fourier transform) of the data to plot a spectrum**

## *Measuring a $^{13}$C NMR spectrum involves*

Steps 2 and 3 can be repeated hundreds of times to enhance the signal-noise ratio

2. Application of a radiofrequency pulse to give an excess of nuclei in the higher spin state
3. Acquisition of free-induction decay data during the time interval in which the equilibrium distribution of nuclear spins is restored

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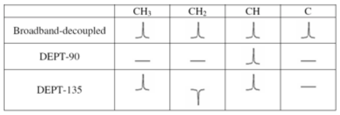
## *Measuring a $^{13}$C NMR spectrum involves*

In DEPT, a second transmitter irradiates $^1$H during the sequence, which affects the appearance of the $^{13}$C spectrum.

some $^{13}$C signals stay the same

some $^{13}$C signals disappear

some $^{13}$C signals are inverted



| | $CH_3$ | $CH_2$ | CH | C |
|---|---|---|---|---|
| Broadband-decoupled | ⊥ | ⊥ | ⊥ | ⊥ |
| DEPT-90 | — | — | ⊥ | — |
| DEPT-135 | ⊥ | ⊤ | ⊥ | — |

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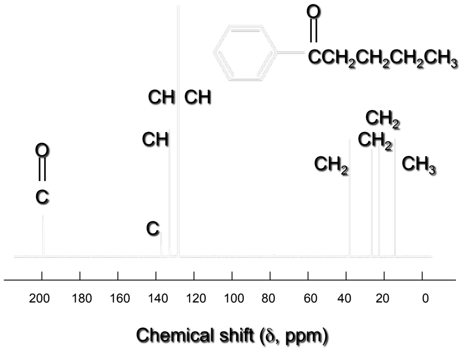
### *Figure #3*



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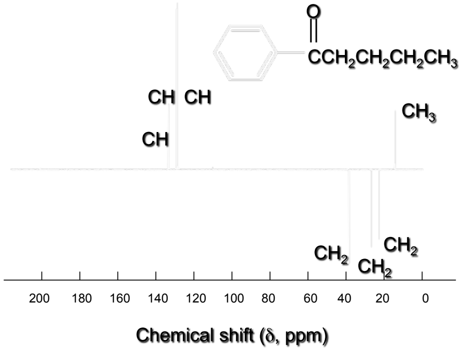
### *Figure #4*



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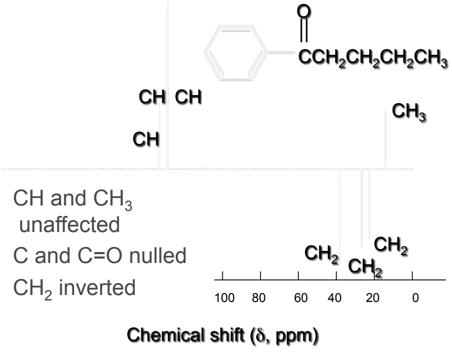
### *Figure #5*



CH and $CH_3$ unaffected

C and C=O nulled

$CH_2$ inverted

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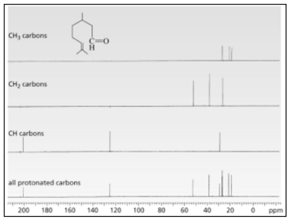
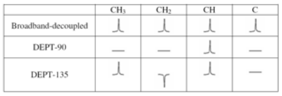
## *DEPT $^{13}$C NMR distinguish among $CH_3$, $CH_2$, and CH groups*





| | $CH_3$ | $CH_2$ | CH | C |
|---|---|---|---|---|
| Broadband-decoupled | ⊥ | ⊥ | ⊥ | ⊥ |
| DEPT-90 | — | — | ⊥ | — |
| DEPT-135 | ⊥ | ⊤ | ⊥ | — |

# Question

- Which isomer of $C_6H_{14}$ is consistent with the following $^{13}$C-NMR spectrum data? $\delta$ 11.1
- ($CH_3$); $\delta$ 18.4 ($CH_3$); $\delta$ 29.1 ($CH_2$); $\delta$ 36.4 (CH)
- A) *n*-hexane
- B) 2,3-dimethylbutane
- C) 2-methylpentane
- D) 3-methylpentane

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# Question

- Identify the $C_4H_{10}O$ isomer on the basis of its $^{13}$C-NMR spectrum data: $\delta$ 31.2 ($CH_3$, 3C); $\delta$ 68.9 (C, 1C)
- A) 2-butanol
- B) 2-methyl-2-propanol
- C) 1-butanol
- D) $CH_3CH_2$-O-$CH_2CH_3$

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# Question

- For an isomer of $C_7H_5Cl_3O$: its IR spectrum indicates an ether function, the $^1$H NMR indicates one methyl group ($CH_3$-) bonded to an oxygen atom. How many isomers (total) are possible for the molecular formula?

- A) *2*
- B) 3
- C) 4
- D) 5
- E) 6

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# Question

- Of the total number of possible isomers of $C_7H_5Cl_3O$ they produce two $^{13}$C NMR sets: one set respectively has 5 peaks and the other 7 peaks in the decoupled $^{13}$C NMR spectra? Which tri-chloro substitution pattern would produce 5 peaks?

- A) 2,4,5
- B) 2,3,4
- C) 2,3,5
- D) 2,4,6
- E) 2,3,6

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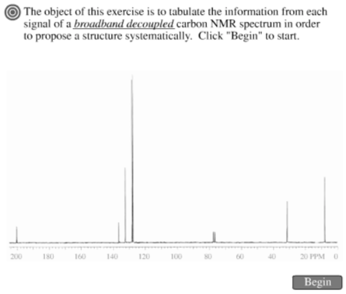
http://chemconnections.org/organic/Movies%20Org%20Flash/nmr-C13-flash/AADFQQZ0.swf



The object of this exercise is to tabulate the information from each signal of a *broadband decoupled* carbon NMR spectrum in order to propose a structure systematically. Click "Begin" to start.

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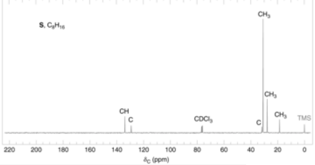
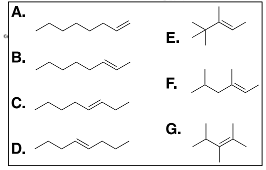
# Question

Which compound corresponds to the 13C NMR spectrum below?





- A. B
- B. D
- C. E
- D. F
- E. G

## 2D NMR Methods

- COSY: Carbon Hydrogen Correlation Spectroscopy
- HETCOR: Heteronuclear Chemical Shift Correlation
- NOESY: Nuclear Overhauser Effects Spectroscopy
- TROSY: Translation Relaxation Optimized Spectroscopy

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## 2D NMR:
## COSY AND HETCOR

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## *2D $^1$H NMR Terminology*

**1D NMR = 1 frequency axis**
**2D NMR = 2 frequency axes**

**COSY = Correlated Spectroscopy**

**$^1$H-$^1$H COSY provides connectivity information by allowing one to identify spin-coupled protons.**

**x,y-coordinates of cross peaks are spin-coupled protons**

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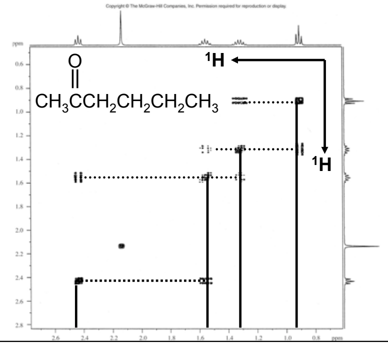
## *$^1$H-$^1$H COSY*



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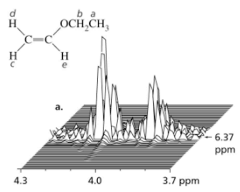
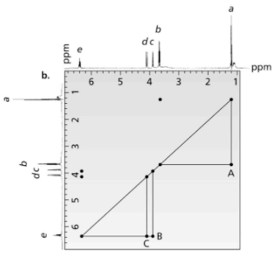
The COSY spectrum identifies protons that are coupled
COSY: Correlation Spectroscopy





Cross peaks indicate pairs of protons that are coupled

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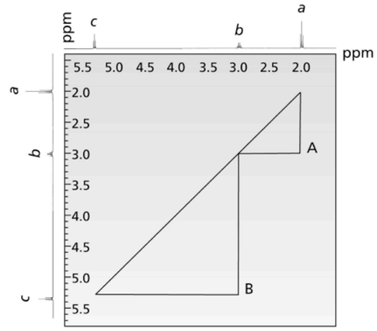
## COSY Spectrum of 1-Nitropropane

$\overset{a}{CH_3}\overset{b}{CH_2}\overset{c}{CH_2}NO_2$



## HETCOR

*Carbon - Hydrogen*

**$^1$H and $^{13}$C spectra plotted separately on two frequency axes.**

**Coordinates of cross peak connect signal of carbon to protons that are bonded to it.**

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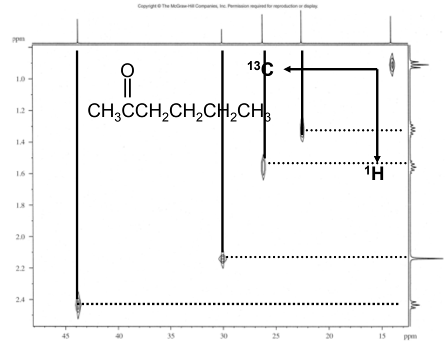
## $^1$H-$^{13}$C HETCOR



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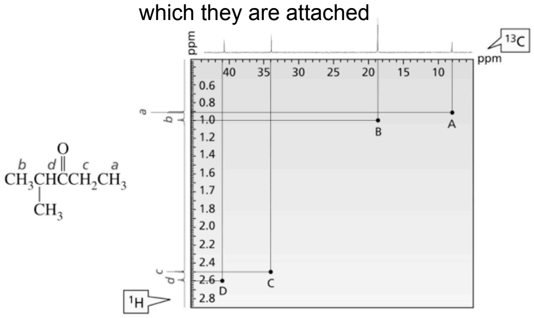
The HETCOR spectrum of 2-methyl-3-pentanone indicates coupling between protons and the carbon to which they are attached



HETCOR: Heteronuclear Chemical Shift Correlation

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# 2D-NMR Methods

- NOESY: Nuclear Overhauser Effects Spectoscopy
- TROSY: Translation Relaxation Optimized Spectroscopy