# 13-Carbon Spectra

## One Pulse and Multi-pulse Experiments

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**Common types of NMR experiments:**

**13-C NMR**

a. Experiment – High field $^{13}$C-NMR; H-decoupled.

b. Spectral Interpretation

i. Chemical Shift (ppm) ~220ppm, indicates chemical environment.
ii. H-BB decoupled spectra; no splitting information.
iii. Solvent peak (**C**$DCl_3$) at ~77 ppm.
iv. Quaternary Cs often give small peaks.
v. Acquisition not optimized for integration; no information on the number of carbon atoms.

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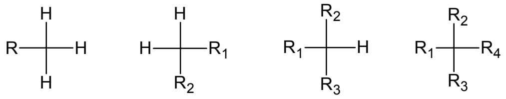
1.1% of naturally occurring carbon is 13C and its has a nuclear spin of ½.

Low abundance and low $\gamma$ leads to lower sensitivity of the 13C-NMR experiment requiring much more scans per spectrum, compared with H-NMR spectroscopy.

The low abundance makes probability of two 13C carbon isotopes occurring next to each other in a given compound is very low.

Organic compounds has four types of commonly encountered C.



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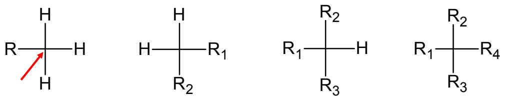
Un-decoupled 13C NMR Spectra.



13-C-NMR spectrum of a methyl 13-C is a quartet.

13-C-NMR spectrum of a methylene 13-C is a triplet.

13-C-NMR spectrum of a methine 13-C is a doublet.

13-C-NMR spectrum of a quaternary 13-C is a singlet.
$J_{C\text{-}H}$ =125 – 250Hz leads to extensive overlap – making Interpretation difficult (‘multiplets are not ‘localized’ well).

The position of resonance (chemical shift) is dependent on the degree of shielding of the particular carbon.

## H–Broad-band decoupled 13C NMR Spectra.

Decoupling protons simplifies the 13C NMR spectra.

Broad-band decoupling is necessary to decouple all H atoms.

The resulting 13-C spectrum consists of singlets. Each singlet arising from each type of C atom in the molecule at specific chemical shifts; carries no coupling information.

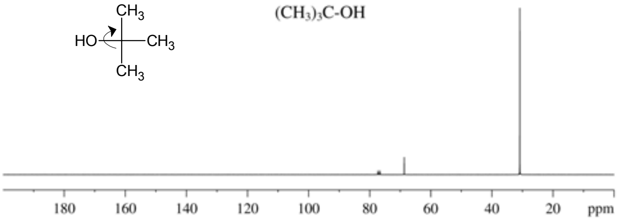
Decoupling gives rise to NOE and NOE is not uniform on all C atoms. Depends on the number of H's attached and other factors. Different relaxation times of 13C nuclei further changes signal intensities.

These makes H – Broad-band decoupled 13C NMR Spectra unsuitable for the quantification of C.

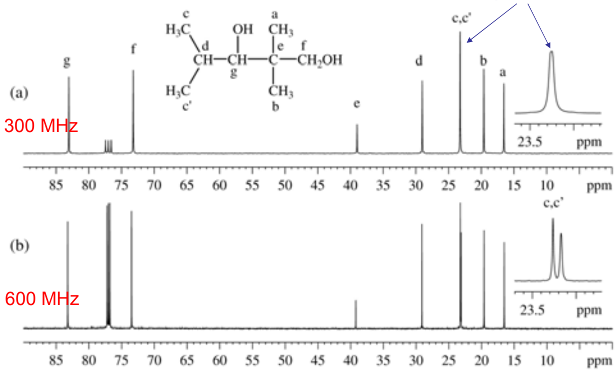
## Chemical Shift Equivalence

Symmetry related C atoms in a molecule have chemical shift equivalence.

Rapid exchange would also make otherwise nonequivalent C atoms equivalent.



Coincidental equivalence

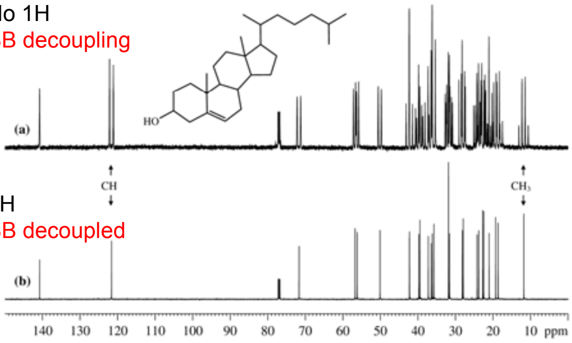


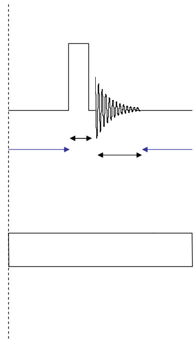
300 MHz

600 MHz

No 1H
BB decoupling

1H
BB decoupled

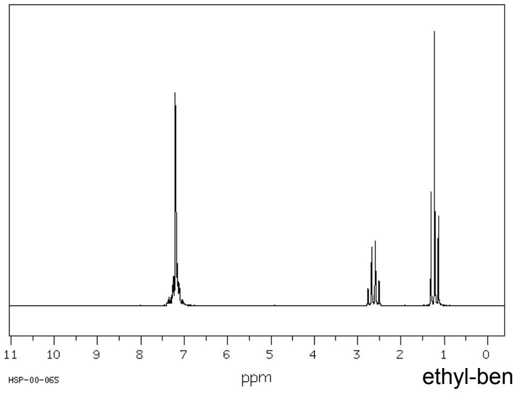




Channel 1
Observe
13C

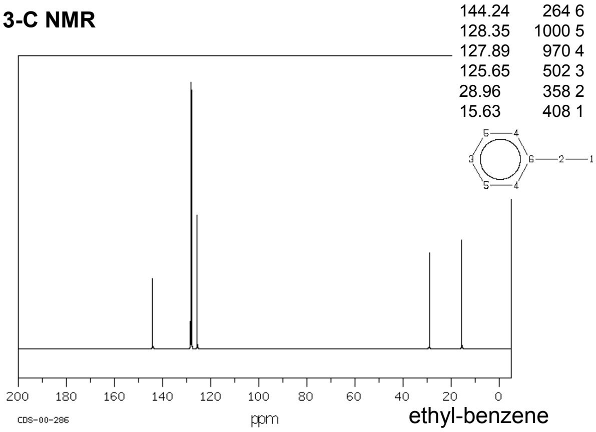
Channel 2
BB decoupling
1H

## 1-H NMR



ethyl-benzene

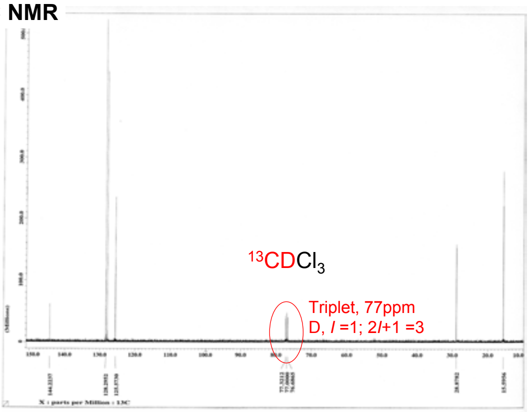
## 13-C NMR



| | | |
|---|---|---|
| 144.24 | 264 | 6 |
| 128.35 | 1000 | 5 |
| 127.89 | 970 | 4 |
| 125.65 | 502 | 3 |
| 28.96 | 358 | 2 |
| 15.63 | 408 | 1 |

ethyl-benzene

## 13-C NMR



$^{13}CDCl_3$

Triplet, 77ppm
D, *I* =1; 2*I*+1 =3

ethyl-benzene

## 13CNMR Chemical shifts

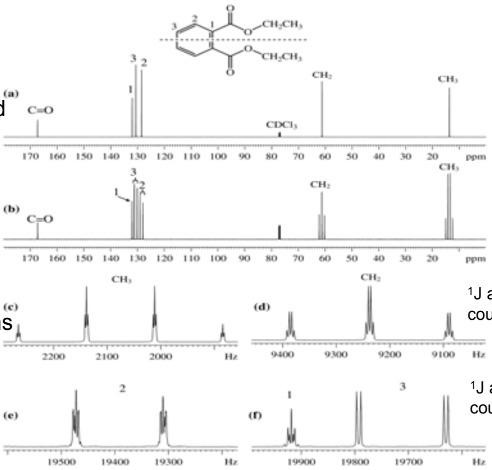
13C spectral chemical shifts ranges to >200ppm.
IR spectral information.

δ depends on the electronic environment.

General rule; δ: $sp^2 > sp > sp^3$
electro-negative atoms cause downfield shift
pi bonds cause downfield shift

Number of signals equals the number equivalent carbons and would reveal information about molecular symmetry

$(CH_3)_4Si$=0.00 ppm (singlet) $CDCl_3$(solvent)=77.0 ppm (triplet)



decoupled

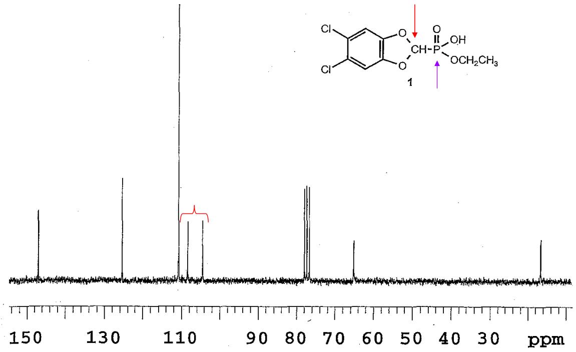
coupled

coupled expansions

$^1J$ and $^2J$ coupling

$^1J$ and $^2J$ coupling

## 13C NMR



## The importance of $T_1$ and NOE in Routine 13C NMR

13C relaxation times has wide variations, depends on the kind of C atom. Relaxation delay is an important issue.

Optimum repetition time $T_r$ (=$T_{aq}$+ $R_d$) used for sample with a lower tilt angle (Ernst angle) θ, different from π/2, using;

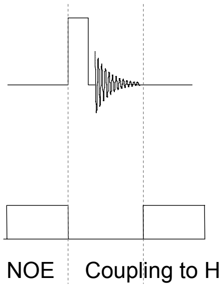
$$\cos\theta = e^{-(T_r/T_1)}$$

H-BB decoupling affects the 13C populations, again depends on the kind of C atoms. Thus BB decoupled 13C spectra are not suitable for quantification.

BB coupling loses coupling with H atoms, and therefore coupling constant information as well.

## Gated Decoupling – Coupled Spectrum

Coupling information $^1J_{CH}$, $^3J_{CCH}$ etc are very useful in solving structural/stereo chemical problems. Gated decoupling allows us to determine J values.



Channel 1
Observe
13C

Channel 2
BB decoupling
1H

NOE    Coupling to H

Allows the NOE to build up before acquiring the FID, *Coupling* occurs during FID (*faster* than NOE decay)

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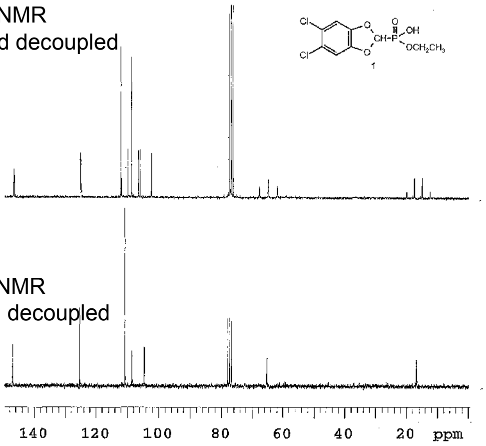

13C NMR
Gated decoupled

13C NMR
H-BB decoupled

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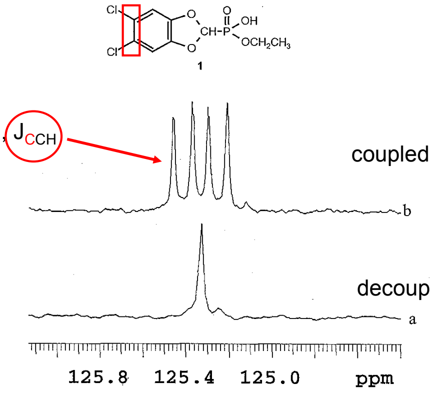

Both $J_{CH}$, $J_{CCH}$

coupled

decoupled

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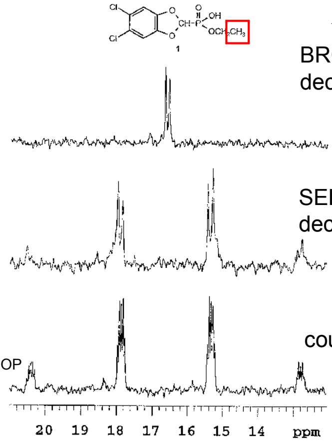


$J_{CCOP}$

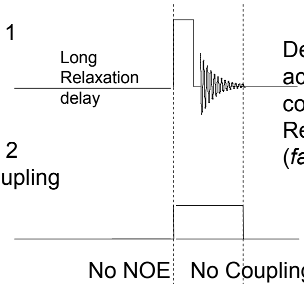
BROADBAND decoupled

SELECTIVE decoupled $OCH_2$

$J_{CH}$, $J_{CCH}$, $J_{CCOP}$

coupled

## Quantitative 13C Spectra (Inverse Gated Decoupling)



Channel 1
Observe
13C

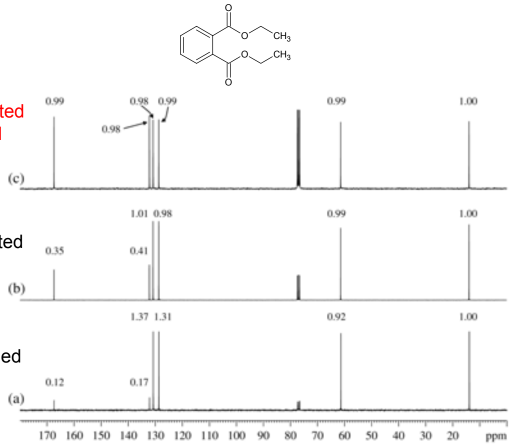
Long
Relaxation
delay

Channel 2
BB decoupling
1H

No NOE

No Coupling to H

Decoupling during the acquisition of *FID*, coupling removed. Retains area information (*faster* than NOE buildup).



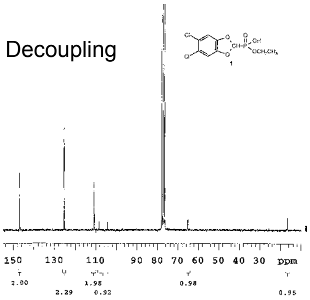
Inversed Gated
H decoupled
Delay>5$T_1$

Inversed Gated
H decoupled
Delay<$T_1$

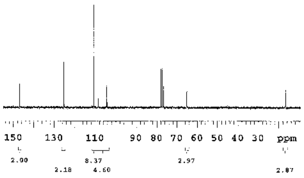
HBB decoupled

13C NMR Inverse Gated Decoupling

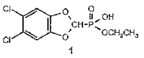
±10% accuracy



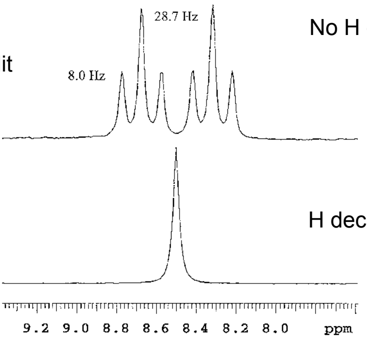
13C NMR



## 31P Spectra



Doublet split
into triplets



No H decoupling

H decoupled

## **APT (Attached Proton Test)**

The multiplicity of the C atom can de determined with a shorter time using the APT procedure.

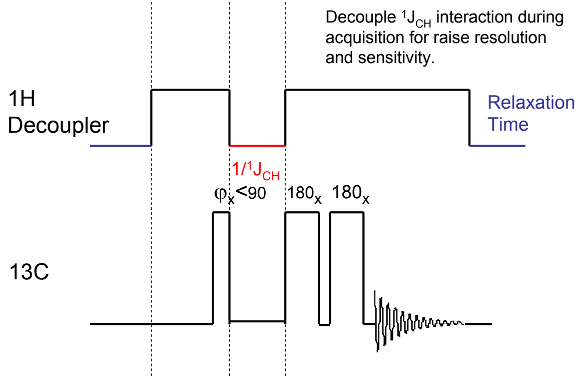
According to their multiplicity, the peaks would appear in the positive and negative direction in the output.

The attached proton test is a 1D $^{13}$C NMR experiment. The APT experiment yields methine (CH) and methyl ($CH_3$) signals positive and quaternary (C) and methylene ($CH_2$) signals negative. It is slightly less sensitive than DEPT but it is a single experiment that generates all carbon signals at once. (DEPT suppresses quaternary carbons and requires up to three different acquisitions to yield full results.)

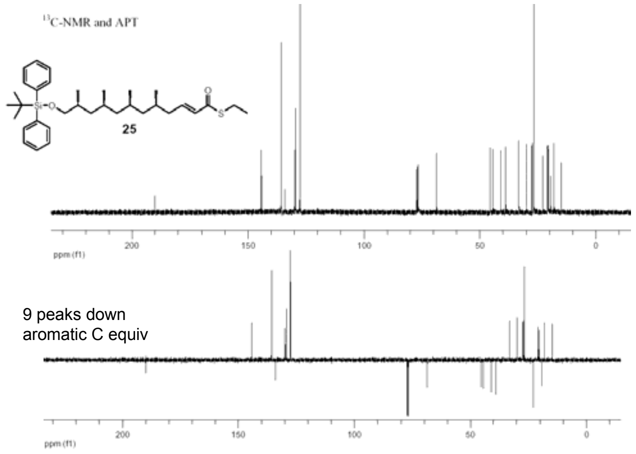
APT uses $^1J_{CH}$ interaction to change sign of peaks and hence yields multiplicity information.

| APT | C | CH | $CH_2$ | $CH_3$ |
|---|---|---|---|---|
| | - | + | - | + |

APT Pulse Sequence



Decouple $^1J_{CH}$ interaction during acquisition for raise resolution and sensitivity.



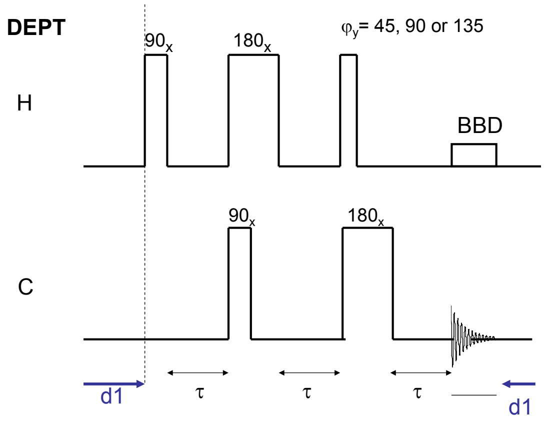
9 peaks down aromatic C equiv

## DEPT (Distortionless Enhancement by Polarization Transfer)

According to the multiplicity, the peaks appear in the positive and negative direction except quaternary C do not produce a signal.

DEPT experiment is slightly more sensitive than APT and can fully separate the carbon signals.

Run three times with different final pulse angles and compare with the regular 1H BB decoupled 13-C spectrum in order to obtain a full analysis.



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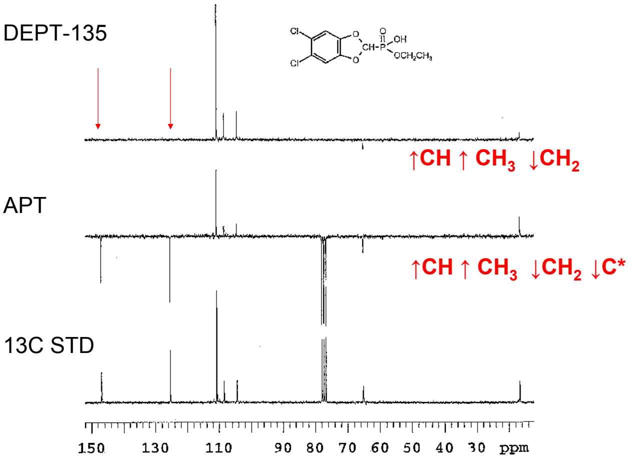
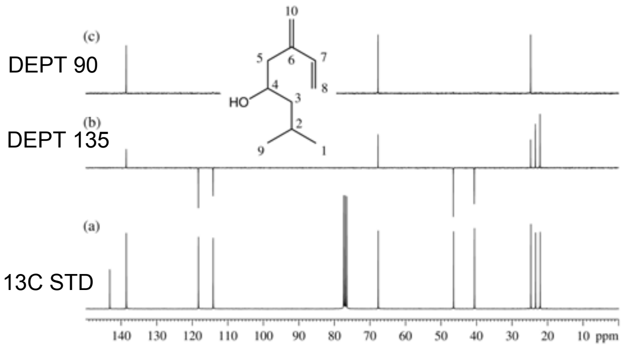
## DEPT (Distortion less Enhancement by Polarization Transfer)

DEPT- 45 yields CH, $CH_2$ and $CH_3$ signals positive, DEPT- 90 yields only CH signals and DEPT-135 yields CH and $CH_3$ positive while $CH_2$ is negative.

Standard procedure; **DEPT-135**. Distinguishes C with odd and even number of attached H atoms (oppositely phased).

| multiplicity | DEPT - 45 | DEPT - 90 | DEPT - 135 | APT |
|---|---|---|---|---|
| C | No signal | No signal | No signal | - |
| CH | + | + | + | + |
| $CH_2$ | + | No signal | - | - |
| $CH_3$ | + | No signal | + | + |




(c)
DEPT 90
10
5
6
7
4
8
HO
3
(b)
DEPT 135
2
9
1
(a)
13C STD
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm