NMR V

Integration

D_2O Exchange

Summary

Practice

Ref 9: 3D, 8; (8th ed.)
9: 2B, 3, 10; (9th ed.)

Prob 9: 29, 31, 33, 39; (8th ed.)
9: 28, 30, 32, 38; (9th ed.)

Adv Rdg 13: (1 - 9); 1, 2B, 7, 9 (both ed^{ns})

Integration

- signal intensity ∝ # of H's

  use:

  - peak height, if signals sharp (esp. singlets)
  - area under signal;

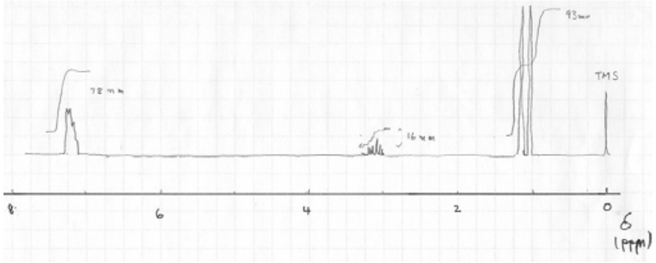
    normally recorded by computer as

    "integration trace"

- to be practiced in lab

  - in exam: (# of H's) / signal will be given

Example



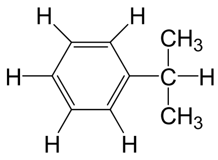
ratio 78 : 16 : 93

÷16

4.87 : 1 : 5.81

nearest integer 5 : 1 : 6

∴

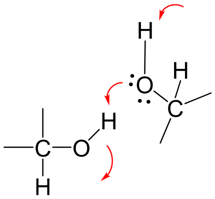


D_2O Exchange Technique

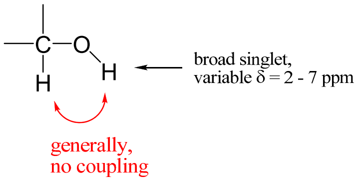
- identifies **acidic H's**
- applies to –OH, –CO_2H & other acidic H's

Explanation

Normally, these kinds of H's are subject to H-Bonding; can easily move , have no fixed partner



H moving too fast and NMR can't see, therefore no coupling



D_2O echange ...

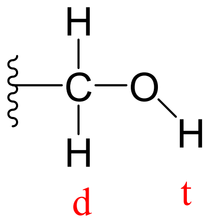
However,

if alcohol (or other acidic ...) sample is very pure,

then exchange process is slow and

NMR can see fixed relationship;

i.e. coupling is apparent.

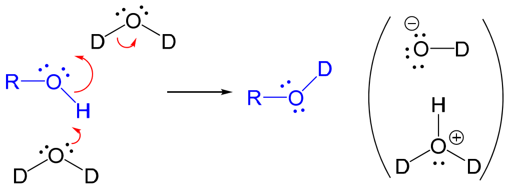


J = 7 Hz

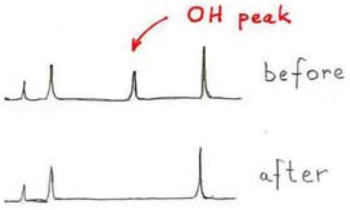
D_2O Exchange Practice

- used to detect O–H, ...
- Process: • run nmr; add D_2O; run nmr again
  • compare "before" and "after" runs

Mech.



Illustration



Steps in NMR Analysis

(spectrum → structure)

1.) # of signals (locate, label, count)

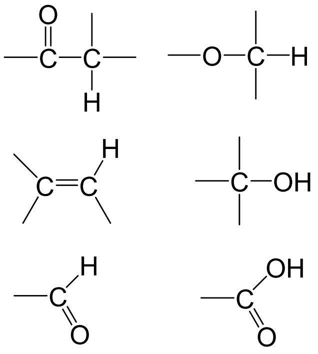
→ # of non- equiv. H's

(may be complicated by overlap of signals)

2.) read δ values ,

assign functionality, tentatively (±); esp.

sat^d H; aromatic H



NMR Analysis

3.) integration

→ # of H's per signal

4.) splitting pattern

→# of neighboring H's &

their structural relationship

5.) take other info. into account, if available:

MM, MF, D of U, IR, UV ....

6.) be flexible;

use trial & error approach

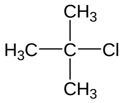
until everything fits.

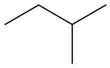
Exercises

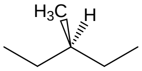
1.) More: “Non-equivalent Protons”

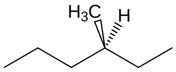
Assess the # of non-equivalent H’s

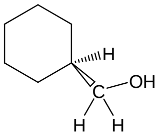
in the following molecules:

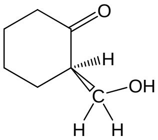




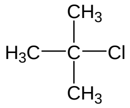
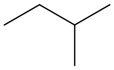
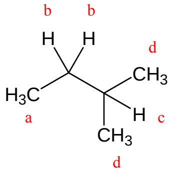
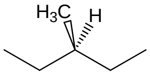
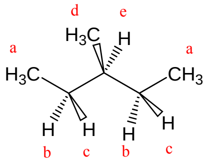
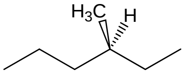
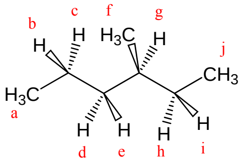




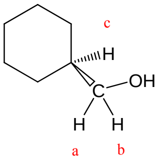




Answers

molecule	analysis	# of non-equivalent H's
	all equivalent	1
		4
		5
		10

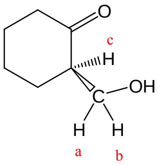
Answers



H_a, H_b are enantiotopic = equivalent
give 1 signal

coupled to H_c only;
therefore 1 doublet (for 2 H's)

H_c has 6 vicinal H's;
let's assume all J's are identical;
then the signal is a septet



H_a, H_b are diastereotopic = non-equivalent
give 2 signals

H_a: coupled to H_b and H_c ;
therefore, 1 doublet of doublets (4 lines)
(expect J_{ab} not same as J_{ac})

H_b: coupled to H_a and H_c ;
1 doublet of doublets (4 lines) ...;

H_c: has 4 vicinal H's;
therefore, in theory, d/d/d/d;
let's assume all J's are identical;
then the signal is a quintet

2.) Inspect and Analyze

NMR Charts from Solomons

8th edn : 9.15, 9.18, 9.20 9.21, 9.23, 9.25

9th edn : 9.17, 9.21, 9.01 9.22, 9.25, 9.27

Solomons Fig. 9.17

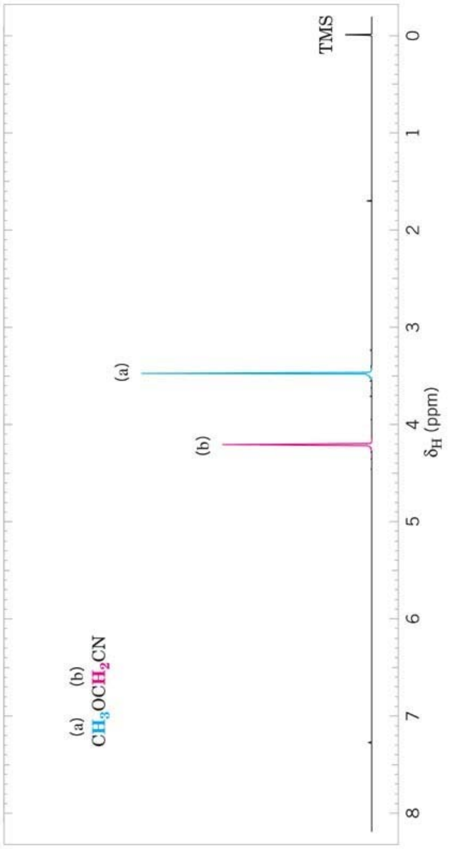


FIGURE 9.17 The 300-MHz ^1H NMR spectrum of methoxyacetonitrile. The signal of the enantiotopic protons *(b)* is not split.

Solomons Fig. 9.21

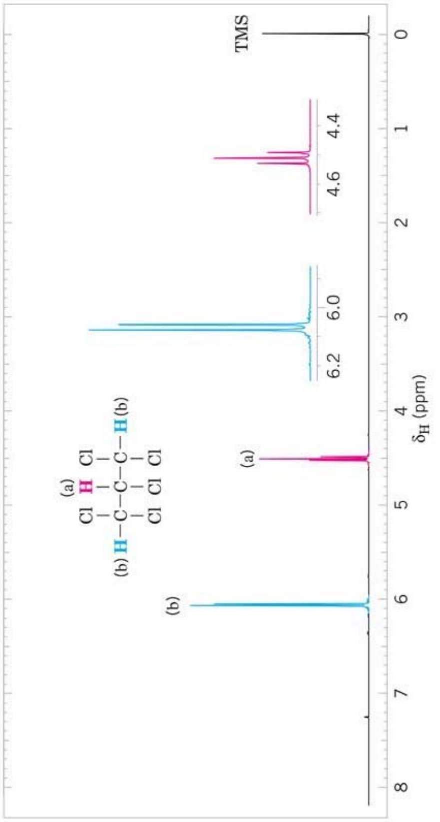


FIGURE 9.21 The 300-MHz ^1H NMR spectrum of 1,1,2,3,3-pentachloropropane. Expansions of the signals are shown in the offset plots.

Solomons Fig. 9.01

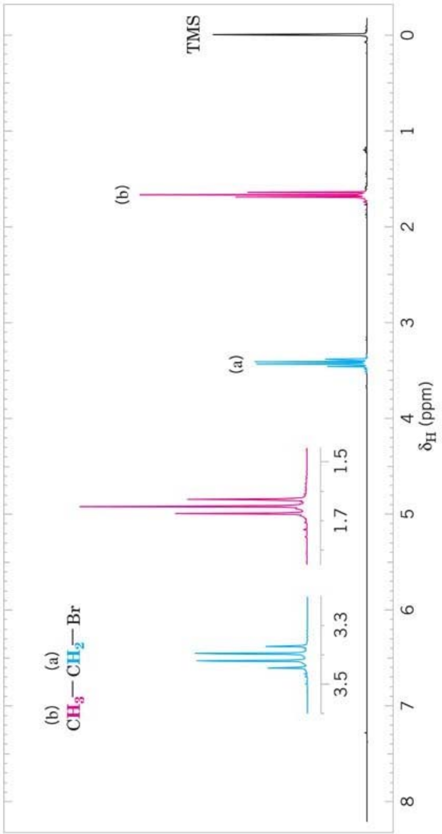
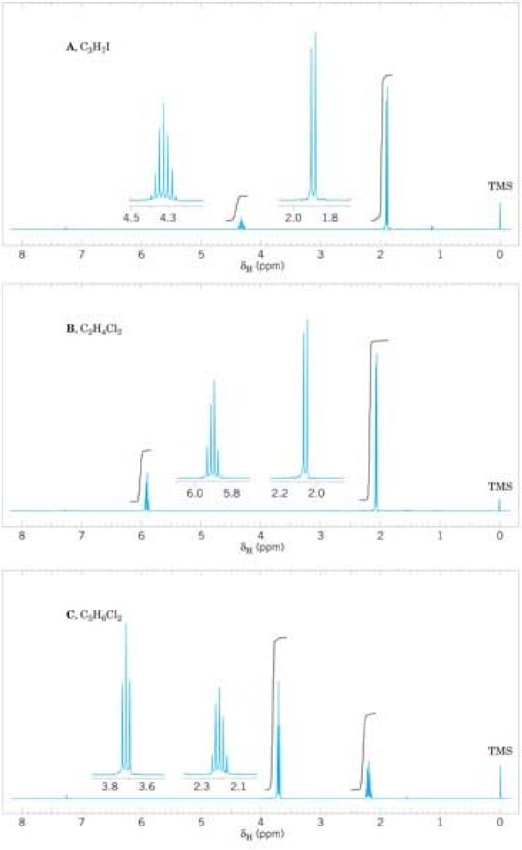


FIGURE 9.1 The 300-MHz ^1H NMR spectrum of 1-bromoethane (ethyl bromide). Expansions of the signals are shown in the offset plots.

Solomons Fig 9.22



Solomons Fig.9.25

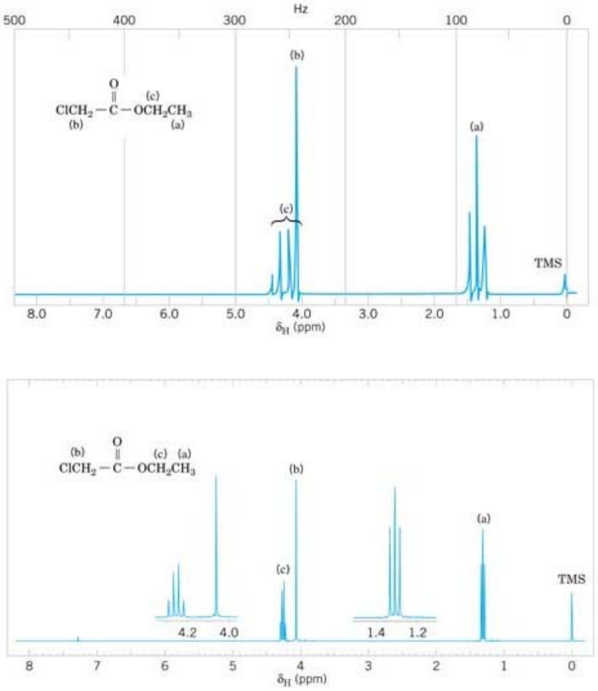


FIGURE 9.25 *(Top)* The 60-MHz ^1H NMR spectrum of ethyl chloroacetate. Note the overlapping signals at δ 4. *(Bottom)* The 300-MHz ^1H NMR spectrum of ethyl chloroacetate, showing resolution at higher magnetic field strength of the signals that overlapped at 60 MHz. Expansions of the signals are shown in the offset plots.

Solomons Fig.9.27

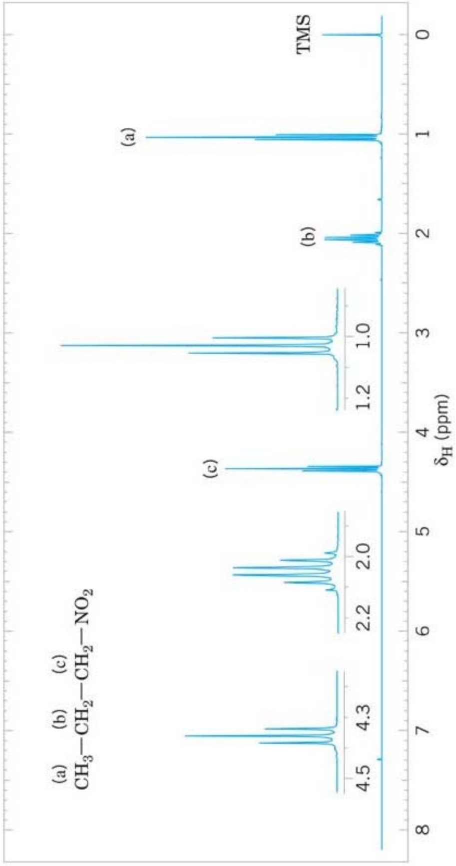
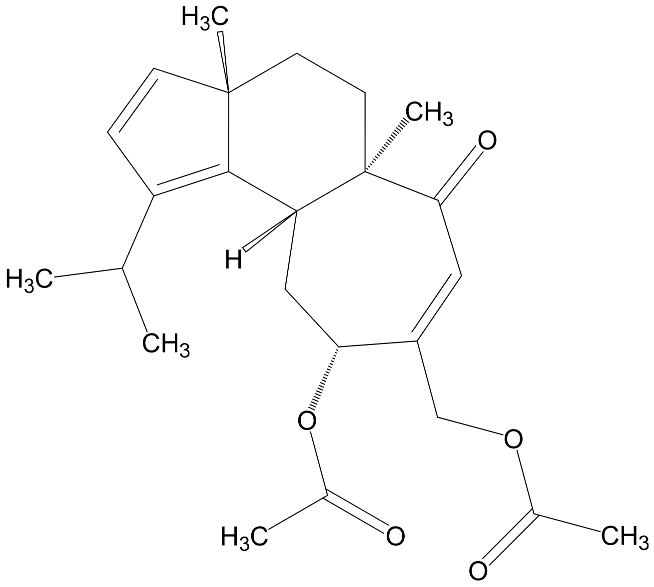


FIGURE 9.27 The 300-MHz ^1H NMR spectrum of 1-nitropropane. Expansions of the signals are shown in the offset plots.

HT Special: Diacetylallocyathin B_3

Molecular Structure



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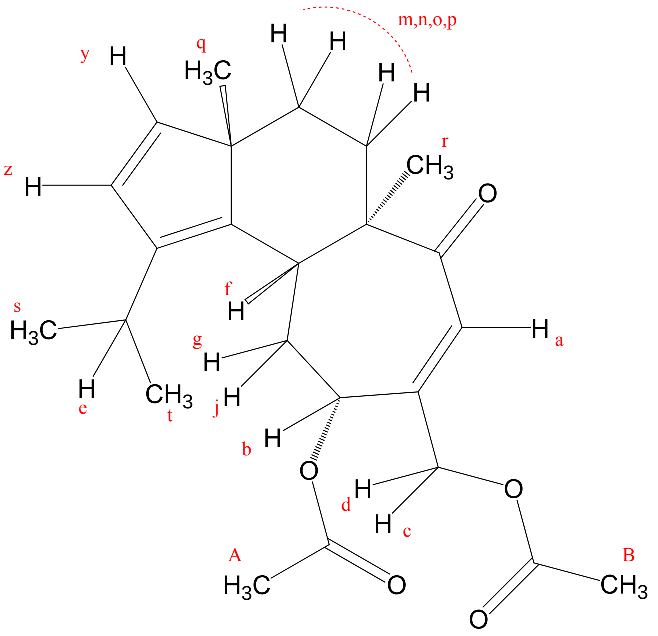
with H's identified

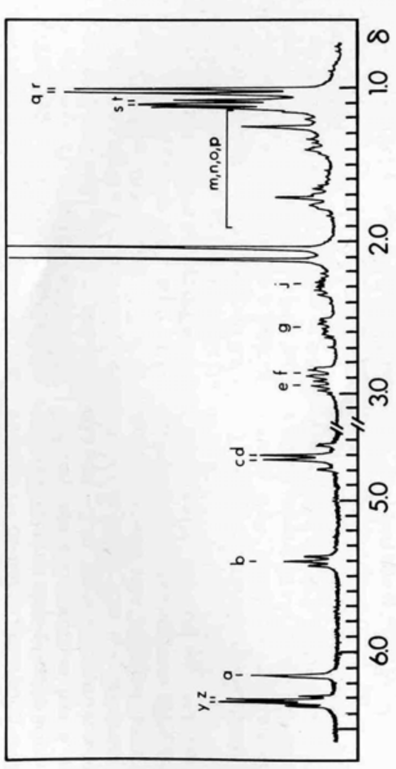


NMR Analysis: diacetylallocyathin B_3

proton ID	δ (ppm)	splitting pattern
y	~ 6.3	d, tilted
z	~ 6.3	d, tilted
a	~ 6.2	s, broad
b	5.5	t (or d of d)
c, d	~ 4.8	2 doublets, tilted
e	~ 3	septet
f	~ 3	d of d (or t)
g, j	2.6, 2.3	2 d of d of d
m, n, o, p	1.2 – 1.9	unresolved
s, t	~ 1	2 doublets
q, r	~ 1	2 singlets
A	~ 2.1	s
B	~ 2.1	s

NMR Spectrum of "Cyathin Derivative"

AYER AND TAUBE: METABOLITES OF CYATHUS HELENAE



1. Nuclear magnetic resonance spectrum (220 MHz) of *O,O*-diacetylallocyathin B_3 in $CDCl_3$.

NMR of "Cyathin", Details

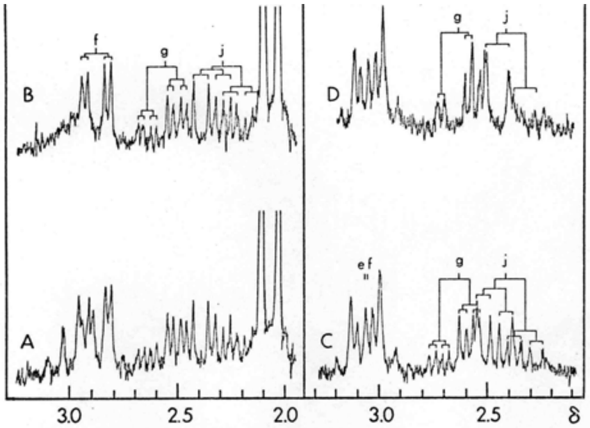


Figure 36. Portions of 100 MHz nmr spectra of O,O-diacetylallocyathin B_3
A, undecoupled ($CDCl_3$); B, signals s and t irradiated (see Fig. 35); C, undecoupled (C_6D_6); D, signal b irradiated.