NMR V

Integration

D_2O Exchange

Summary

Practice

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

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

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

Integration

• signal intensity $\propto$ # of H's

use:

• peak height, if signals sharp (esp. singlets)

• area under signal;

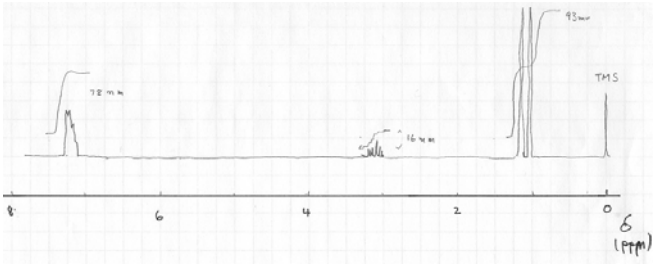
normally recorded by computer as

"integration trace"

• to be practiced in lab

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

Example



ratio

nearest
integer

$\therefore$

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 exchange ...

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.

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.

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

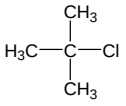
until everything fits.

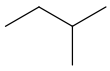
Exercises

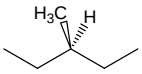
1.) More: "Non-equivalent Protons"

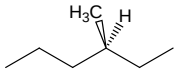
Assess the # of non-equivalent H's

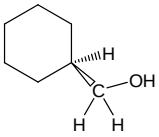
in the following molecules:

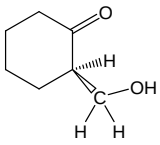






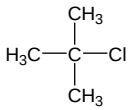


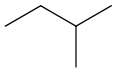


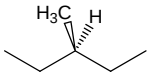


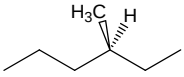
Answers

molecule	analysis	# of non-equivalent H's

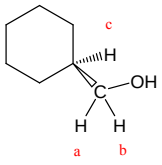


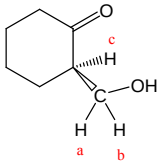






Answers





2.) Inspect and Analyze

NMR Charts from Solomons

8th ed^n : 9.15, 9.18, 9.20 9.21, 9.23, 9.25

9th ed^n : 9.17, 9.21, 9.01 9.22, 9.25, 9.27

Solomons Fig. 9.17

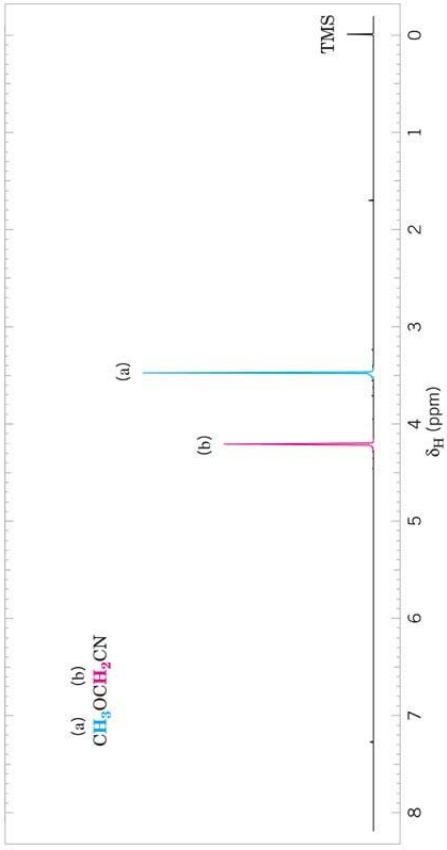


FIGURE 9.17 The 300-MHz ^{1}H NMR spectrum of methoxyacetonitrile. The signal of the enantiotopic protons *(b)* is not split.

Solomons Fig. 9.21

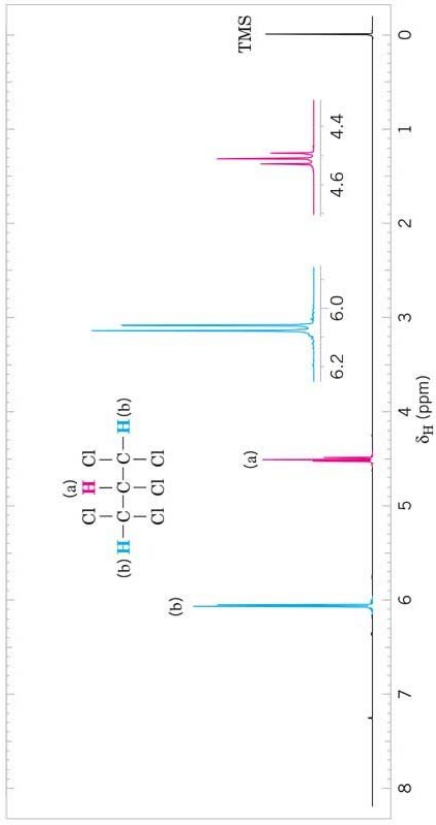


FIGURE 9.21 The 300-MHz ^{1}H NMR spectrum of 1,1,2,3,3-pentachloropropane. Expansions of the signals are shown in the offset plots.

Solomons Fig. 9.01

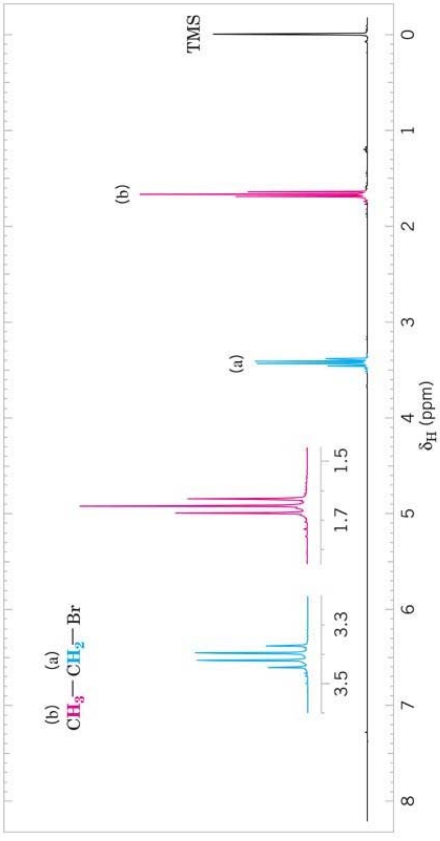
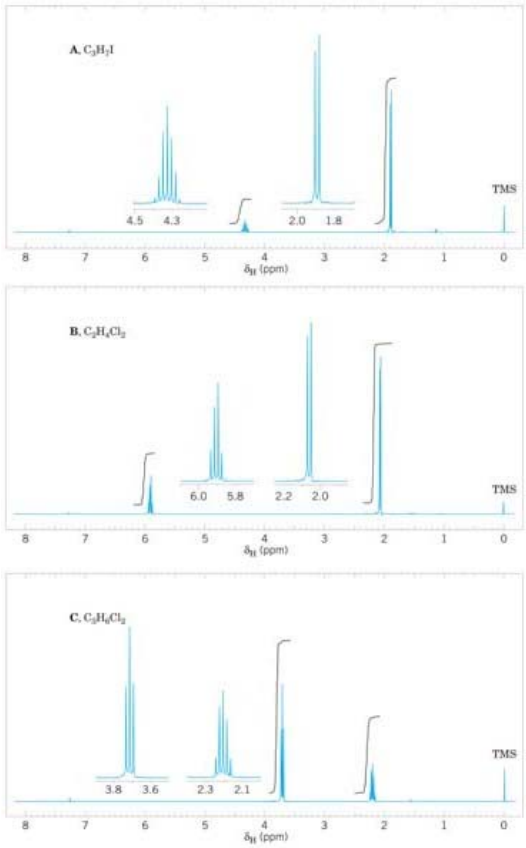


FIGURE 9.1 The 300-MHz ^{1}H NMR spectrum of 1-bromoethane (ethyl bromide). Expansions of the signals are shown in the offset plots.

Solomons Fig 9.22



Solomons Fig.9.25

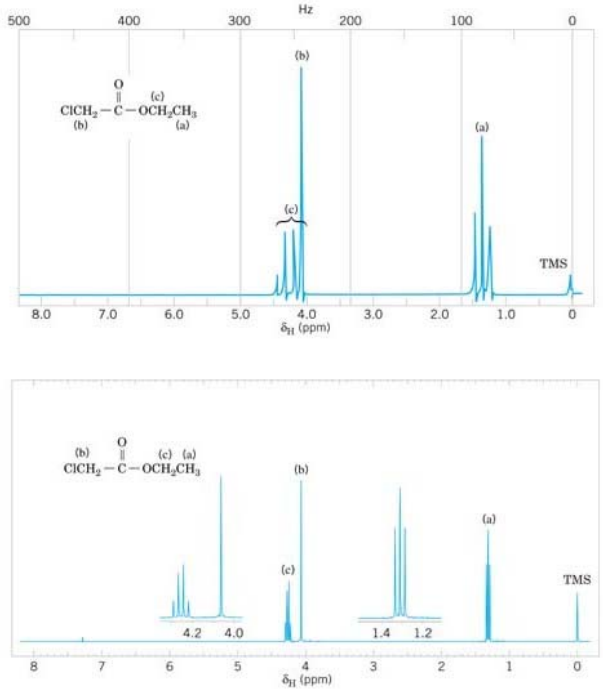


FIGURE 9.25 *(Top)* The 60-MHz ^{1}H NMR spectrum of ethyl chloroacetate. Note the overlapping signals at δ 4. *(Bottom)* The 300-MHz ^{1}H NMR spectrum of ethyl chloroacetate, showing resolution at higher magnetic field strength of the signals that overlapped at 60 MHz. Expansions of the signals are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

Solomons Fig.9.27

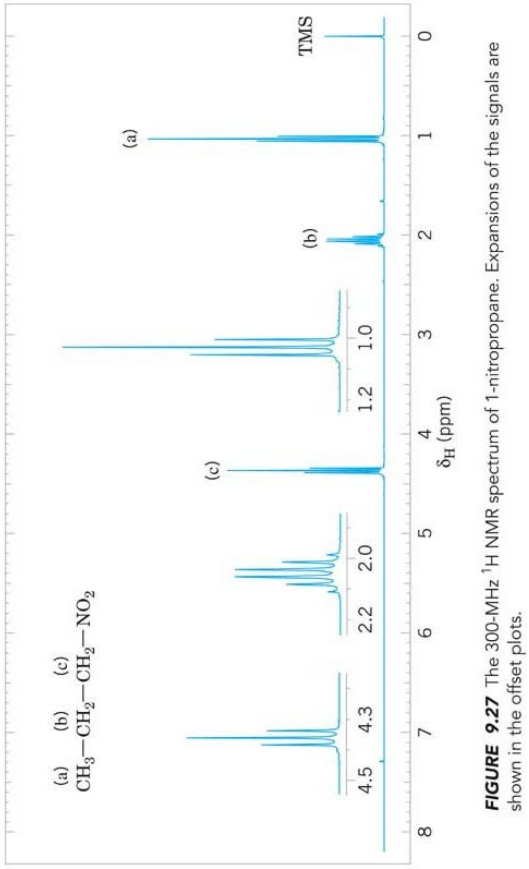
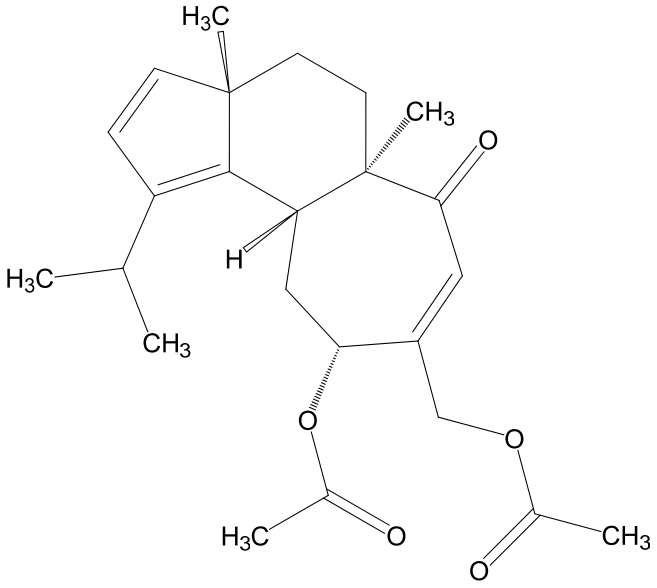


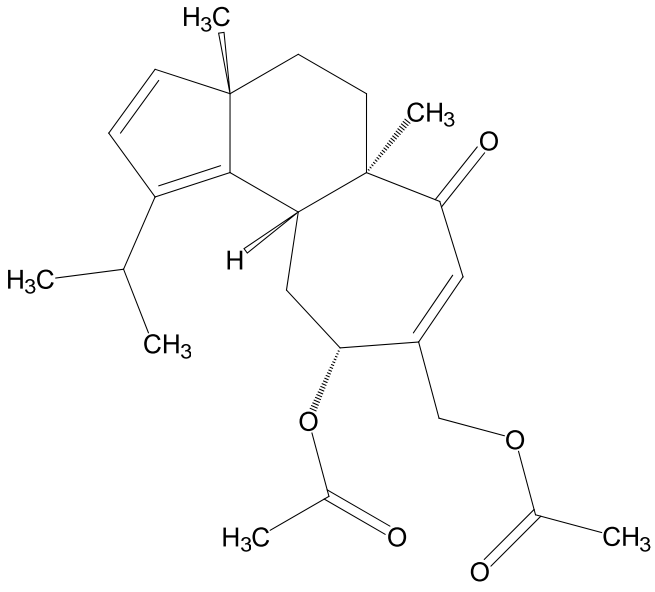
FIGURE 9.27 The 300-MHz ^{1}H NMR spectrum of 1-nitropropane. Expansions of the signals are shown in the offset plots.

HT Special: Diacetylallocyathin B_3

Molecular Structure



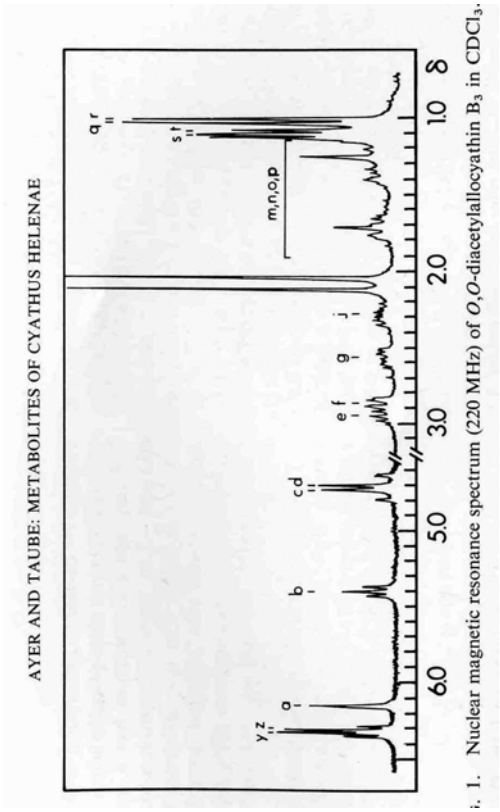
with H's identified



NMR Analysis: diacetylallocyathin B_3

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

NMR Spectrum of "Cyathin Derivative"



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

NMR of "Cyathin", Details

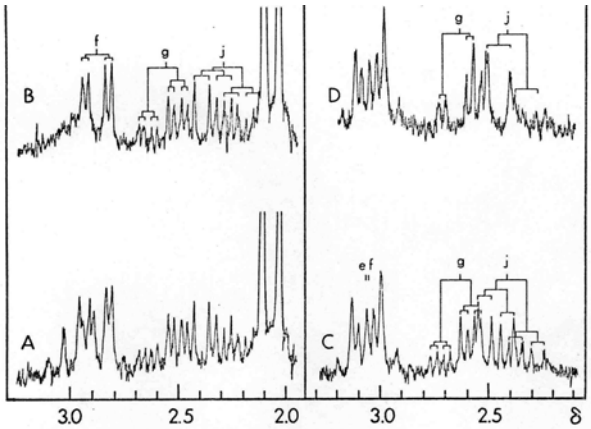


Figure 36. Portions of 100 MHz nmr spectra of O,O-diacetyl-allocyathin B_3
A, undecoupled ($CDCl_3$); B, signals s and t irradiated (see Fig. 35); C, undecoupled (C_6D_6); D, signal b irradiated.