Problem Set #6 ANSWERS

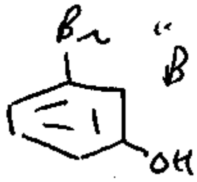
Chapt 6 #3: C_6H_5BrO # sites of unsat'n = $7 - \frac{6}{2} = 4$

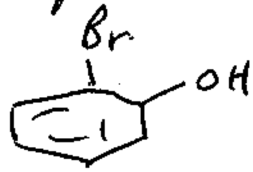
Broad solvent dependent peak is due to OH proton.

Integration results: looks like 4 aromatic protons

Possible Structures:


" " A


" " B


" " C

A can be ruled out because a symmetrical pattern would be seen in the aromatic region.

Need to analyze the spectrum to distinguish between B + C.

7.44 ppm region

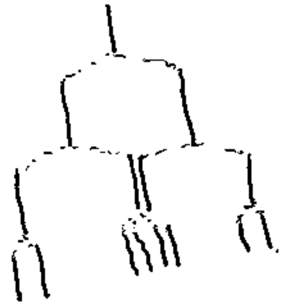
2236.67
− 2228.58
8.09 Hz

2235.06
2227.05
8.01 Hz

average = 8.05 + 1.6 Hz.

analysis & 7.0 ppm region is similar

7.22 ppm region



2168.00
2159.91
4.09.

2168.00
2160.68
7.32

2158.31
2150.99
7.32

8.09
7.32
1.6

Analysis of 6.8 ppm region is similar

∴ ortho disubstituted

must BE "C"

P.S#6 Answers

Chapt 6 #5: Here the spectral resolution does not permit ^4J's to be resolved.

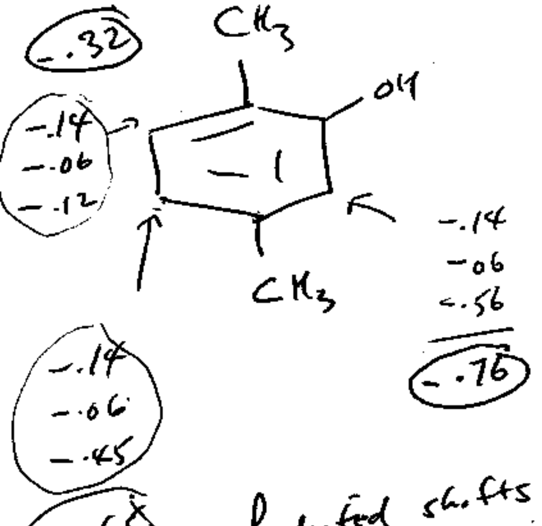
Hence peak at 6.65 is a singlet

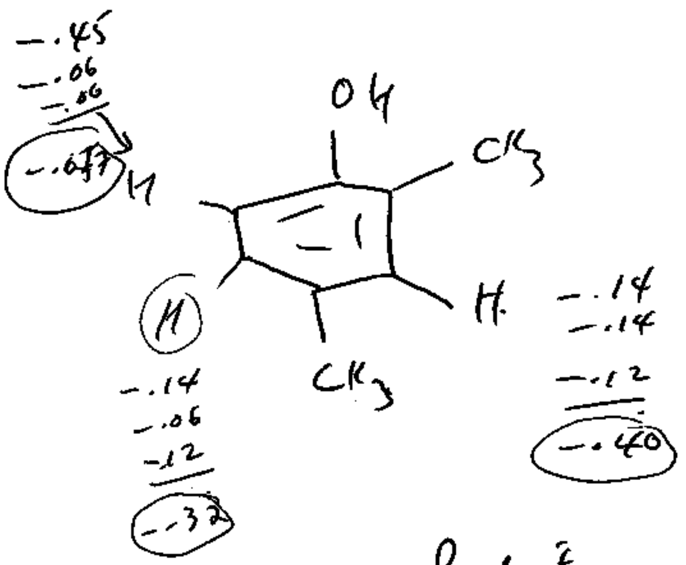
^3J is observed twice:

2094.31	1978.13
2086.59	1970.04
7.72	8.09

∴ Average is 7.9 ± 0.2 Hz

Using Appendix 6





Predicted shifts

$7.27 - .32 = 6.95$ (d)

$7.27 - .65 = 6.62$ (d)

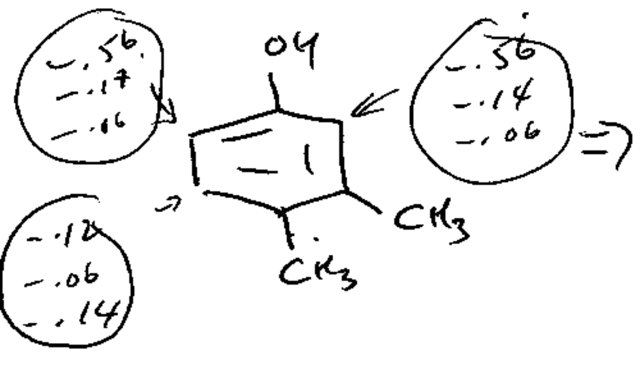
$7.27 - .76 = 6.51$ (s)

Predict

$7.27 - .57 = 6.70$ (d).

$7.27 - .32 = 6.95$ (d)

$7.27 - .40 = 6.87$ (s)



Predict:

$7.27 - .79 = 6.48$ (d).
$7.27 - .32 = 6.95$ (d)
$7.27 - .76 = 6.53$ (s)
} Best fit

P.S #6 ANSWERS

Chapt 6 #9: $C_{10}H_{15}N$: # sites unsat'n $= 11 - \frac{15}{2} + \frac{1}{2} = 4$

Integration of ¹H spectrum: $\underbrace{2:2:2:2:2:2:3}_{15\ H\text{'s}}$

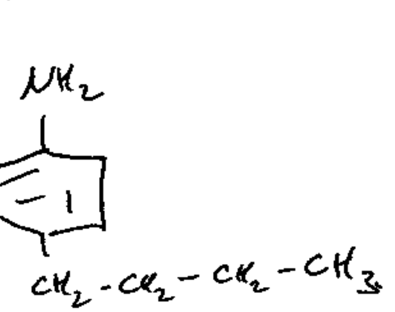
4 aromatics : 2 doublets ∴ Para-disubst'd.

peak at 3.5 – must be NH_2.

must also have (from coupling pattern) $\underset{\text{triplet}}{-CH_2} - \underset{\text{quartet}}{CH_2} - \underset{\text{doublet}}{CH_2} - CH_3$

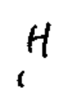
observed sextet is really an overlapped "triplet of quartets"

∴ Must be



Chapt 6 #13: $C_3H_7NO_2$: # sites of unsat'n $= 4 - \frac{7}{2} + \frac{1}{2} = 1$

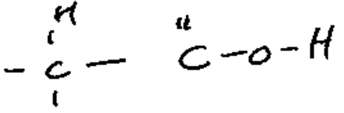
Must have a



$CH_3-\overset{H}{C}$

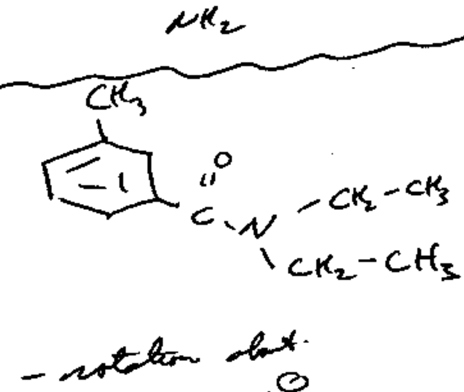
unit (doublet + quartet in ¹H).

So, must be



$CH_3-\underset{NH_2}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-H$ (alanine).

Chapt 6 #18:



At 360°, rapid rotation about $N-\underset{O}{\underset{\|}{C}}$ bond on nmr "timescale" – thus single triplet + quartet.

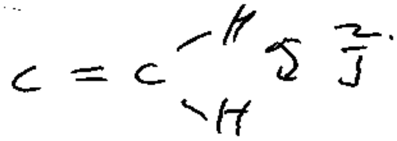
As temp goes down – rotation slows.

becomes slower, so at 290°, almost two sets of quartets (~3.4ppm) & two sets of triplets (~1.2ppm).

Chapt 6 #19: C_4H_7Cl; # sites of unsatn = $5 - \frac{8}{2} = 1$

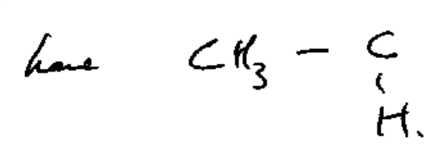
^1H integration

* Since a ^2J is present, must have



Also, since the CH_3 is a doublet (J = 6.62 Hz).

must have



$CH_3 - \underset{H}{C}$

Extracting J's from decoupled spectra: pattern centered at 5.96 ppm

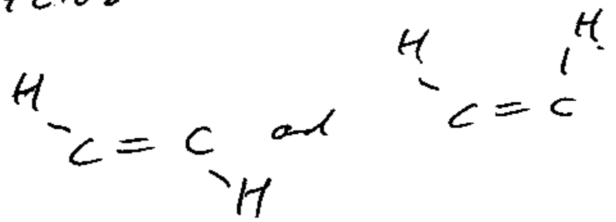
J = 1802.01 - 1792.08 = 9.93; 1785.09 - 1775.17 = 9.92.

∴ 9.9 Hz

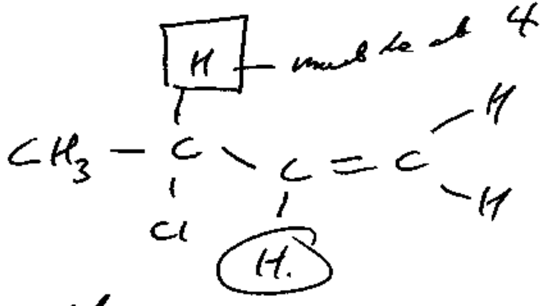
and 1802.01 - 1785.09 = 16.92; 1792.08 - 1775.17 = 16.91

16.9 Hz

Such couplings would arise from



So structure must be



— must be at 4.52 ppm.

at peak at 5.95 ppm. must be

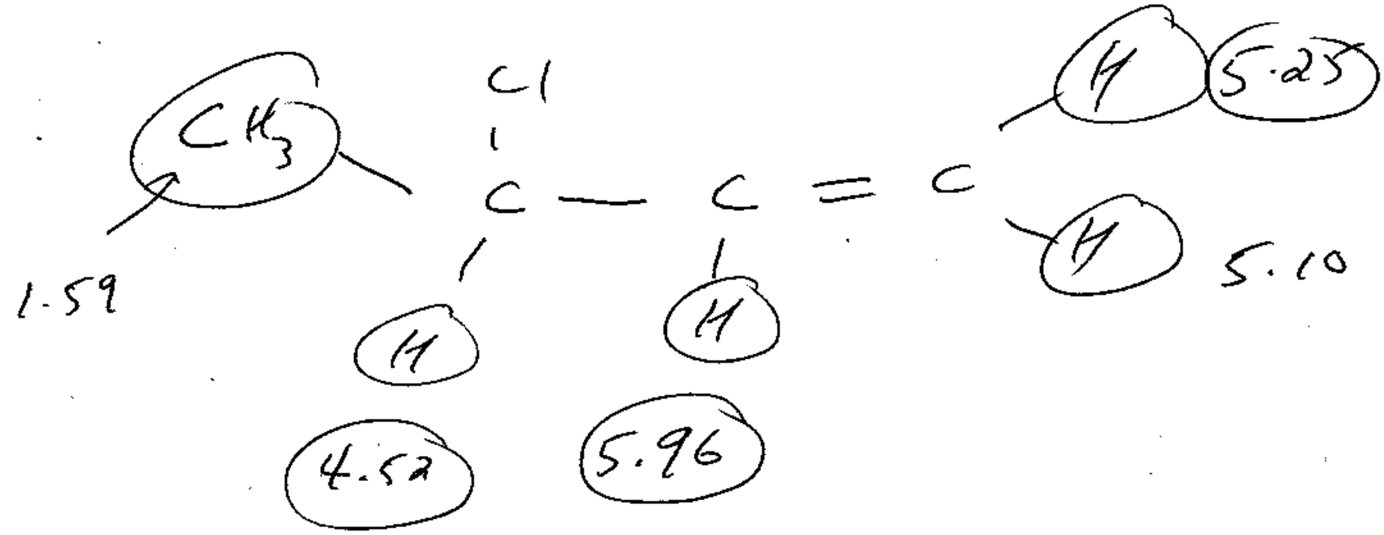
irradiation at 1.59 ⇒ doublet for this proton, J = 1362.64 − 1355.28 = 7.36 Hz

Peaks at 5.25 ppm J = 1584.71 − 1567.79 = 16.92

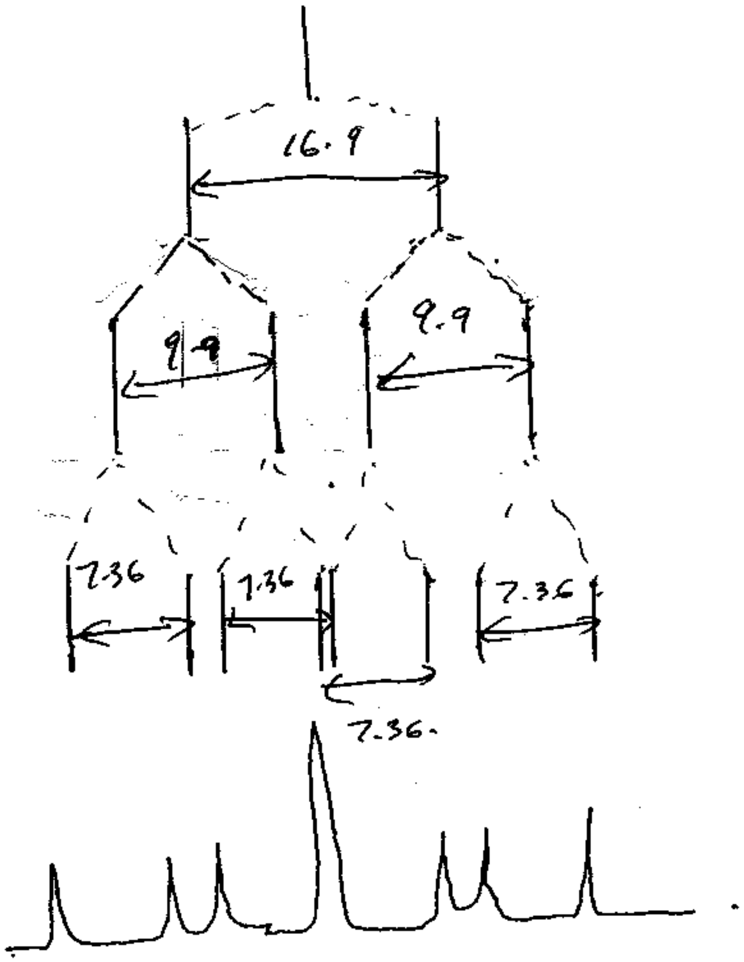
must be proton trans to proton at 5.95

P.S. #6 ANSWERS.

So, peak assignment is this.



"tree" for 5.95 pattern is below



3 coupling constants (shown to scale)

pattern observed