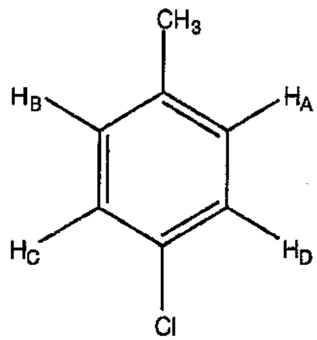
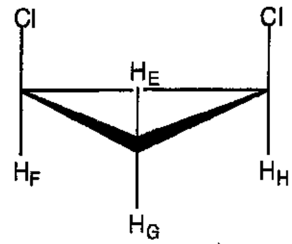
Handout 6: Advanced concepts in NMR

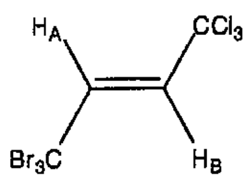
1. Determine if each of the sets of protons listed below are chemically equivalent and/or magnetically equivalent. Fill in each blank with "yes" or "no."





Are protons B and C chemically equivalent? __No_____
Are protons A and B chemically equivalent? ___Yes______
Are protons B and C magnetically equivalent? ____No______
Are protons A and B magnetically equivalent? ____No_____
Are protons E and G chemically equivalent? _No_____
Are protons F and H chemically equivalent? ____Yes_____
Are protons E and G magnetically equivalent? ____No______
Are protons F and H magnetically equivalent? ___Yes______

2. When Sample A (below) is run on a 100 MHz NMR, the proton spectrum is second order, but when it is run on a 500 MHz instrument, the spectrum is first order. Explain this difference, using the necessary calculations.



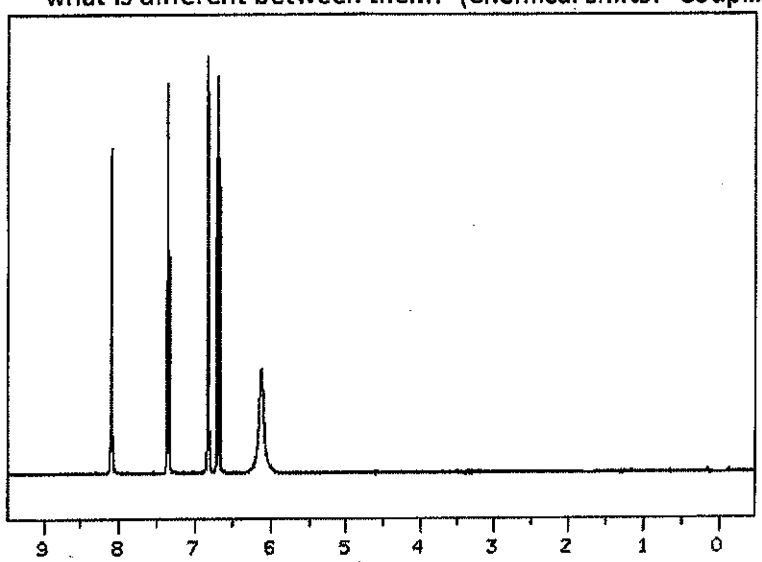
shift of H_A = 6.573
shift of H_B = 5.992

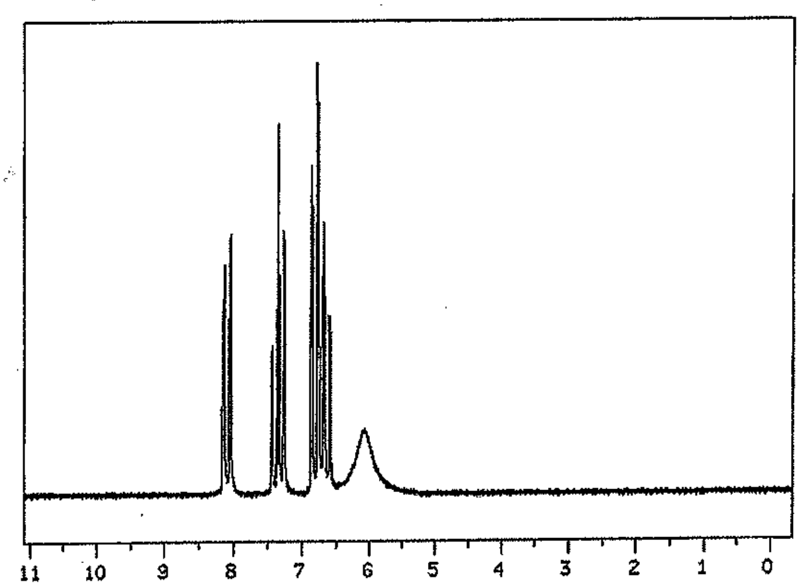
J_{AB} = 18Hz

At 100 MHz, Δv=(6.573-5.992ppm)(100 Hz/ppm) = 58.1 Hz, only3.2 times bigger than J

At 500 MHz, Δv=(6.573-5.992ppm)(500 Hz/ppm) = 290.5 Hz, which is 16 times bigger than J

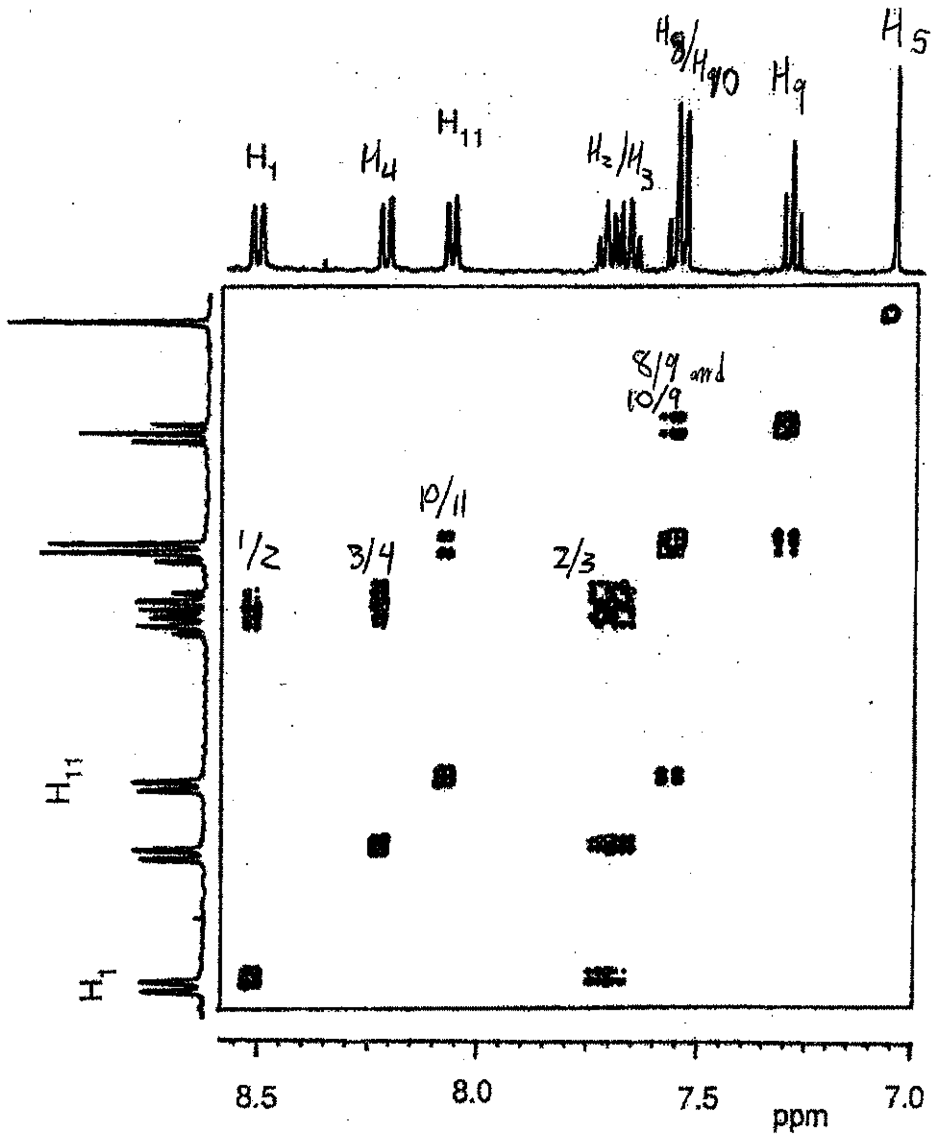
3. Magnet strength greatly affects the appearance of a spectrum. Below are spectra of o-nitro aniline taken on a 90 MHz spectrometer and a 400 MHz spectrometer. Which is which, and what is different between them? (Chemical shifts? Coupling constants?)

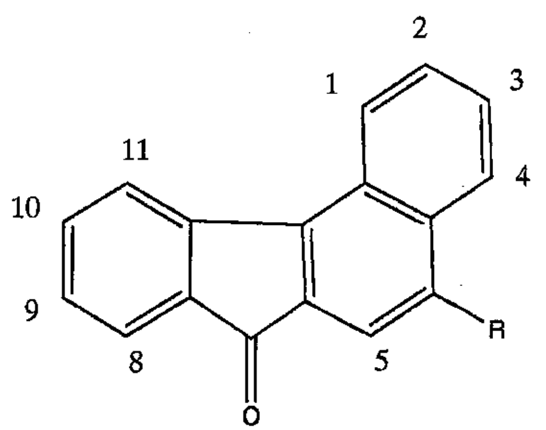




The top spectrum was taken on a higher field (400MHZ) instrument. The coupling constants remain the same, but look closer together because there are more Hz per ppm on the stronger magnet. The bottom spectrum has overlapping peaks because it is at 90 MHz.

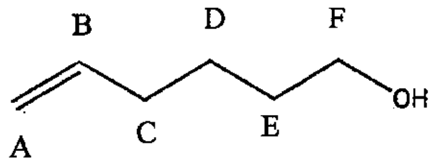
4. Given the COSY spectrum and the assignments of H_1 and H_{11} of this compound, assign the remaining ^1H aromatic signals.



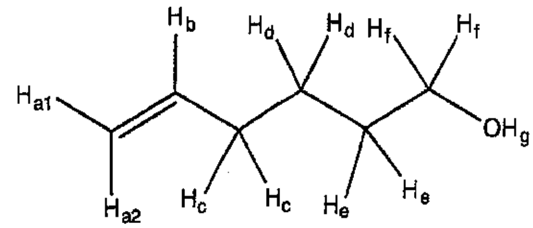


5. Label the proton and carbon-13 NMR with the appropriate letters based on the structure below. Label all of the COSY correlations (all that are not on the diagonal) directly on the spectrum, and indicate which protons they refer to. Note – this spectrum was obtained in $CDCl_3$, which is a solvent where acidic protons are visible, and coupling with acidic protons is also visible.

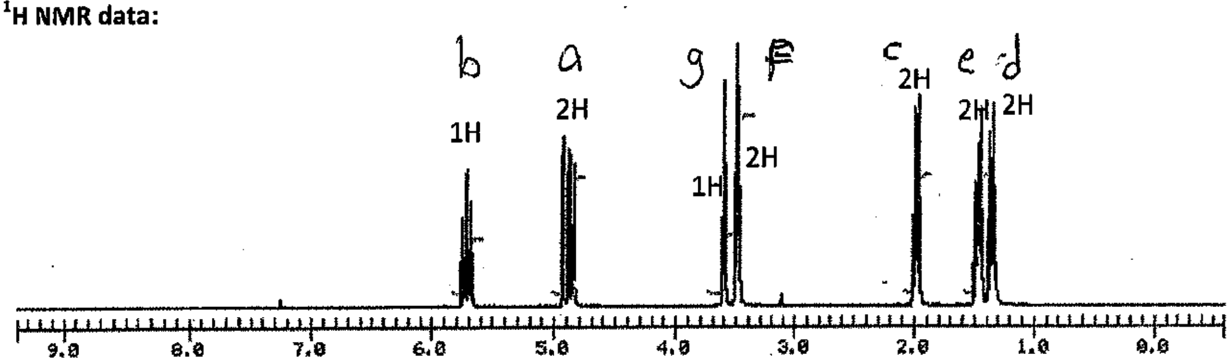
Carbon letters:



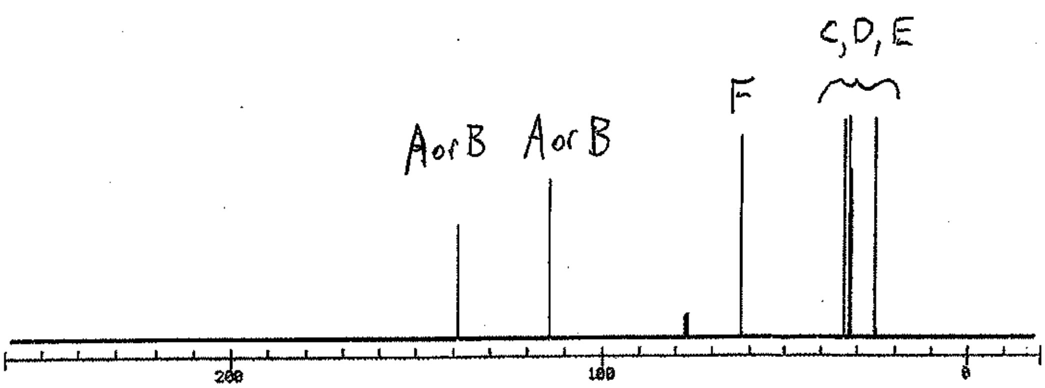
Proton letters:



^{1}H NMR data:

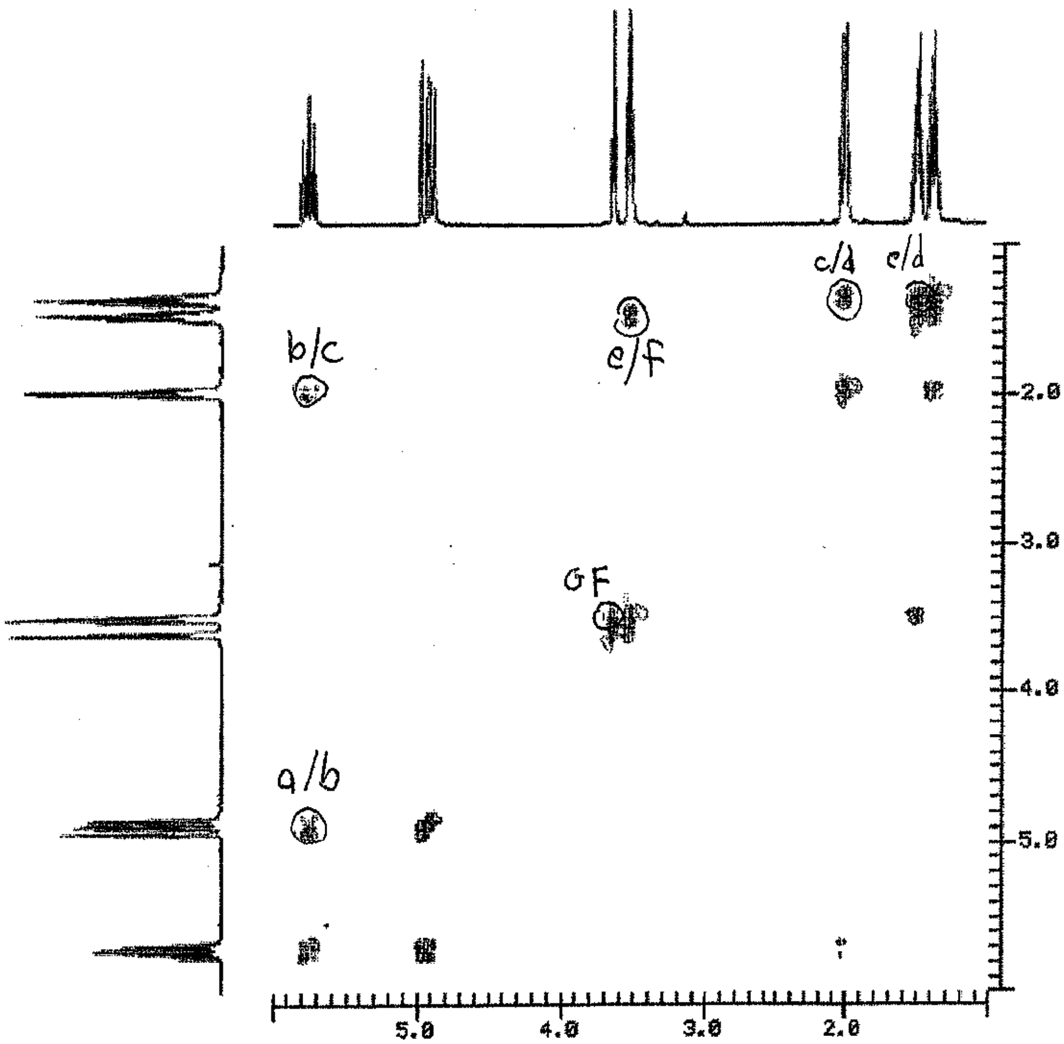


^{13}C NMR Data:



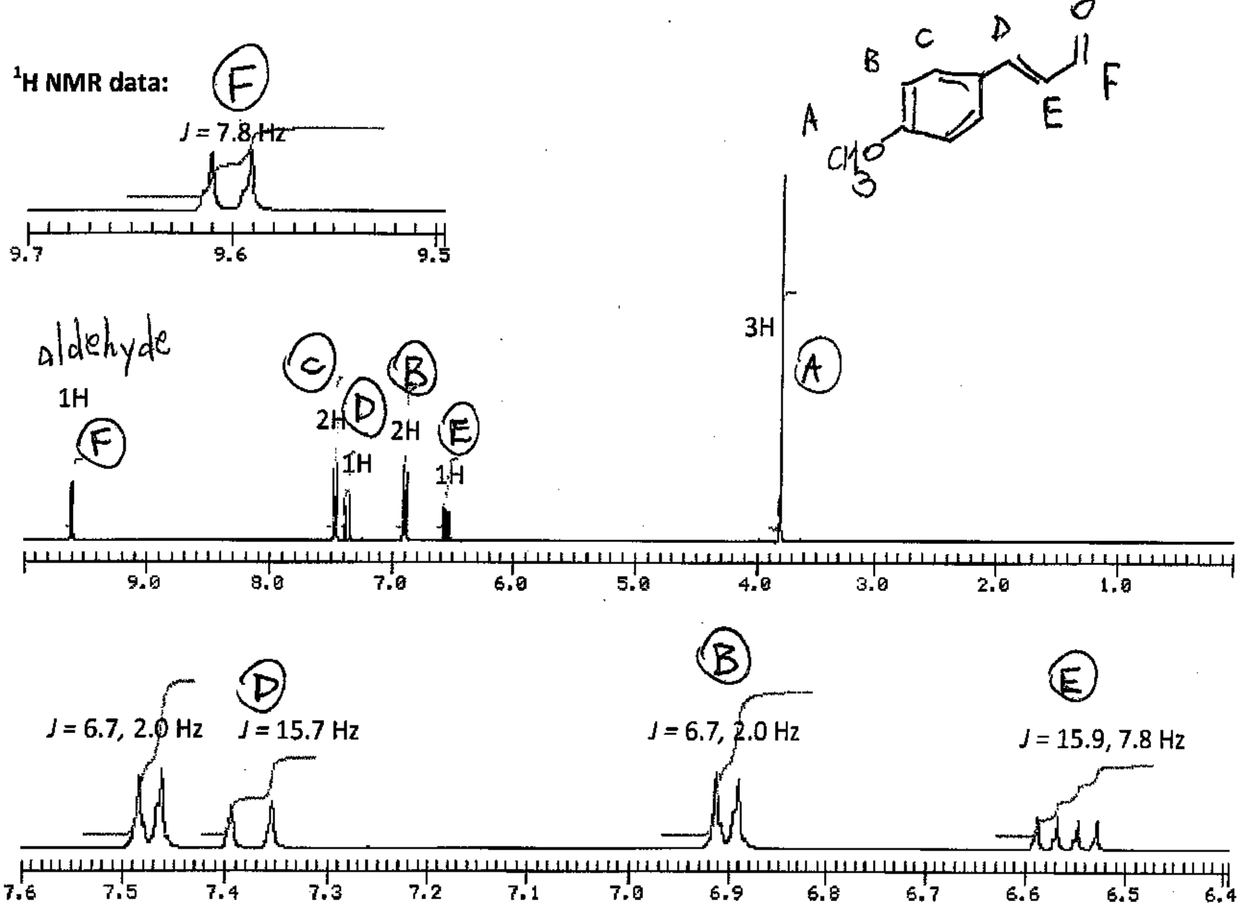
5. cont.

COSY Data



6. Given the ^1H, ^{13}C DEPT, and COSY data provided on the following pages, determine the structure of the following compound which has the molecular formula $C_{10}H_{10}O_2$. Label all COSY correlations directly on the spectrum, and indicate which protons they refer to.

^1H NMR data:



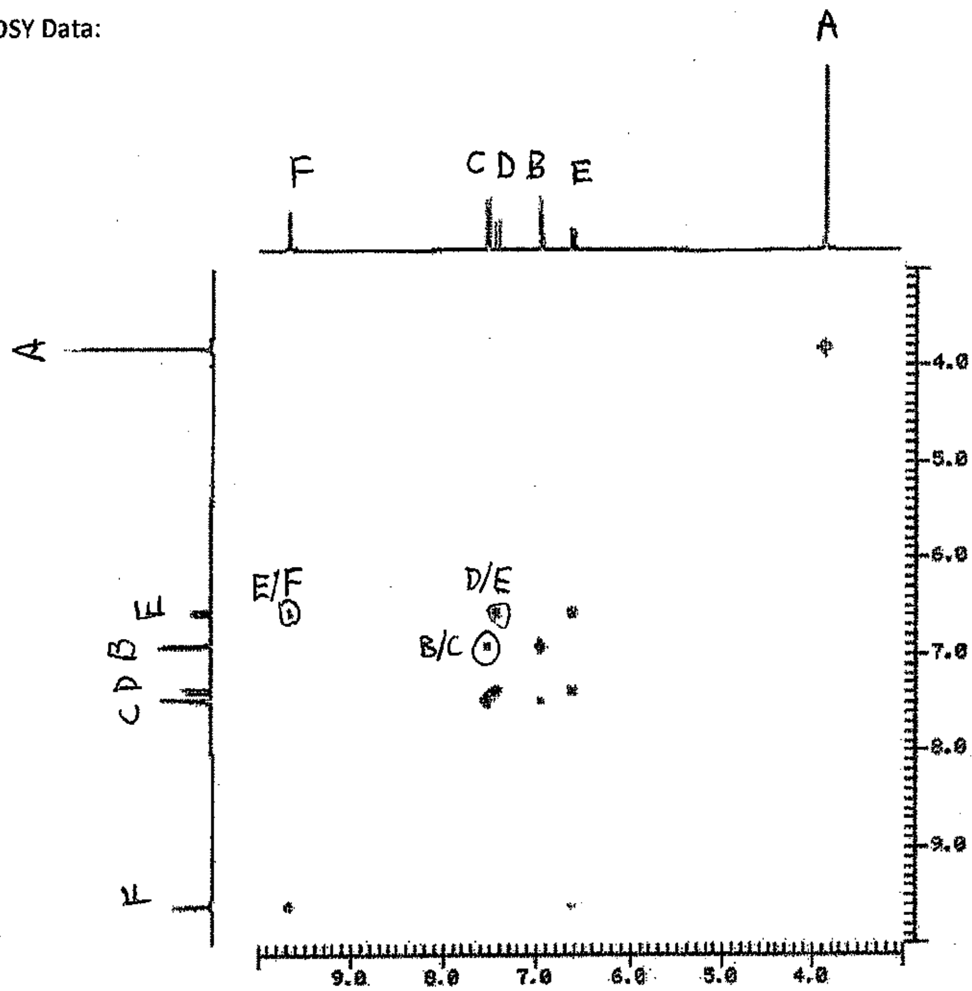
^{13}C NMR data:

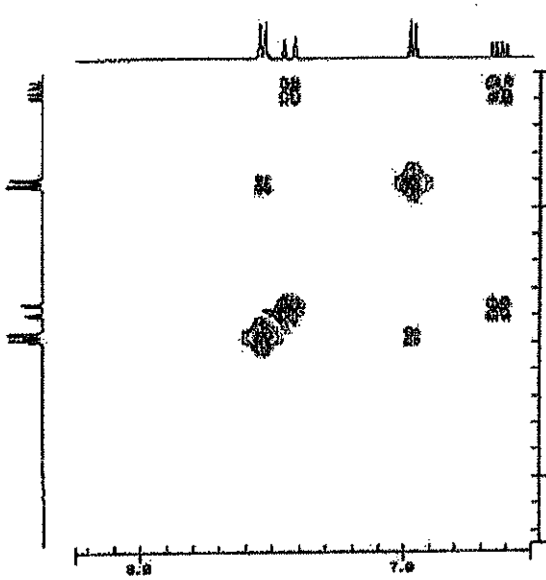
δ ppm	DEPT 135	DEPT 90	
[illegible]	+	+	CH (aldehyde)
162.2	no signal	no signal	C
[illegible]	[illegible]	[illegible]	CH
130.4	+	+	CH
[illegible]	no signal	no signal	C
126.4	+	+	CH
114.6	[illegible]	[illegible]	CH
55.4	+	no signal	CH_3

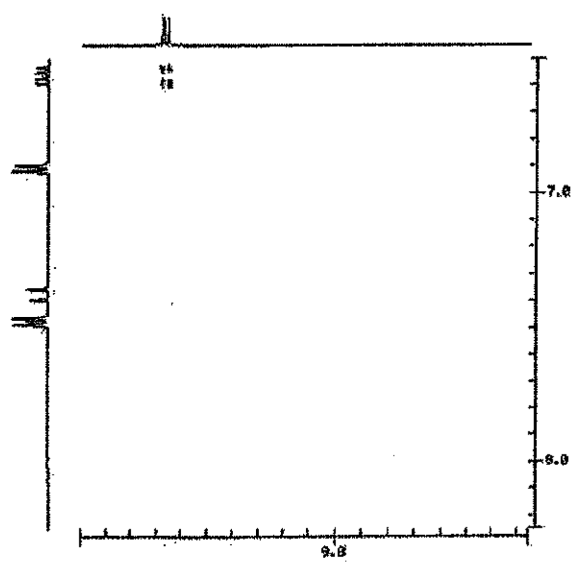
B is more shielded than C by resonance of methoxy

J = 2 Hz para coupling
J = 6.7 Hz ortho coupling
J = 7.8 Hz aldehyde
J = 15.7 Hz trans

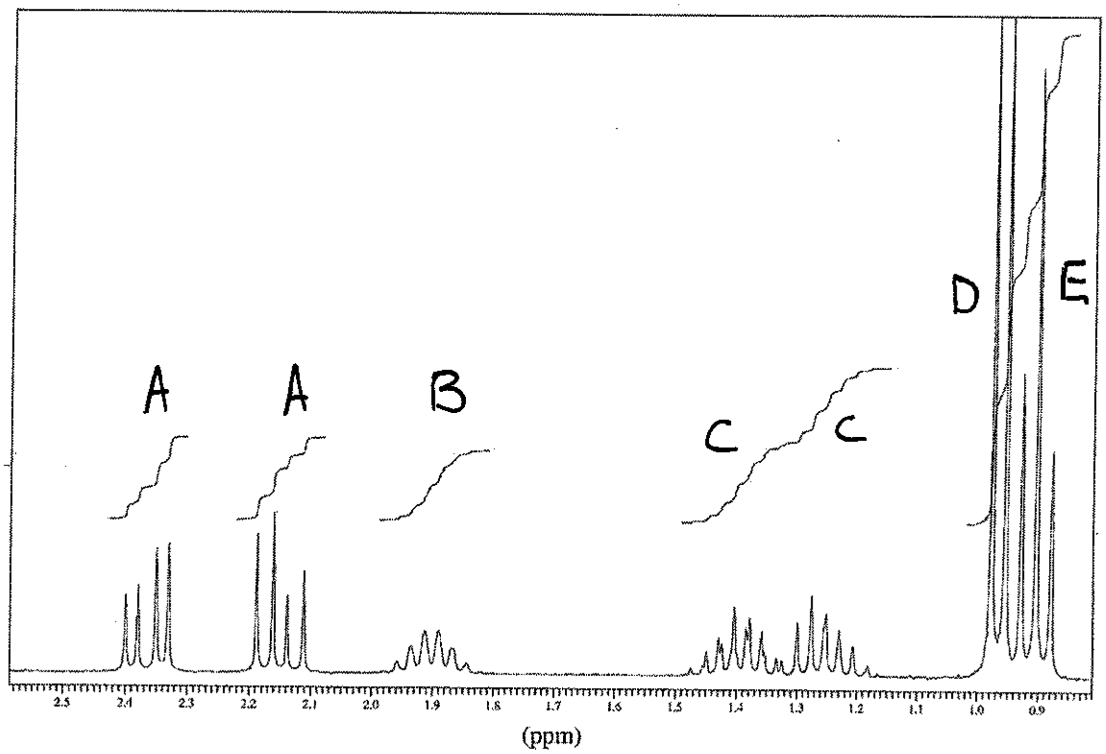
6. COSY Data:

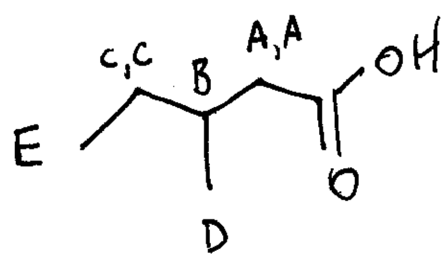






7. Given the ^1H and HETCOR data provided on the following pages, determine the structure of a compound which has the formula $C_6H_{12}O_2$. Comment on the carbon peaks appearing at 29 and 41 ppm in the HETCOR spectrum. Assign all protons and carbons for this compound





A dd, 1H

B octet, 1H

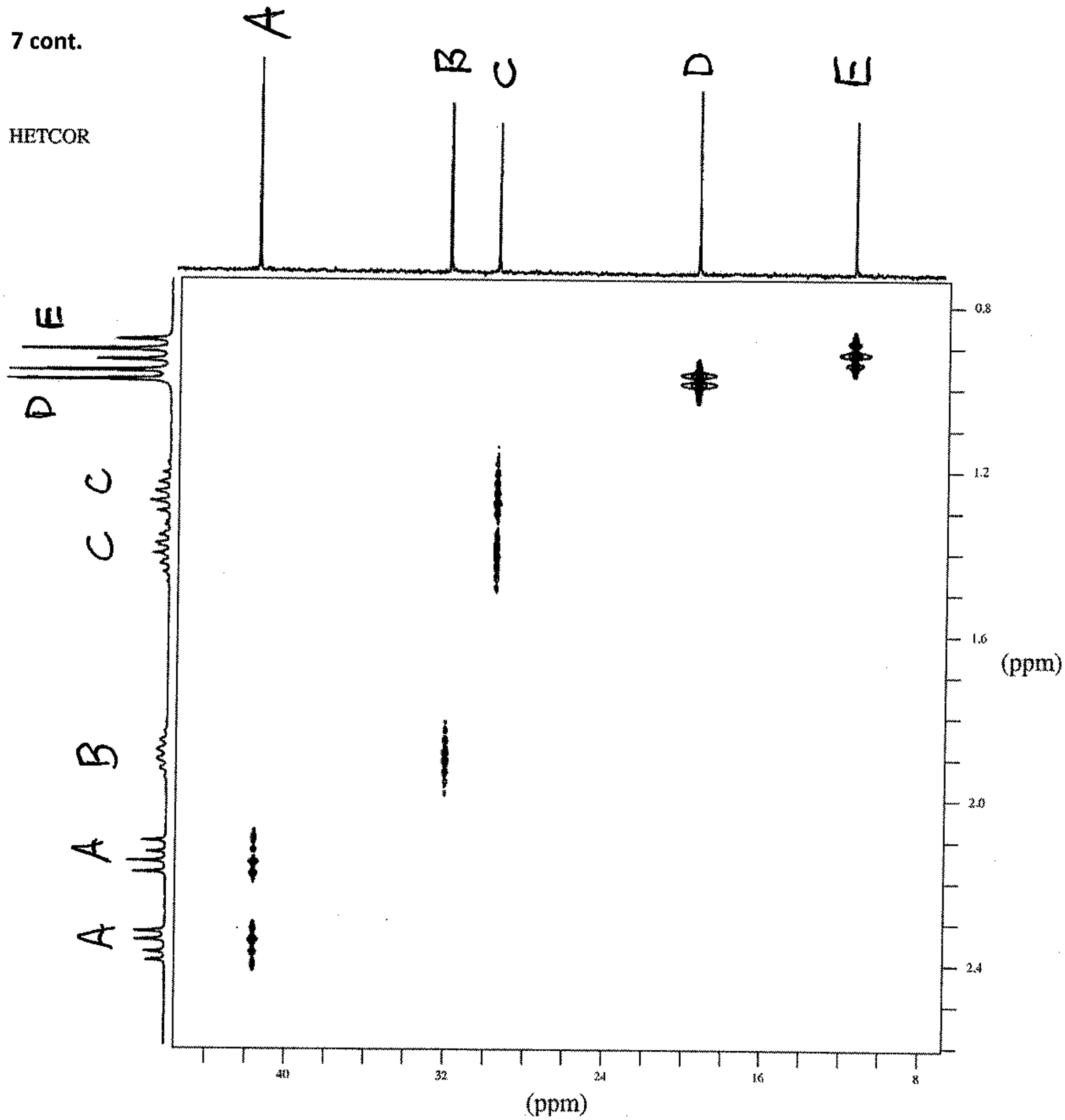
C ddq, 1H

D d, 3H

E t, 3H

7 cont.

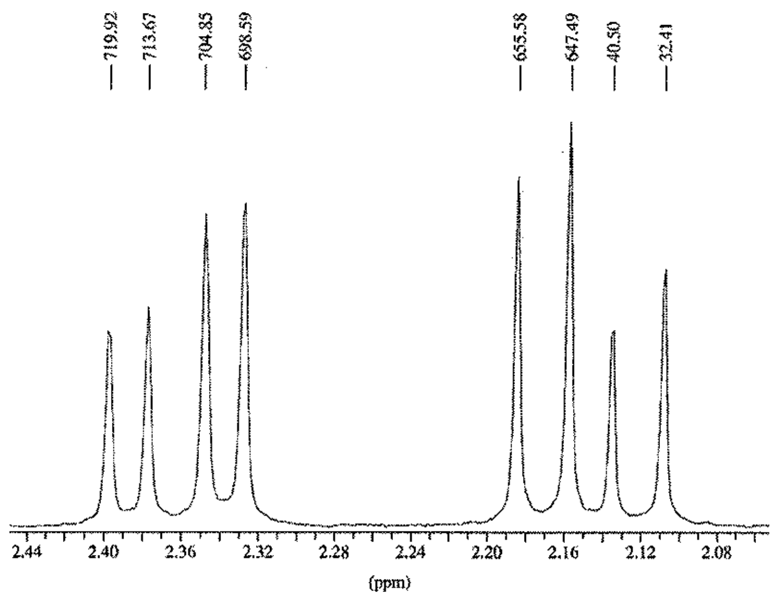
HETCOR



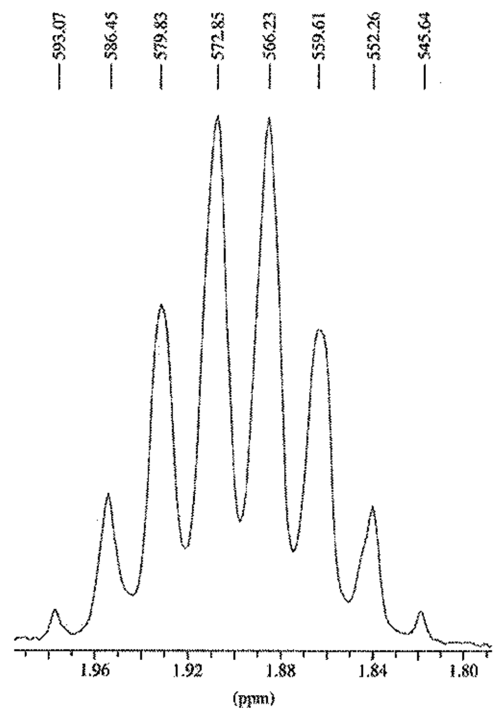
carbons A + C have diastereotopic protons

7 cont.

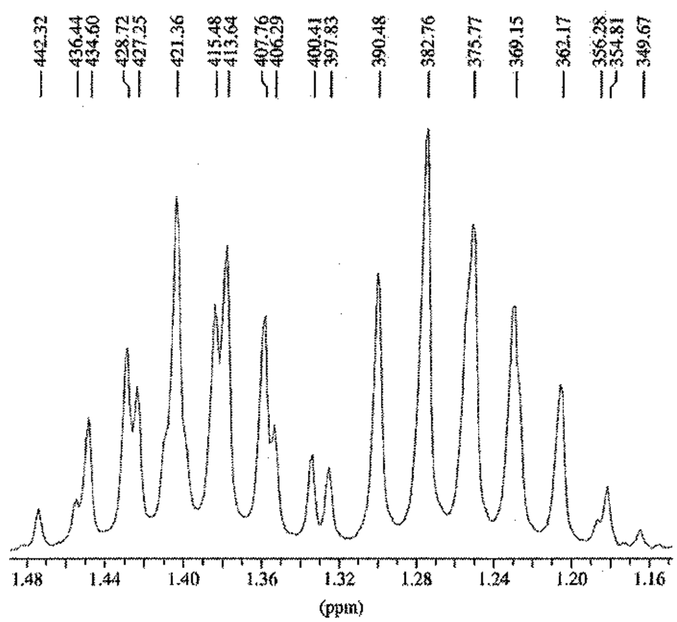
dd J= 6.25 Hz
J= 15.1 Hz

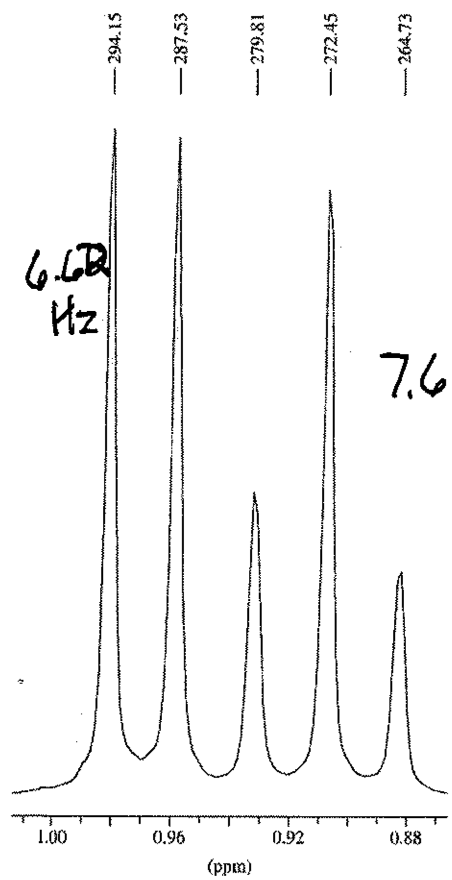


octet J= 6.62



ddq





7.6 Hz