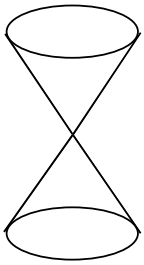
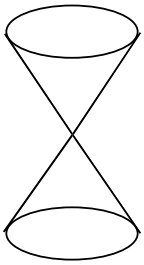
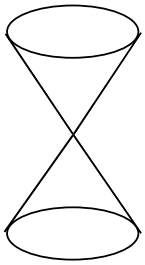
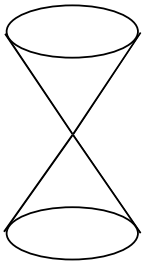
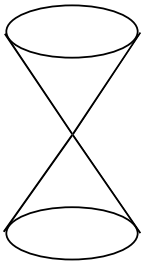
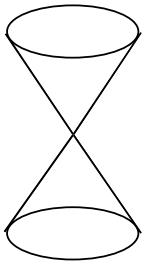
Your Name:_____

Question 1. NMR Basics. (20 points)

(a) In the top row, indicate schematically the "magnetic moments of individual nuclei" (draw some 10-15) as arrows for the following situations. In the bottom row, draw the direction of the "macroscopic magnetization" of the sample. Assume that the external magnetic field is pointing straight up (z-direction). (12 points)

	After sample is placed in magnetic field. (But no pulses as yet).	After one "90° pulse."	One hour after applying one "90° pulse."
Draw individual nuclear magnetic momenst in this row.			
Draw the macroscopic magnetization in this row.			

(b) Draw a scheme of the Zeeman levels for one H atom. On the left, draw the Zeeman levels for the one H atom assuming that it is not coupling. On the right, draw the Zeeman levels for the one H-atom assuming that it is coupling to one neighbor with a nuclear spin of ½. (8 points)

Without Coupling	With Coupling

Question 2. NMR Solvents. (20 points)

(a) The rows of the "Pascal Triangle" and of the "Trinominal Triangle", respectively, list the relative intensities of the (2•n•I + 1) lines of the multiplets caused by n equivalent neighbors with nuclear spin I = __ or I = __, respectively. Fill in the missing numbers. (8 points)

Pascal Triangle	**Trinominal Triangle**
1	1
1 1	1 _ 1
1 _ 1	1 _ _ _ 1
1 _ _ 1	1 _ _ _ _ _ 1
1 _ _ _ 1	1 _ _ _ _ _ _ _ 1
1 _ _ _ _ 1	1 _ _ _ _ _ _ _ _ _ 1

(b) Suppose you use **acetone-d_6** as a solvent for **^{13}C-NMR**. (4 points)

The "acetone signals" are caused by **acetone-*d*_**. The ^{13}C-NMR signal for the methyl-carbon appears at a chemical shift of δ = ___ ppm as a _____ (specify the multiplet). The intensities of the lines of this multiplet are _____ (*i.e.*, 1:1:1, 1:3:1, etc.)

(c) Suppose you use **acetone-d_6** as a solvent for **^{1}H-NMR**. (4 points)

The "acetone signal" is caused by **acetone-*d*_**. The ^{1}H-NMR signal appears at a chemical shift of δ = ___ ppm as a _____ (specify the multiplet). The intensities of the lines of this multiplet are _____ (*i.e.*, 1:1:1, 1:3:1, etc.)

(d) Suppose you use **tetrahydrofuran-d_8** as a solvent for **^{1}H-NMR**. (4 points)

There will be two "THF signals", one at 3.57 ppm and one at 1.73 ppm, and both signals look like broad singlets. What causes these two signals? Are we seeing true singlets? What causes the peaks to be so broad?

Question 3. Chemical Shift Computations for ^{1}H-NMR and ^{13}C-NMR. (20 points)

(a) Nitrobenzene ^{13}C-NMR Chemical Shifts: δ = 123.5, 129.4, 134.7 and 148.3 ppm. (12 points)

Using increment systems and/or look-up tables in Pretsch 4/e, predict the chemical shifts for the four types of carbon in nitrobenzene. Then assign the spectrum by writing the appropriate measured value in the appropriate column. Then determine the difference between the computed and measured values.

	C_{ipso}	C_{ortho}	C_{meta}	C_{para}
Calculated:				
Measured:				
Deviation:				

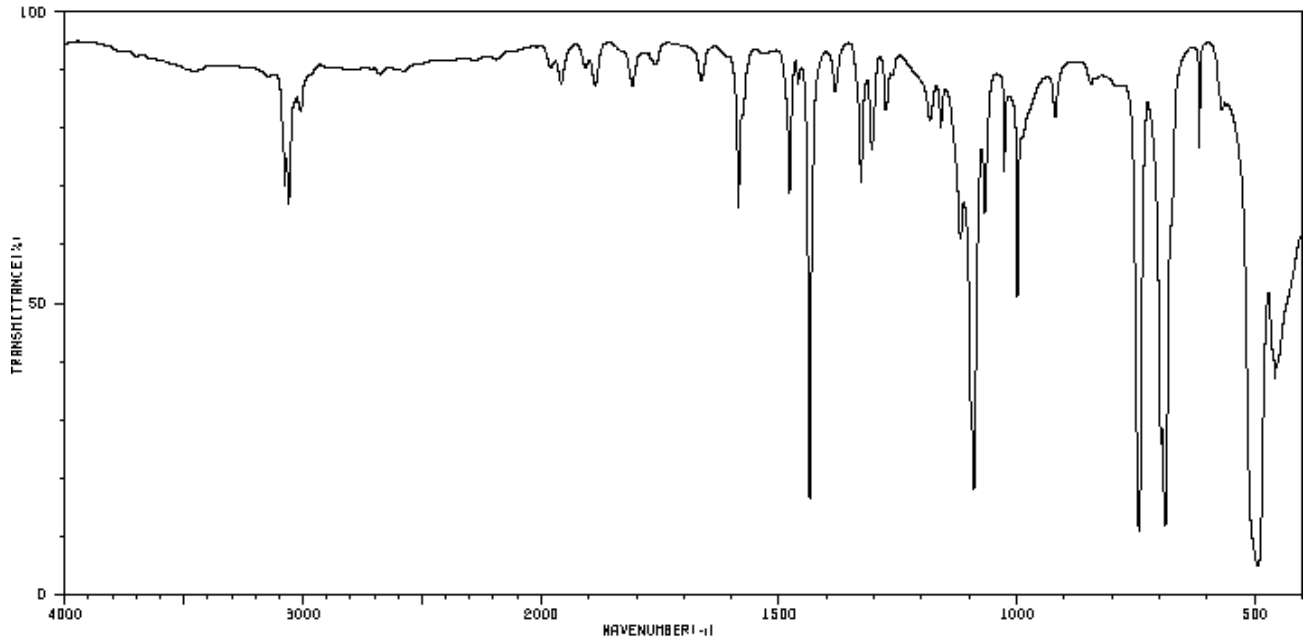
(b) para-Nitroaniline ^{1}H-NMR Chemical Shifts of Aromatic Hydrogens: δ = 6.8 and 8.0 ppm. (8 points)

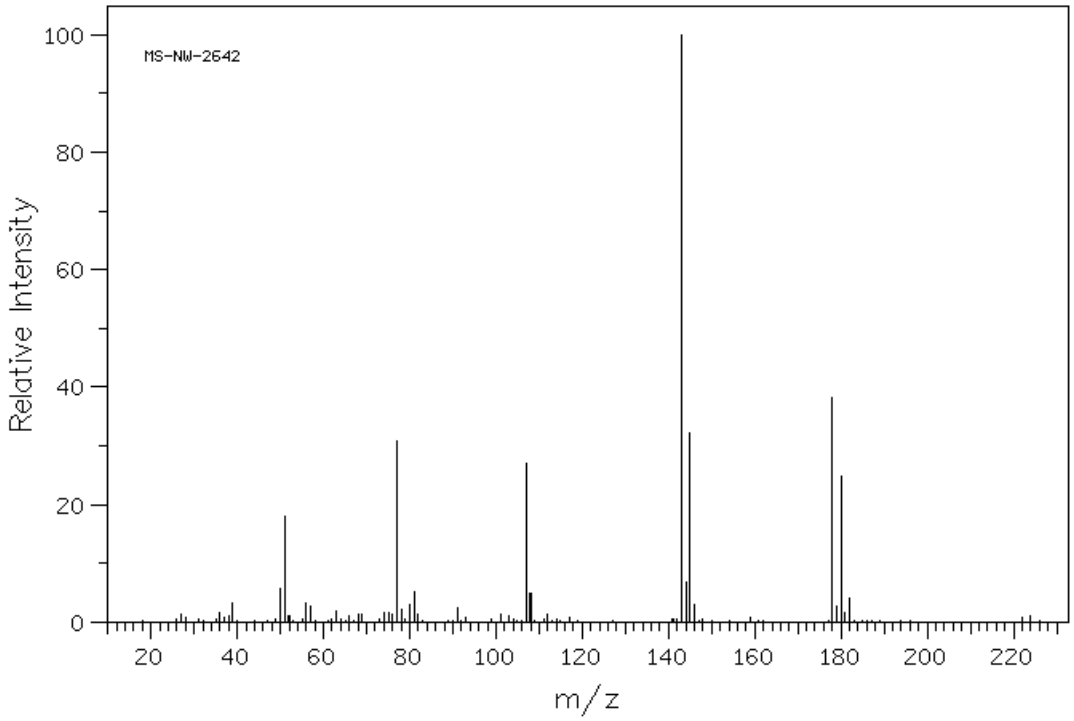
Using increment systems and/or look-up tables in Pretsch 4/e, predict the chemical shifts for the two types of aromatic hydrogens in para-nitroaniline. Then assign the spectrum by writing the appropriate measured value in the appropriate column. Then determine the difference between the computed and measured values.

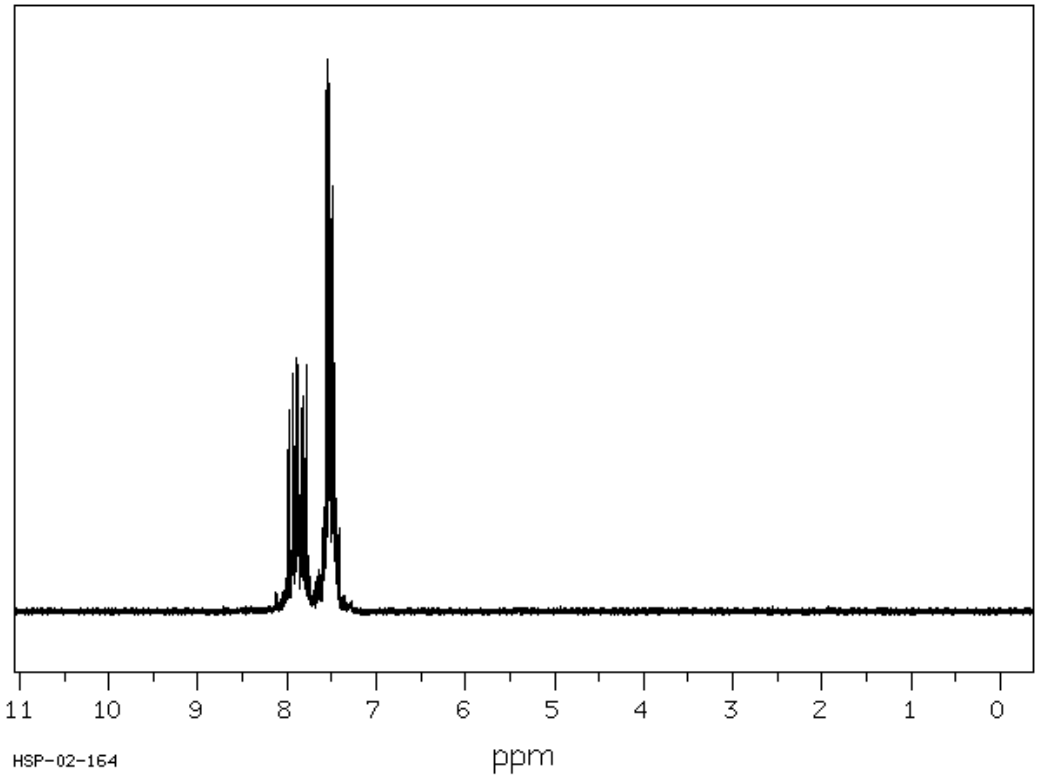
	H ortho to NO_2	H ortho to NH_2
Calculated:		
Measured:		
Deviation:		

Question 4. Structure Determination. (40 points)

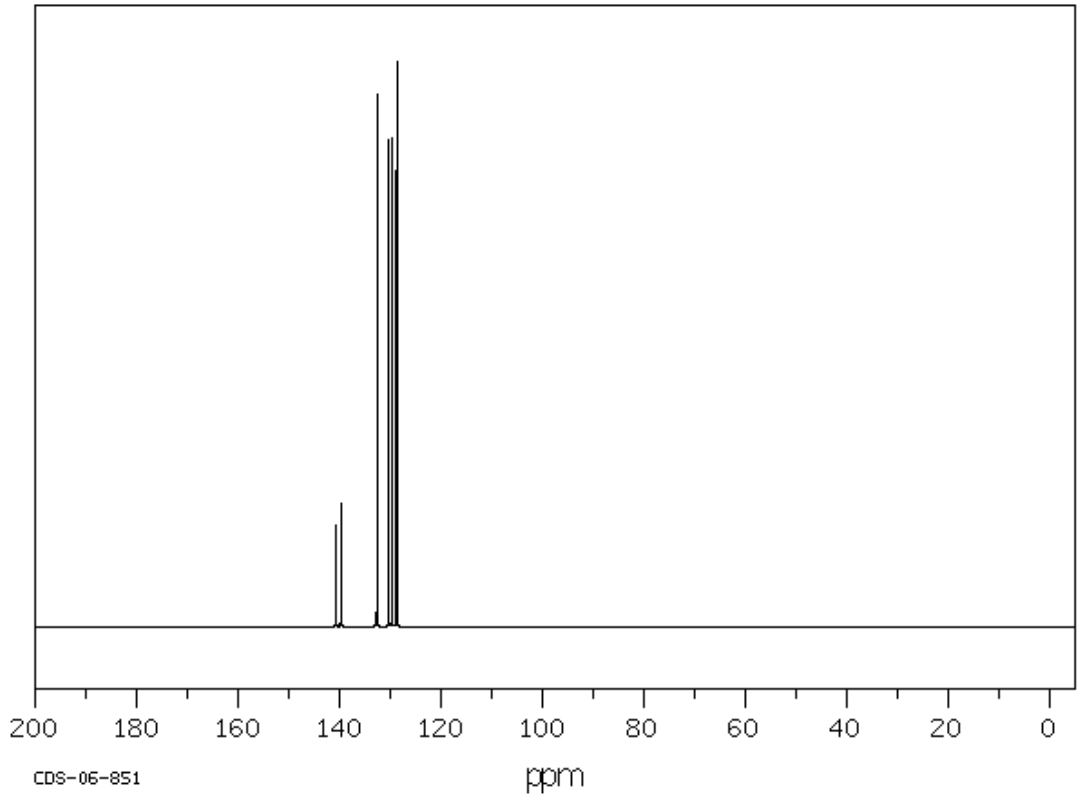
IR, MS, and NMR spectra are provided for a molecule with formula $C_6H_5PCl_2$. Deduce the structure of this compound and assign the spectra. Specific questions follow after the spectra.







^{1}H-NMR: 90 MHz, 0.05 ml : 0.5 ml $CDCl_3$



^{13}C-NMR (H-decoupled): 50 MHz, 0.05 ml : 0.5 ml $CDCl_3$

Your Name:_____

(a) Draw the structure of the compound:

(**b)** Directly on the IR spectrum, assign all characteristic bands. Also indicate significant absences (if any).

(**c)** Directly on the MS spectrum, assign all peaks with relative intensity > 20.

(d) The ^{13}C-NMR spectrum contains seven lines and their locations and intensities are listed to the right. Explain as best as you can how your structure explains the features of this spectrum (number of lines and their location).

ppm	Int.
140.82	180
139.77	219
132.62	943
130.31	863
129.70	867
128.90	804
128.75	1000