Chemistry 416 "Spectroscopy"
Fall Semester 1993
Dr. Rainer Glaser

Fourth "Take Home" Examination
"NMR Spectroscopy"

Hand-out: Wednesday, December 1, 1993
Collect: Friday, December 3, 1993

Name:

|		
Question 1 (Coupling)	21	
Question 2 (Fluoro Azine)	29	
Question 3 (^{1}H Increments)	30	
Question 4 (^{13}C Inc. Sys.)	20	
Total	100	

Question 1. Heteronuclear Coupling. (21 points)

The deprotonation of 4-*tert*-butylcyclohexanone followed by reaction with Me$_3$SiCl at -78°C may yield two non-identical TMS enol ethers. Draw these two products. (3 points).

	Deprotonation at A	Deprotonation at B

The reaction can be made enantioselective by use of chiral bidentate lithium amides of the type shown. (The Li-N bond is shown covalent although it most likely is dominantly ionic, of course). The solid state structure of the base was determined by X-ray crystallography and it is shown. Now, there always is the question as to whether the solid state structure also is the most abundant structure in solution and, moreover, then there is still the more important question as to whether that is in fact the reactive species.

X-ray structure
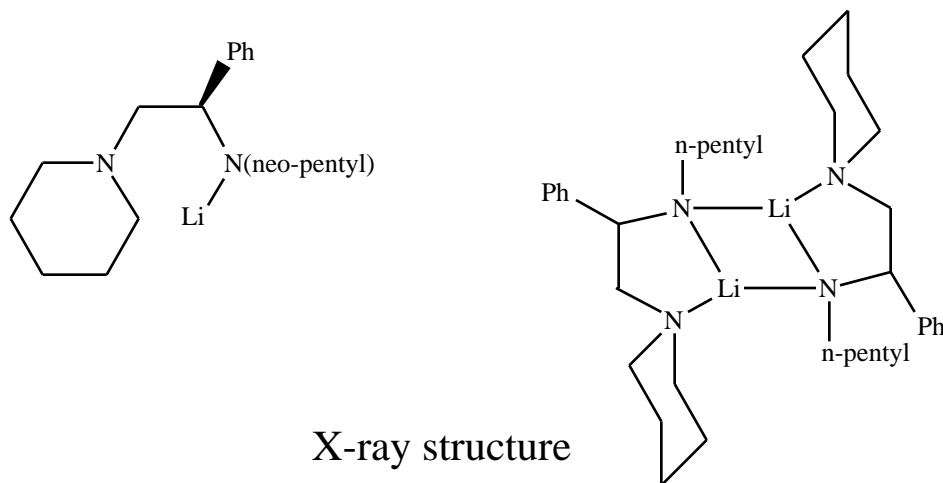
Sato *et al.* carried out ^{6}Li and ^{15}N NMR experiments to study these questions. The spectra obtained with ^{6}Li and ^{15}N enriched material are reproduced in Figure 2. For each of the three sets of NMR spectra, describe what the spectra (multiplicities) tell you about Li-N contacts (number of neighbors, are they equivalent or not). Then conclude whether under those conditions the structure found in the solid state also is that found in solution. If not, suggest a structure that is compatible with the spectra in each case. (4 points for cases A - C each)

Remember that ^{15}N has a spin = 1/2 and ^{6}Li has a spin = 1.

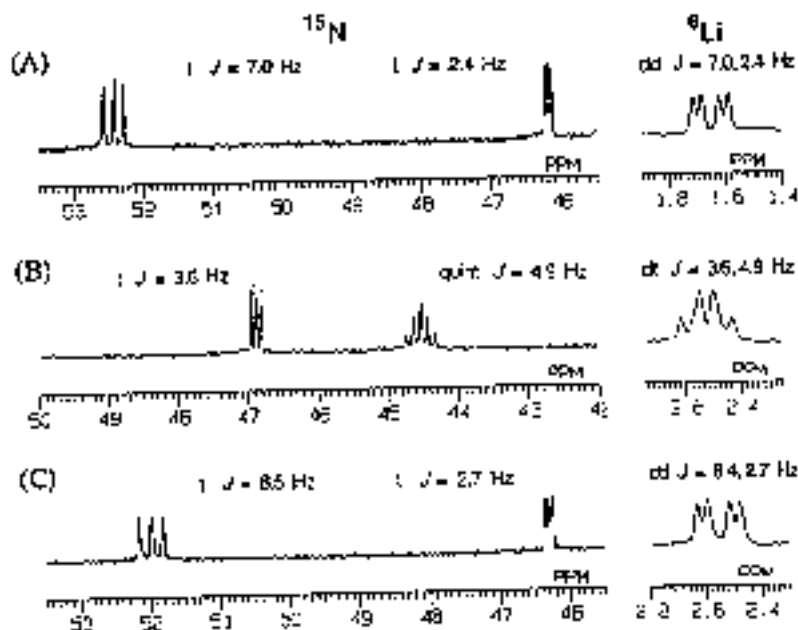**Figure 2.** (A) ^{15}N and ^{6}Li NMR spectra of [^{6}Li,^{15}N$_2$]-(*R*)-1a in THF-d_8 (Table 1, entry 1); (B) in toluene-d_8 (Table 1, entry 6); (C) in toluene-d_8 with 2 equiv of HMPA (Table 1, entry 7).

Predict the multiplicities and the line intensities (e.g. 1:1) for the following structures. (6 points)
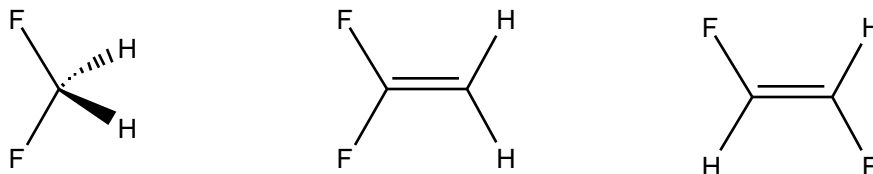
Structure	^{6}Li NMR	^{15}N NMR

CASE (A): in THF-d$_8$

CASE (B): in toluene-d$_8$

CASE (C): in toluene-d$_8$ with 2 equivalents of HMPA

Question 2. *Para*-Fluoroacetophenone Azine. (29 points)

(a) Difluoromethane and difluoroethene. (9 points)

|	difluoro-methane	1,1-difluoro-ethene	1,2-difluoro-ethene
C_2 Symmetry present? (Yes,no)			
C_s Symmetry present?			
H-atoms are homo-, enantio- or diastereotopic?			
H-atoms are chemically equivalent?			
H-atoms are magnetically equivalent?			
Spin system type?			

**(b)** Consider *para*-fluoro-chlorobenzene. (8 points)
* The *meta*-Hs (next to F) are chemically _____ (equivalent / not equivalent). The *ortho*-Hs (next to Cl) are chemically _____ (equivalent, not equivalent).
* The *meta*-hydrogens are magnetically equivalent only if the long range coupling between the *meta*-hydrogens is _____.
* The spin system is of the general type _____ (e.g. AB_n)

(c) The benzene portion of the spectrum of *para*-fluoroacetophenone azine is shown.
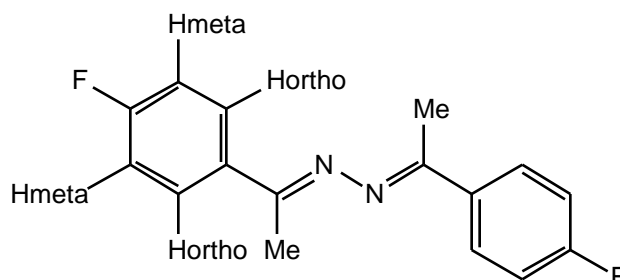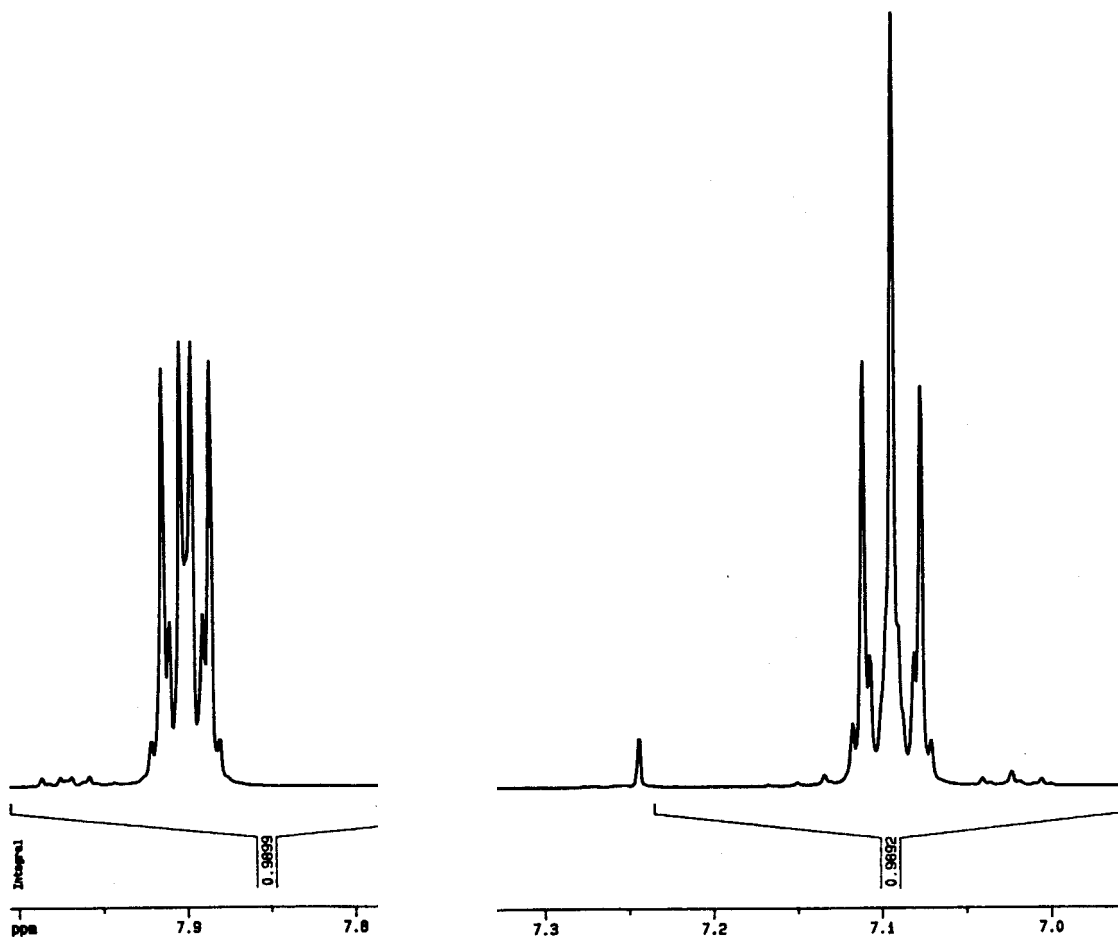
* Essentially, there occur a dublet of dublets and a triplet in the benzene region. The dublet of dublets is caused by the (*meta* or *ortho*) _____ H-atoms since they couple with _____ and _____. The triplet is caused by the (*meta* or *ortho*) _____ H-atoms because (H,H) and (F,H) coupling with these H atoms happen to be _____. (8 points)

* From the chemical shifts of these signals, we can see that the F substituent is _____ (more or less) electronegative compared to the azine substituent. (2points)

* It is also clear that the aromatic rings rotate _____ (essentially free, greatly hindered). (2 points)

Question 3. Proton Increment Systems: Shoolery's Rule, PMS and the like ... (30 points)

It is the purpose of the following questions to get you to study and apply the increment systems that exist to approximate the chemical shifts of protons and ^{13}C atoms. You should refer to the book by Fribolin as well as to the book by Pretsch et al.

(a) Shoolery's rule is only one of several increment systems for the estimation of ^1H NMR chemical shifts of disubstituted methylene groups. See pages H15 and H16 (Shoolery) in Pretsch. Note that the base value is different and so are the increments. The base value in Shoolery's system (0.23) is the chemical shift of the compound _____. Calculate the ^1H NMR chemical shifts for the methylene groups in the following compounds using both increment systems. Show your work, that is, do not only give the final value but show the sum of terms that got you there. (1+8=9 points)

	Using H15	Using H16 (Shoolery)
Dichloromethane (exp. 5.33)		
Phenylchloromethane		
Malonic Acid		
Fluorochlormethane		

(b) Chemical shift also are effected by -substituents. H17 shows the increment system used in thoses cases. Here we have Z_R values for -substituents and $Z_{R'}$ values for -substituents. Let's look at the Z_R values first. Note that the Z_R values differ for this increment system and the ones discussed in (a). For example, the values listed in Tables H15 - H17 for Cl are _____, _____, and _____. Next we notice that the -substituent R values are additive in this system. Calculate the ^1H NMR chemical shifts for the methylene groups in the following compounds using this increment system. Show your work, that is, do not only give the final value but show the sum of terms that got you there. (4 points)

|	Using H17
1,2-Dichloroethane	
1,1,2-Trichloroethane	
1,1,1,2-Tetrachloroethane	

(c) The ***Pascual-Meier-Simon*** rules consist in an increment system for the determination of the ^{1}H NMR chemical shifts of alkenes. Refer to Table H215ff in Pretsch's book. Table H225 lists the actual values for several isobutenes. Let's see how well the PMS system works. (6 points)

Isobutene Me$_2$C=C$\underline{H}$R	PMS	Actual (H225)
R = Br		
R = COH		
R = CN		

(d) This increment system allows you to determine the effects of substituents on the benzene proton chemical shifts. The base value for the system, 7.26, is the chemical shift of the proton in _____. Calculate the ^{1}H NMR chemical shifts for the protons in the following compounds using this increment system. Show your work, that is, do not only give the final value but show the sum of terms that got you there. (1+1+1+2=5 points)

|	Using H225
The H in the *para*-position in nitrobenzene	
The H in the *para*-position in aniline	
The H with the highest chemical shift in *meta*-dichlorobenzene	

(e) Putting it together. Predict the chemical shifts of all protons in the molecule shown. Indicate what increment system was used and show the terms that lead to the estimated chemical shift. Also give the J(H,H) values. (6 points)
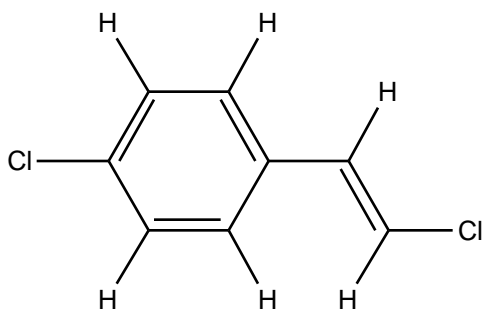
Question 4. Increment Systems in ^{13}C NMR Spectroscopy. (20 points)

(a) *Alkanes.* (10 points) This is somewhat more complicated than the H NMR increments because we need to consider a so-called <u>steric correction S</u> and a <u>conformation correction for substituents</u>. For now, let's assume that the conformation correction is zero (free rotation). Note that equations 6-4 in Fribolin and C10 in Pretsch are the same once you consider the entries in row 2 of table C20.
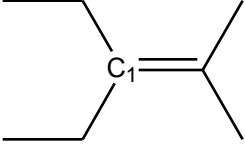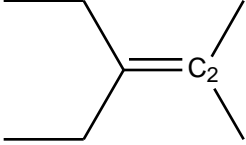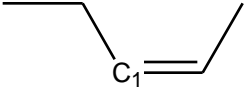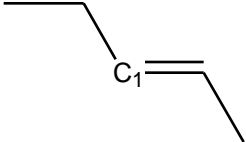
The use of the steric corrections is not all that simple! Easiest to follow the guidelines given by Fribolin on page 149. First you decide whether the C atom is primary, secondary and so on; this gives the *row* in Table 6-4 (or Table C15-top). The *column* is decided by the number of substituents on the attached C-atom. (Note that the numbers in Table 6-4 and C15-top differ slightly. Use Fribolin's numbers).
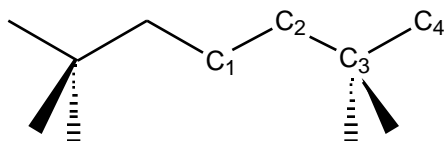
	C1	C2	C3	C4
# of substituents (*9.1)				
# of -substituents (*9.4)				
# of -substituents (*-2.5)				
# of -substituents (*0.3)				
Sum of Steric Corrections				
Total Estimated Carbon Shift				

Explain the "Sum of Steric Correction" for C2. (4 points)

(b) *Alkenes*. (10 points) On page 151 in Fribolin and on page C85 in Pretsch, the rules are given as to how one can estimate the chemical shifts of alkene C-atoms. Again one needs to consider the number and type of the substituents and a steric correction. Determine the expected chemical shifts for the molecules shown. Show your work.

The END