Chemistry 416 "Spectroscopy"
Fall Semester 1997
Dr. Rainer Glaser

First 1-Hour Examination
"NMR Spectroscopy"

Monday, October 6, 1997, 8:40 - 9:30

Name:
Answer Key

Question 1 (Spectra)	20	
Question 2 (Equivalence)	20	
Question 3 (Shielding)	20	
Question 4 (-Ionone)	40	
Total	100	

Question 1. Larmor Frequencies, Chemical Shifts and Coupling Constants. (20 points)

The chemical shift δ is defined as $\delta = (\nu_{sample} - \nu_{reference})/\nu_{reference} \cdot 10^6$. As usual, TMS is the reference compound. The Larmor frequency of the H-nuclei in TMS is exactly 90 MHz if the magnetic field is selected to be 2.11 Tesla.

(a) What is the chemical shift of an uncoupled nucleus H_a that resonates at 90,000,450 Hz? (2)

$\delta = (90,000,450 - 90,000,000)/90,000,000 \cdot 10^6$
$= 450/90 = 5$

(b) Now let's assume that the nucleus H_a is coupled to one nucleus H_b via a $^3J(H,H)$ coupling constant of 18 Hz. Of course, the H_a signal will now be split into a doublet. What are the Larmor frequencies of the two lines of this doublet? What are the chemical shifts of the two lines of the doublet? What will be the chemical shift difference between the two lines of the doublet?

Larmor frequency of line 1: 90,000,459 (2 p.)	Chemical shift of line 1: 5.1 ppm (1 p.)
Larmor frequency of line 2: 90,000,441 (2 p.)	Chemical shift of line 2: 4.9 ppm (1 p.)
Chemical shift difference between the doublet lines: 0.2 ppm (1 p.)	

(c) Suppose you measure the ^1H-NMR spectrum again but now on a 450 MHz spectrometer. What will be the Larmor frequency for the nucleus H_a when it is uncoupled. What will be the Larmor frequencies of the doublet lines of the H_a signal resulting from coupling to one nucleus H_b via a $^3J(H,H)$ coupling constant of 18 Hz? What will be the chemical shift difference between the two lines of the doublet?

| Larmor frequency of the uncoupled nucleus H_a: 450,002,250 MHz (2 p.)	
Larmor frequency of line 1: 450,002,259 (2 p.)	Chemical shift of line 1: 5.02 ppm (1 p.)
Larmor frequency of line 2: 450,002,241 (2 p.)	Chemical shift of line 2: 4.98 ppm (1 p.)
Chemical shift difference between the doublet lines: 0.04 ppm (1 p.)	

(d) Suppose the gyromagnetic constant of the ^{13}C nucleus were exactly one quarter the value of the gyromagnetic constant for the H-nucleus. At what resonance frequency (in MHz) would we find the ^{13}C resonance on a "90 MHz spectrometer" (B-field is 2.11 T)?

The ^{13}C resonance occurs at: 22.5 MHz (2 p.)

Question 2. Chemical and Magnetic Equivalence. (20 points)

Source: The Absolute Configuration of Bromochlorofluoromethane from Experimental and ab Initio Theoretical Vibrational Raman Optical Activity. Costante, J.; Hecht, L.; Polavarapu, P. L.; Collet, A.; Barron, L. D. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 885-887.

Several attempts have been made to separate the enantiomers of bromochlorofluoromethane (**1**) and to measure their optical activities. Collet et al. prepared **1** by decarboxylation of a partially resolved strychnine salt of (R)-(-)-**2**. The enantiomeric excess was estimated at 36 % by ^{1}H-NMR in the presence of enantiomerically pure cryptophane C (shown) as a chiral host shift reagent. The cryptophane C can form a 1:1 inclusion complex with **1**. Explain the ^{1}H-NMR shown. Why are there are four lines? What is the function of the "chiral host shift reagent"? What causes the coupling seen in the spectrum? How does this spectrum reflect the enantiomeric excess? For maximum score, use correct terminology.
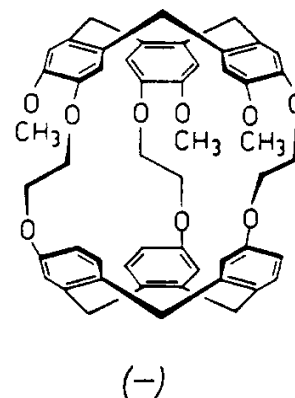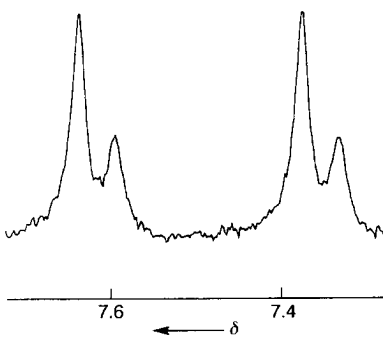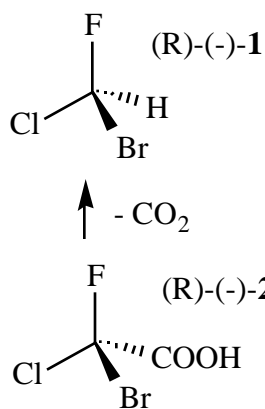
The 1:1 inclusion complex between **1** and the enantiomerically pure cryptophane comes as diastereoisomers. Hence, the H in **1** in the complexes are in different environments and show different chemical shifts; they are diastereotopic. (7 p.)

Each H shows up as doublet due to coupling to F. Doublet of doublets. (7 p.)

Integrate the set of large signals to get Area 1
Integrate the set of small signals to get Area 2.
Enantiomeric excess = 100% (Area 1 - Area 2) / (Area 1 + Area 2) (6 p.)

Question 3. Chemical Shift and Molecular Charge. (20 points)

Data from: ^{17}O and ^{13}C NMR/*ab initio*/IGLO/GIAO-MP2 Study of Oxonium and Carboxonium Ions (Dications) and Comparison with Experimental Data. Olah, G. A.; Burrichter, A.; Rasul, G.; Gnann, R.; Christie, K. O.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1997**, *119*, 8035-8042.

Computed (gas phase) and measured (condensed phase) ^{17}O-NMR chemical shifts of protonated and diprotonated water.

Molecule	[ppm], Comp. I GIAO-SCF	[ppm], Comp. II GIAO-MP2	[ppm], Expt.
H_2O	0.0	0.0	0.0
H_3O^+	18.2	24.4	10.2
H_4O^{2+}	30.2	39.2	not known

Explain the increase in ^{17}O-NMR chemical shift with the degree protonation. The naive explanation "ahh, well, the charge increases and therefore the chemical shift increases ..." will not suffice. Provide a careful and reasonable discussion of the effects of protonation on the oxygen's atomic shielding. In particular, consider in detail the effects of protonation on the diamagnetic and paramagnetic shielding.

The more protonation, the less is the shielding.
That is what everybody expects and it is true. Why is it true?
Could be (a) diamagnetic shielding <u>decreases</u> and/or (b) paramagnetic shielding <u>increases</u>
with degree of protonation.

With protonation, the diamagnetic shielding ...
H-atoms carry most of the charge and protonation withdraws a very small amount of
electron density from the O. The diamagnetic shieding should not vary all that much.

With protonation, the paramagnetic shielding ...
(a) electron density of O contracts and the $<1/r^3>$ term increases   (MAIN EFFECT)
(b.1) in cations,   E is reduced and paramagnetic shielding thus increases
(b.2) but in dication the lone pairs get engaged, no n-to- * left,   E grows,   p drops
(c) drops as the molecule becomes more symmetric (Q terms)

Every reasonable comment received partial credit. Every good argument wins 5 points.

Question 4. ^{13}C-NMR Spectra of -Ionone: Selective Decoupling, INEPT & DEPT. (40 points)

Source: One- and Two-dimensional NMR Spectra by Modern Pulse Techniques. Edited by Koji Nakanishi. Kodansha, University Science Books, Mill Valley, California, **1990**.

-ionone
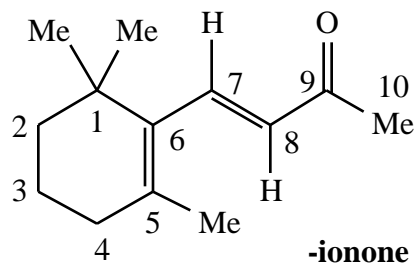
(a) The carbonyl-C couples with the H-atoms at C8 with ^{2}J(C,H), at C7 with ^{3}J(C,H) and at C10 with another ^{2}J(C,H). Sketch the ^{13}C-NMR signal of C9 for the three conditions specified:

(**I**) Broadband proton decoupled (2 points)	(**II**) Hydrogens at C10 are selectively irradiated (3 points)	(**III**) Hydrogens at C7 and C8 are selectively irradiated. (3 points)
a singlet	doublet of doublets Hs at C8 and C7 each couple to make doublet	a quartet due to coupling with 3 methyl-Hs only

(b) Appendix 1 shows the 62.5 MHz ^{13}C-NMR (CDCl$_3$) of -ionone with complete decoupling and selective decoupling of the J(C,H) couplings of C7 and C2. Note that the selective ^{1}J(C,H)-decoupling of C7 is indeed selective in that only the C7 signal becomes a singlet while the other signals all show ^{1}J(C,H)-splitting. Now look at the "selective decoupling" of the C2. The irradiation of the Larmor frequency of the H-atom attached to C2 not only makes the C2 resonance a strong singlet but also has other consequences. Describe these consequences and comment as to why the situations differ for these two selective proton decouplings. (8 points)
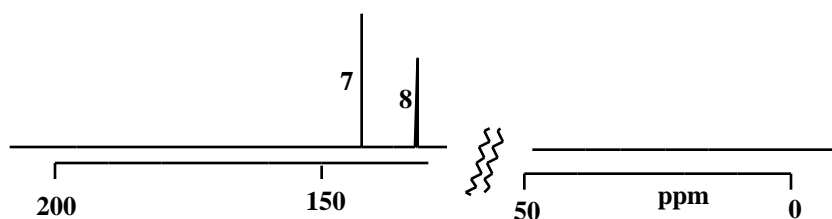
Irradiation of the H at C2 makes the C2 signal a strong singlet. In addition, other parts of the spectrum show collapsing multiplets. The reason is that the H at C2 is very close to the chemical shift of the Hs at C3 and the methyl groups at C5 and attached to C1.

(c) In the DEPT pulse sequence, one records several spectra that differ in the pulse length of the last pulse in the H-channel. Depending on the length of this pulse, one records the 45°, 90° and 135° DEPT spectra. The normal decoupled 62.5 MHz ^{13}C-NMR (CDCl$_3$) spectrum of -ionone is shown at the bottom of the page. Sketch the 45°, 90° and 135° DEPT spectra in the spaces provided. (4+4+4 pts.)
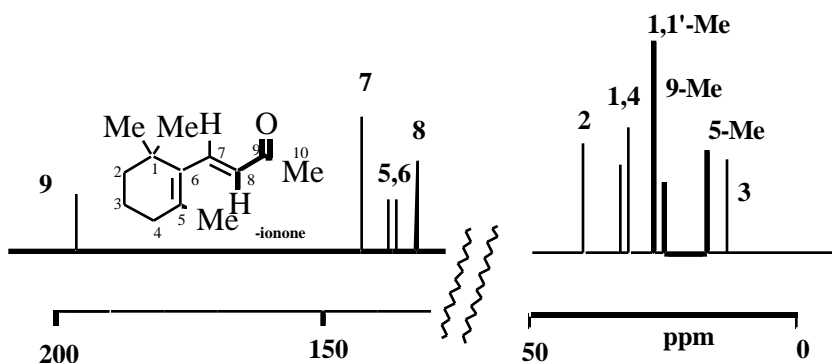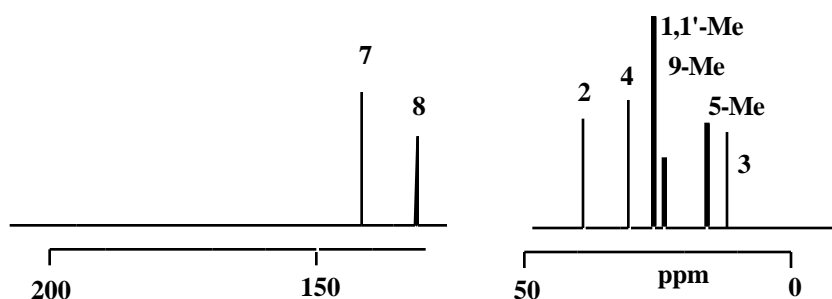
DEPT(135) "no quats" and CH$_2$ on negative side

1,1'-Me
9-Me
5-Me
7
8
2 4
3
200 150

DEPT(90) CH only!

7
8
200 150 50 ppm 0

DEPT(45) no quat. C!

1,1'-Me
9-Me
5-Me
7
8
2 4
3
200 150 50 ppm 0

1,1'-Me
1,4 9-Me
5-Me
2
9
7
8
5,6
3
Me Me H   O
7   9   10
2 1   Me
3 6 8
4 5 Me
H
-ionone
200 150 50 ppm 0
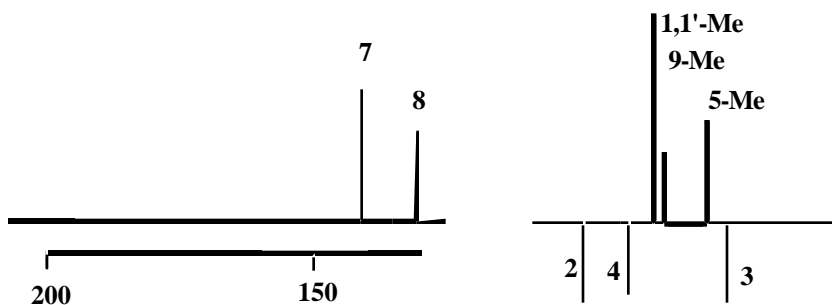
(d) Appendix 2 shows the INEPT spectrum of -ionone. In INEPT, the delay time is an important factor. Appendix 2 shows the normal decoupled 62.5 MHz ^{13}C-NMR (CDCl$_3$) spectrum of -ionone as spectrum A. Spectra B, C and D were obtained with delay times of 1/4J, 1/2J and 3/4J. The J value used was about 130 Hz, which is a typical value for a C-H coupling constant involving an sp^3 hybridized carbon atom. (3+3+3+3 pts.)

Which carbons show up in INEPT spectrum B and which don't?

All carbons that have H-atoms attached show up. Quaternary C-atoms don't show up.
Like the DEPT(45)

Which carbons show up in INEPT spectrum C and which don't?

All CH carbons show up. This is like the DEPT(90)

Which carbons show up in INEPT spectrum D and which don't?

All CH and CH$_3$ are up and all CH$_2$ are down.
This is like the DEPT(135).

Which two of the three INEPT spectra B - D do you consider most relevant to determine the multiplicities of all signals?

Need C and D. B is not so important.

The END