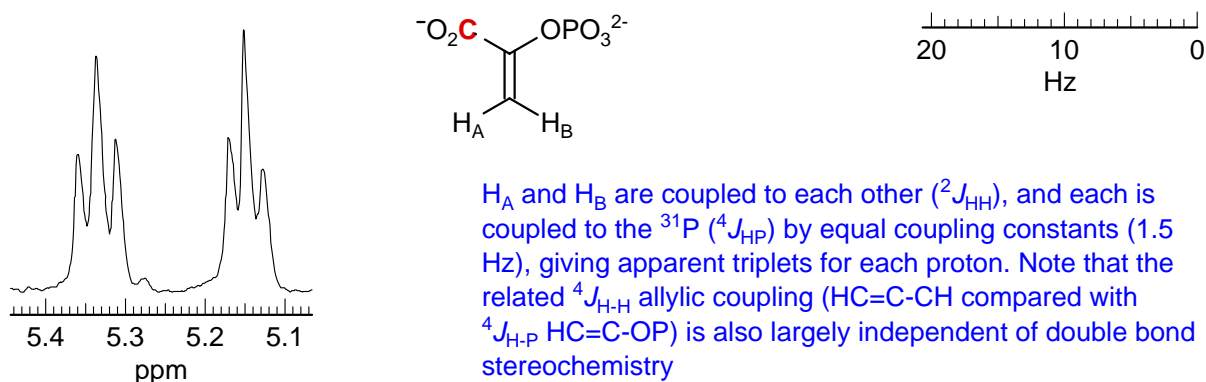


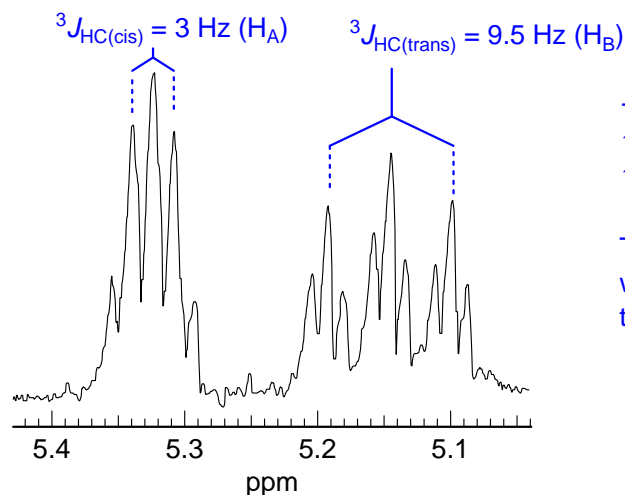
Problem Set 11 - 2014 - Answer

Problem R-85K (*J. Am. Chem. Soc.* **1970**, 92, 4095)

(a) The 60 MHz ^1H NMR spectrum of phosphoenolpyruvate (PEP) is shown below. Analyze the multiplets and assign the couplings



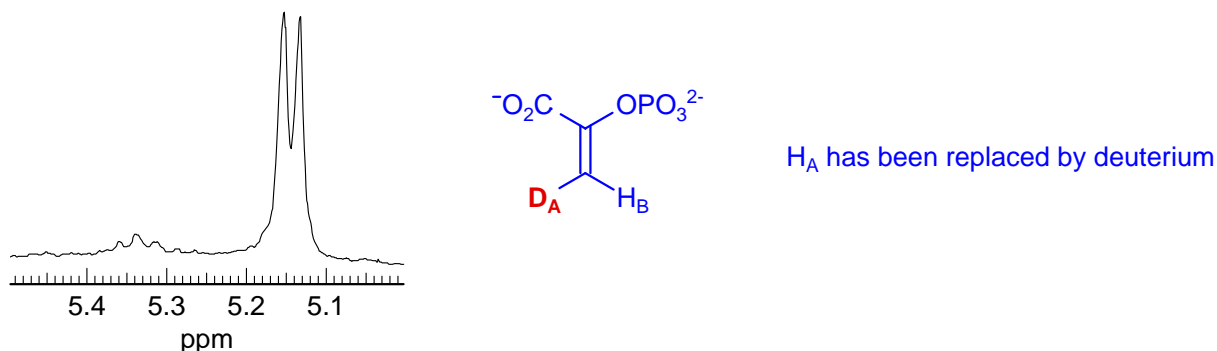
(b) The 100 MHz ^1H NMR spectrum of PEP labeled 60% with ^{13}C at the carboxyl carbon is shown below. Analyze the multiplets and assign the chemical shifts and couplings.



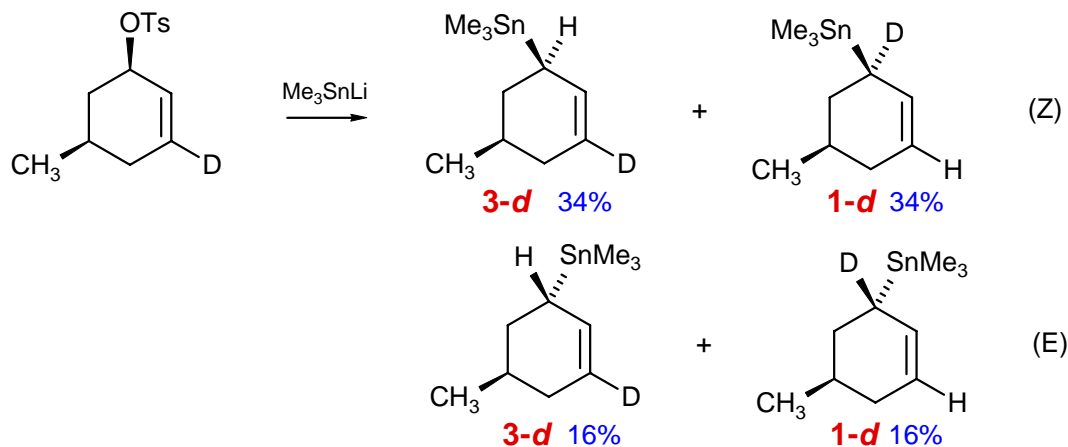
The central peaks are from the 40% of the sample that has ^{12}C at the carboxyl carbon, the satellites are from the 60% ^{13}C .

This allows assignment of the two protons - the upfield one with the large $^3J_{\text{HC}}$ is trans to the carboxyl group (H_B) and the other H_A ($^3J_{\text{HC(trans)}}$ is always larger than $^3J_{\text{HC(cis)}}$)

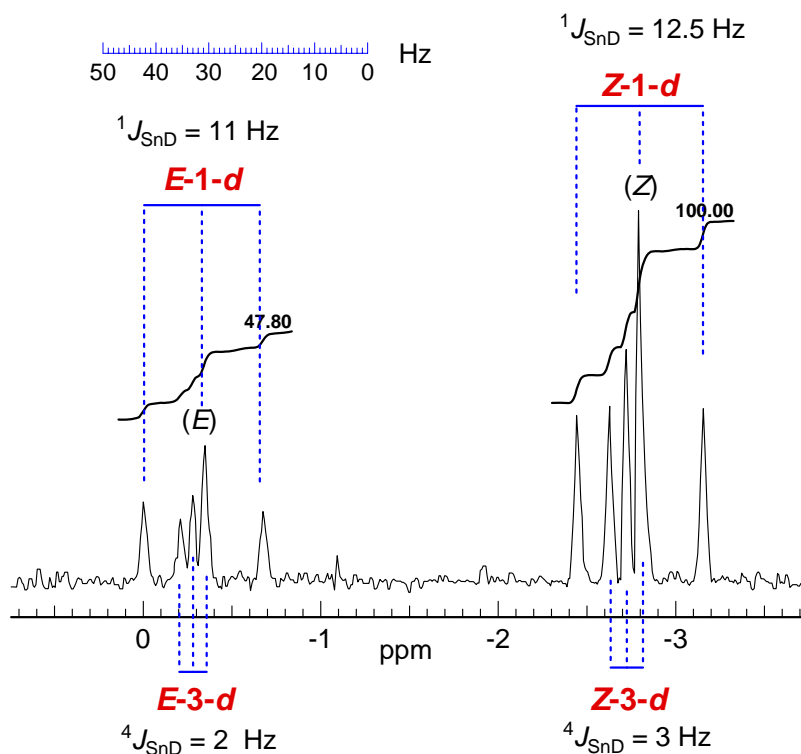
(c) The 60 MHz ^1H NMR spectrum of PEP labeled with one deuterium atom is shown below. Draw the structure of the compound, include stereochemistry.



Problem R-306 ($C_{10}H_{20}Sn$). Below is the 33.54 MHz $^{119}Sn\{^1H\}$ NMR spectrum of a reaction product from the reaction shown (Quintard, J.-P.; Degueil-Castaing, M.; Dumartin, G.; Barbe, B.; Petraud, M. *J. Orgmet. Chem.* **1982**, 234, 36):



Estimate the ratio of the four isomeric products from the NMR spectrum. All materials are racemic.



Each of the ^{119}Sn signals is coupled to the deuterium, to give overlapping 1:1:1 triplets

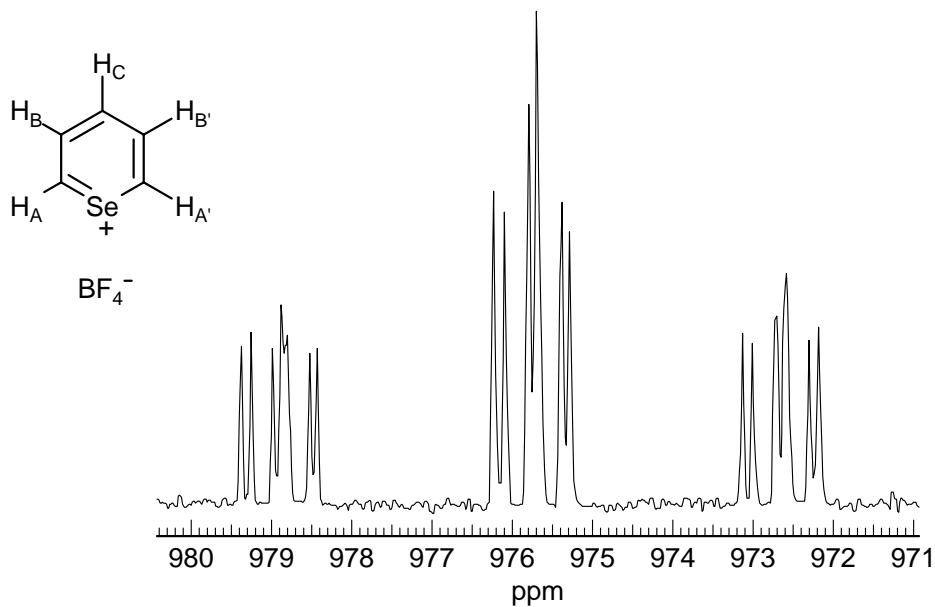
We would expect the $^2J_{SnD}$ (1-d) to be larger than $^4J_{SnD}$ (3-d).

The ratio of 3-d to 1-d is 1:1

The *E* to *Z* ratio is 48/100 (32/68)

This experiment was carried out to determine the mechanism of the nucleophilic substitution at carbon. A direct S_N2 substitution would have given only the *E*-3-d isomer (inversion at carbon), so either a carbonium ion (S_N1 through the allyl cation) or, more likely, a radical mechanism ($S_{RN}1$ through the allyl radical) is involved.

Problem R-307 ($C_5H_5BF_4Se$). Shown below is the 15.17 MHz ^{77}Se NMR spectrum of selenapyrylium fluoroborate. Interpret the splitting pattern (Sandor, P.; Radics, L. *Org. Magn. Reson.* **1981**, 16, 148).

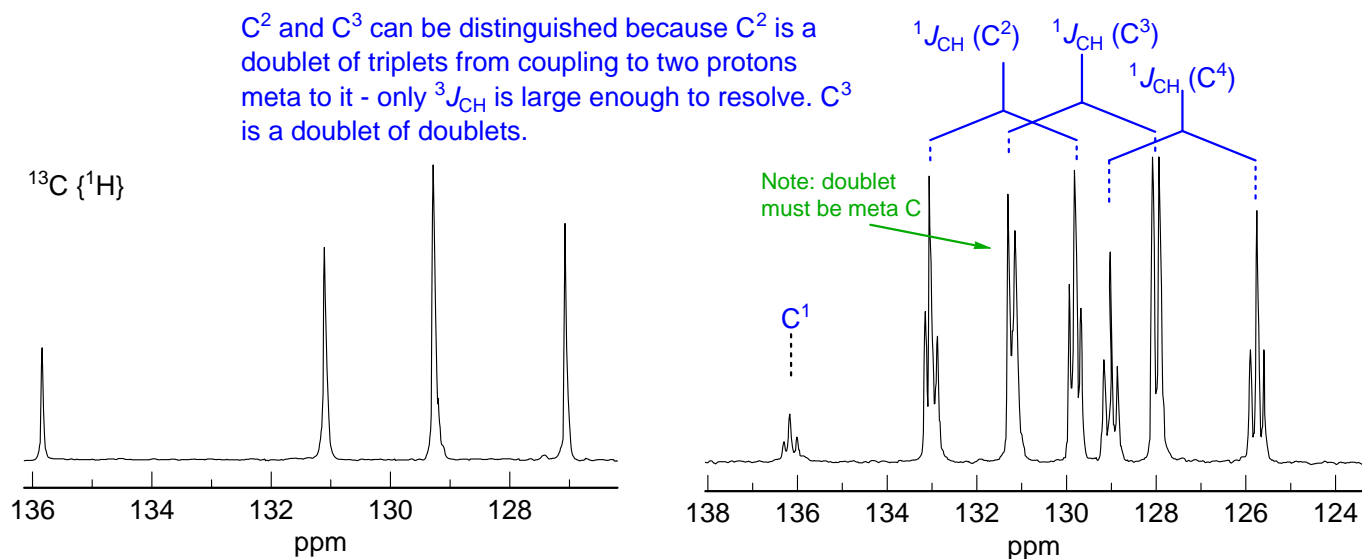


The ^{77}Se NMR signal is an apparent ttd, $J = 47, 6, 3$ Hz from coupling to H_A , H_B and H_C . The pattern is actually the X part of an $AA'BB'CX$ spin system ($X = Se$), which is not strictly first order. Hence the somewhat irregular intensities of the peaks, and small additional splittings.

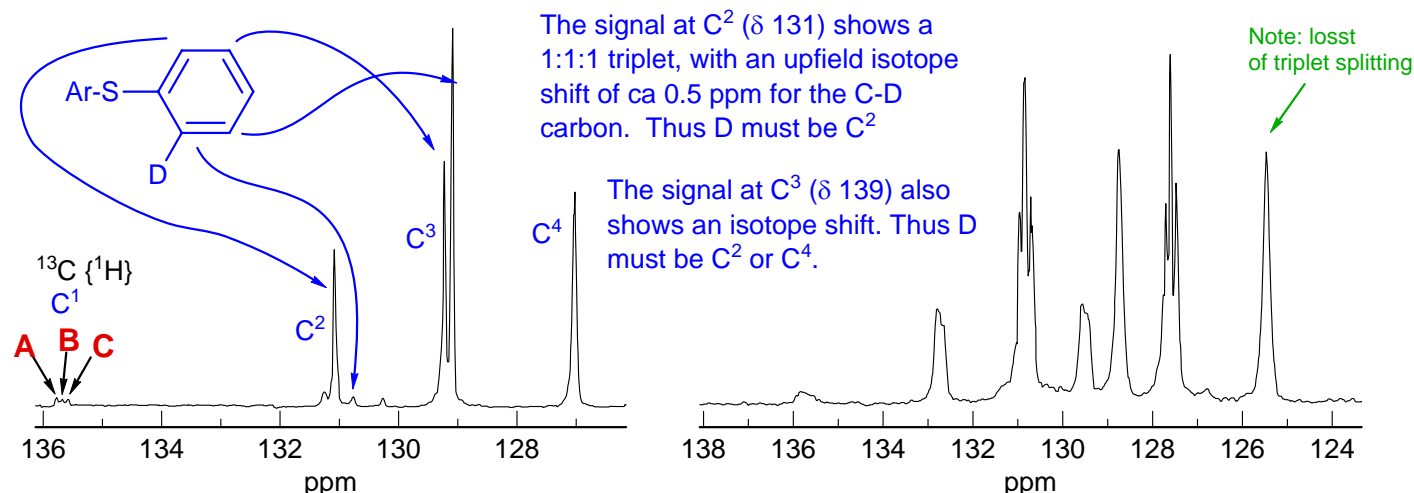
Problem R-64 ($C_{12}H_{10}S$). Below are four ^{13}C NMR spectra (50 MHz). The upper spectra are of diphenyl sulfide (Ph_2S). The lower spectra are of Ph_2S partially deuterated. The left set of spectra are proton-decoupled, the right set is fully coupled. Have PLT

(a) Assign the resonances in the unlabelled spectra (C^1 , C^2 , C^3 , C^4).

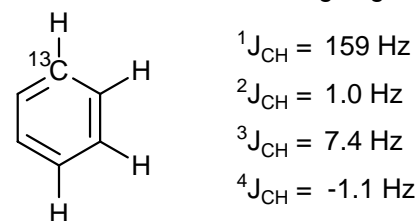
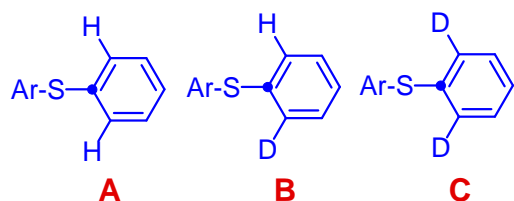
JOC 1981, 46, 4950



(b) Assign the various peaks in the D-labelled spectra.



(c) Determine the **position(s)** and roughly estimate the **extent** of deuteration indicated by the upper spectra. Briefly give your reasoning. Hint: calculate the expected C-D couplings and compare to the observed ones before assigning the signals.



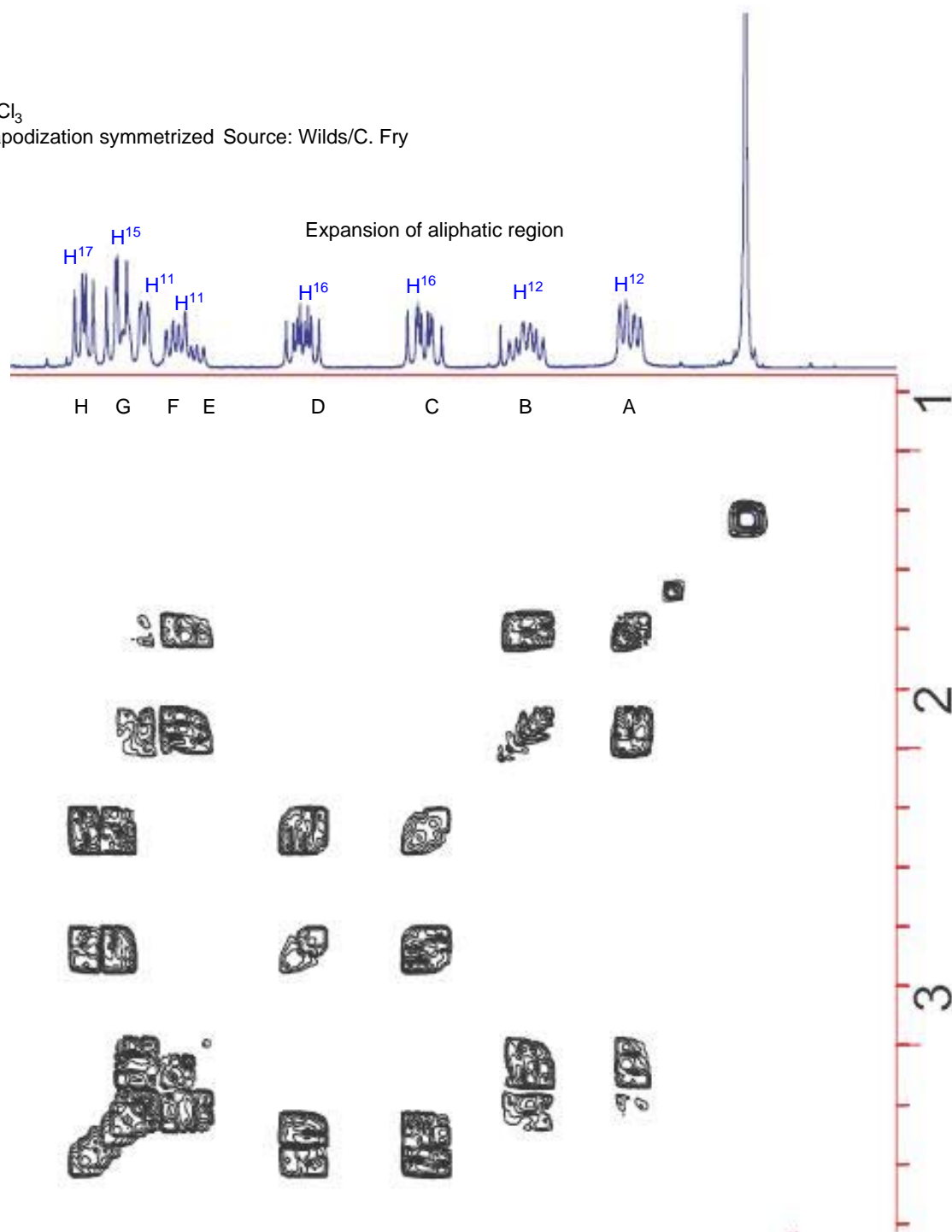
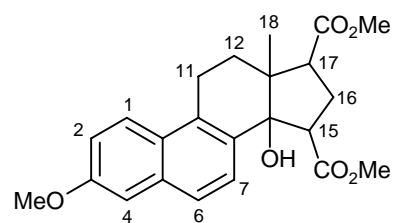
The three peaks for C^1 (labelled A, B, C) are separated by 6 Hz. These cannot be due to $^3J_{CD}$ since this would be at most $1/6 \times 7.4 \text{ Hz}$ (if D was meta), or to $^2J_{CD}$, if D was ortho (as it actually is) since it would be only $1/6 \times 1.0 \text{ Hz}$.

The deuterium seems to be almost entirely at C^2 (this is the only carbon that shows $^1J_{CD}$). The best estimate of the level of labelling at C^2 is probably from the two peaks at C^3 (two-bond isotope shift), (60% D, 40% H). There must be a significant amount of 2,6-dideutero, to account for peak C at C^1 , and very little 2,6-diprotio (structure A), otherwise peak A at C^1 would be taller. Peaks B and C are very weak because they would have long T_1 due to loss of CH DD relaxation, leading to saturation, and possible loss of NOE enhancement.

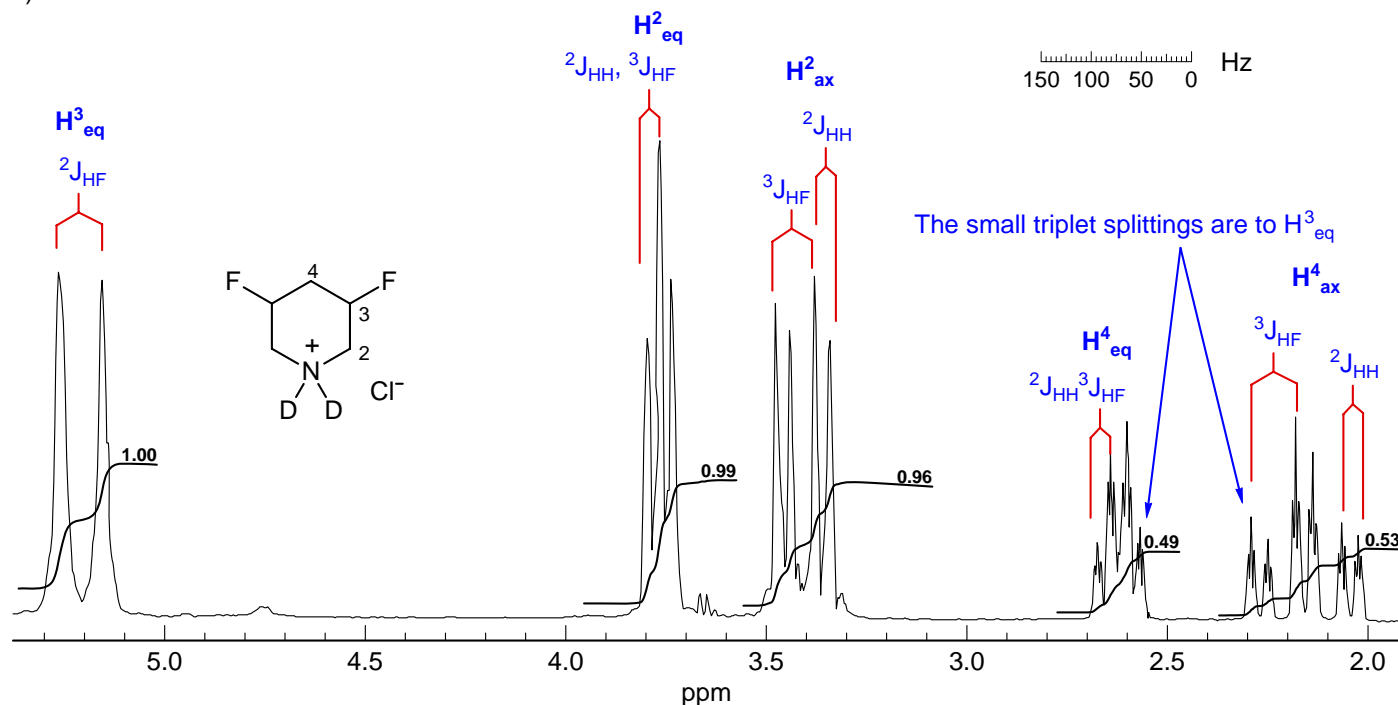
Problem R-28A ($C_{23}H_{26}O_5$)

300 MHz 1H COSY 2D NMR spectrum in $CDCl_3$

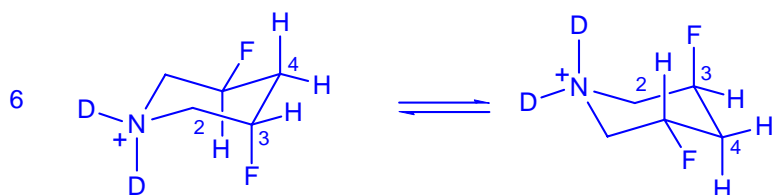
512x128 FT'd to 512x512, sinebell-squared apodization symmetrized Source: Wilds/C. Fry



Problem R-10M. Interpret the room temperature 400 MHz ^1H NMR spectrum of a difluoropiperidine ammonium salt (D_2O solvent, expansions on next page) and determine stereochemistry and conformation (*J. Am. Chem. Soc.* **2000**, 122, 544).



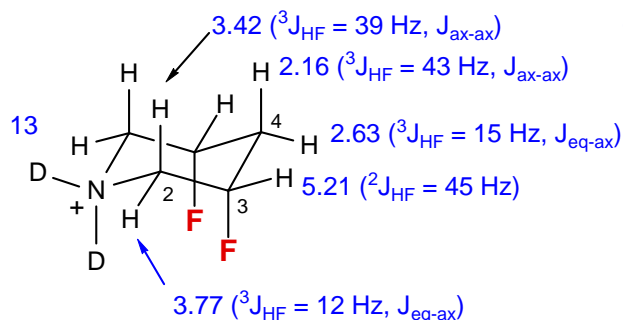
(a) Are the two fluorines cis or trans to each other? Explain briefly.



There are two signals for the protons on H^4 (2.15, 2.60). If the two fluorines were cis, rapid inversion of the ring would give only one chemical shift for the H^4 protons.

Similarly, the protons at H^2 (3.4, 3.8) would have only one shift, two are observed

(b) Add the fluorines to the cyclohexane conformation below, and explain how you arrived at this conformation. Write the chemical shifts next to the protons on carbons 2,3, and 4 on the structure, and, in parenthesis, the approximate $J_{\text{H-F}}$ coupling for each proton (δ 0.00, $^nJ_{\text{H-F}} = 0.00$ Hz).



The two fluorines have to be cis, and both are axial:

- There are large $J_{\text{Hax-Fax}}$ couplings to both H^2 and H^4 (ca 40 Hz)
- H^4_{ax} shows only one additional large coupling ($^2J_{\text{H-H}}$)
- H^2_{ax} shows only one additional large coupling ($^2J_{\text{H-H}}$) and no $^3J_{\text{Hax-Hax}}$
- If H^3 was axial, there should be a ca 10 Hz J to both H^2_{ax} and H^4_{ax}

(c) Why are the signals at δ 3.3-5.4 broadened compared to the signals at δ 2-2.7?

H^2 : The signals at δ 3.4-3.8 are probably broadened by small unresolved coupling to the N-D. There are also unresolved $^3J_{\text{HH}}$ couplings to the equatorial H^3 protons

5 H^3 : There are several unresolved H-H couplings ($J_{\text{eq-eq}}$ and $J_{\text{eq-ax}}$) to H^2 and H^4 ; also a possible unresolved coupling to ^{14}N - there is an anti relationship between H^3 and N, and the N could be undergoing relatively slow quadrupolar relaxation (high symmetry).

Problem R-10M ($C_5H_{10}ClF_2N$).400 MHz 1H NMR spectrum in D_2O (Source: *J. Am. Chem. Soc.* **2000**, 122, 544 / Reich 11/18)