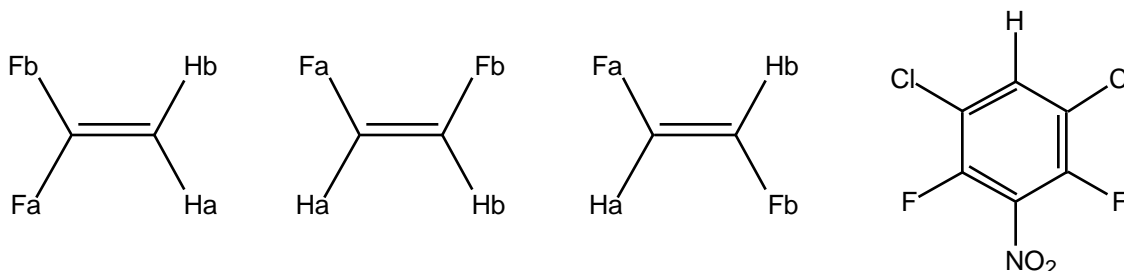


Chemistry 416, Fall Semester 1997, Dr. Glaser

Quiz 1: "NMR Spectroscopy", Monday, September 22, 1997, 35 minutes, announced.

Your Name:

Question 1. Coupling in Difluoro Compounds. (12 points)



(a) We talked about the 1,1-isomer and we decided that H_a and H_b are chemically _____ (equi., not equi.) because they were related by _____ (no, a C_s , a C_2) symmetry element. The term "homotopic" _____ (would, would not) apply to H_a and H_b . Moreover, it is clear that H_a and H_b _____ (are, are not) magnetically equivalent and hence the 1H -NMR spectrum will be _____ (simple, complex). (5 points)

(b) Now let's turn to the two 1,2-isomers. The atoms H_a and H_b in the *cis* isomer are chemically equivalent because of the _____ symmetry element. Because of this chemical equivalence, the H nuclei are chemical shift equivalent and they _____ (are, are not) magnetically equivalent. The *trans* isomer represents a _____ (A_2X_2 , $AA'XX'$) spin system. (4 points)

(c) For the benzene compound, the two F-atoms _____ (are, are not) chemically equivalent and they _____ (are, are not) magnetically equivalent since the ${}_nJ(F,H)$ coupling constant (give the value of "n" in front of the J) is the same for both H/F couplings. (3 points)

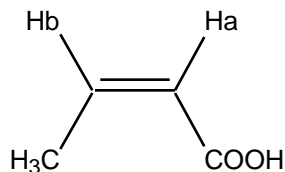
OVER

Points for Question 1:	/12		
Points for Question 2:	/12		
Points for Question 3:	/12		
Points for Question 4:	/4	Total Points:	/40

For each of the estimates you make in Questions 2 and 3, show your work (give equation and values of the various parameters) and do **state your source** (e.g. "Pretsch C194" or "Friebolin, p. 139").

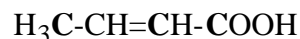
Question 2. H-NMR Increments. (12 points)

Estimate the chemical shifts of the methyl H-atoms and of the vinylic H-atoms in *cis*-crotonic acid.



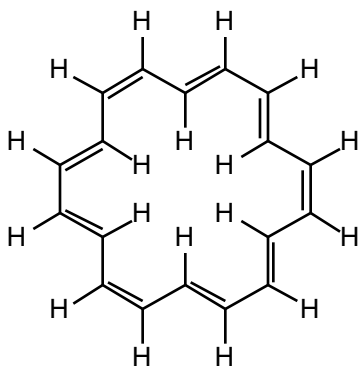
Question 3. ¹³C-NMR Increments. (12 points)

Estimate the chemical shifts of the methyl-C, the =C and the acid-C in crotonic acid.



Methyl-H chemical shift:	H ₃ C- chemical shift:
H _a chemical shift:	=CH- chemical shift:
H _b chemical shift:	-COOH chemical shift:

Question 4. Ring Current Effects. (4 points)



A spectacular example of shielding and deshielding by ring currents is furnished by some of the annulenes. At low temperatures, the protons outside of the ring of [18]annulene are strongly _____ and occur at much _____ (lower, higher) chemical shift and those inside are strongly _____ and occur in the _____ (positive, negative) chemical shift region (rel. to TMS). (1 point each)