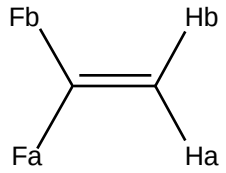
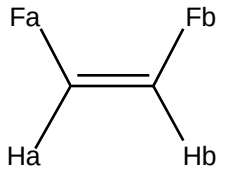
Chemistry 416, Fall Semester 1997, Dr. Glaser

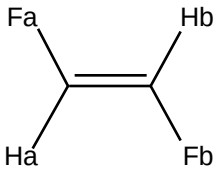
Quiz 1: "NMR Spectroscopy", Monday, September 22, 1997, 35 minutes, announced.

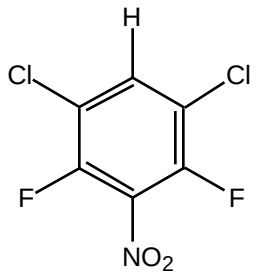
Your Name:

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 equiv.) because they were related by _____ (no, a $\mathbf{C_s}$, a $\mathbf{C_2}$) 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 ^{1}H-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 __ $\mathbf{C_s}$ or $\mathbf{C_2}$__ 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)

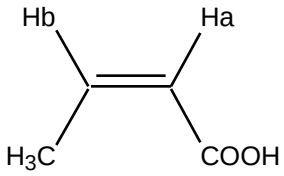
(c) For the benzene compound, the two F-atoms _____ (**are**, are not) chemically equivalent and they _____ (**are**, are not) magnetically equivalent since the **_4_**J(F,H) coupling constant (give the value of "n" in fromt of the J) is the same for both H/F couplings. (3 points)

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.

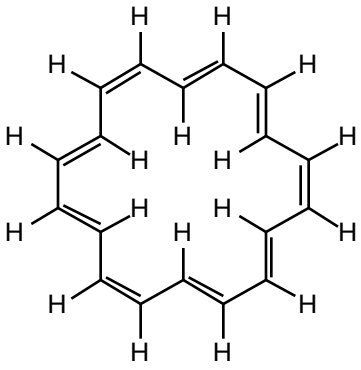


Question 3. ^{13}C-NMR Increments. (12 points)
Estimate the chemical shifts of the methyl-C, the α-C and the acid-C in crotonic acid.

H_3**C**-CH=**C**H-**C**OOH

Methyl-H chemical shift: F. p. 141/2 0.23 + 1.32 = 1.55 ppm	H_3**C**- chemical shift: F. p. 150 or P. C10 -2.4 + 19.5 - 2.8 = 14.4 ppm
H_a chemical shift: F. p. 142: 5.28 + 0.69 + 0 - 0.29 = 5.68 ppm P. H225: 5.25 + 0.80 + 0 - 0.28 = 5.77 ppm	=**C**H- chemical shift: F. p. 152: 123.3 + 4.2 - 7.9 = 119.6 ppm P. C90: 123.3 + 5.0 - 7.4 = 120.9 ppm
H_b chemical shift: F. p. 142: 5.28 + 0.39 + 0.44 = 6.11 P. H215: 5.25 + 0.32 + 0.45 = 6.02 ppm	-**C**OOH chemical shift: P. C186: 171.7 P. C184: 166 + 5.0 - 1.0 = 170 ppm

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 ___**deshielded**___ and occur at much __**higher**___ (lower, higher) chemical shift and those inside are strongly ___**shielded**___ and occur in the ____**negative** ___ (positive, negative) chemical shift region (rel. to TMS). (1 point each)