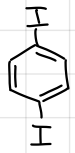
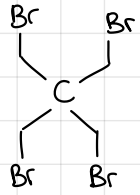
Good job!

2/2

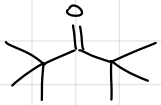
Exercise 1

a) 

b) 

c) 

d) 

e) 

2/2

Exercise 2

a) $\Delta E = h\nu = h\left|\left(-\frac{\gamma B_0}{2\pi}\right)(1-\sigma)\right| \cong h\frac{\gamma B_0}{2\pi} = 6.626\cdot10^{-34}\cdot\frac{2.68\cdot10^{8}\,s^{-1}T^{-1}\cdot 11.7\,T}{2\pi} = 3.307\cdot10^{-25}\,J$

1. $T = 298\,K \rightarrow \frac{N_\beta}{N_\alpha} = \exp\left(-\frac{\Delta E}{kT}\right) = \exp\left(-\frac{3.307\cdot10^{-25}}{1.381\cdot10^{-23}\cdot 298}\right) = 0.9999196$

2. $T = -150 + 273.15 = 123.15\,K \rightarrow \frac{N_\beta}{N_\alpha} = 0.999806$

b) We would choose -150°C to do the NMR, because if the temperature decreases, then the nuclear polarization is bigger and the NMR signal will also be bigger (NMR signal $\propto P$, NMR signal $\propto \frac{1}{T}$).
Also, it is important to know that the noise is proportional to $\sqrt{T}$.

2/2

Exercise 3

- alkanes (sp^3) : 10 eV.
- alkenes (sp^2) : 8eV.

From the theory, $\sigma_p \propto -\frac{1}{\Delta}\left\langle\frac{1}{R^3}\right\rangle$, where Δ = average excitation energy ; R = distance nucleus - electrons.
The absolute value of the excitation energy is higher for alkenes (because σ_p is more negative).

The shielding constant $\sigma = \sigma_d + \sigma_p$, where σ_d = diamagnetic contribution, σ_p = paramagnetic contribution.
Assuming that σ_p is the dominant contribution, $\sigma \cong \sigma_p$. Thus, the σ of alkenes is more negative than σ alkanes.

Also, greater shielding gives smaller chemical shift : $\delta = 10^6\left(\frac{\sigma_{ref}-\sigma}{1-\sigma_{ref}}\right)$
Thus, δ is larger for very negative σ $\Rightarrow$ alkenes.

The assumption was that the paramagnetic contribution is dominant. It could maybe be explained by the fact that, there is not much polarization in a C-C bond or C=C bond. So if we added an EN group, it would probably move the electrons and thus we would have had a bigger diamagnetic contribution.

Grup 1A :

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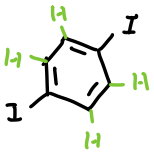
Jigsaw 2A

all the H are equivalent

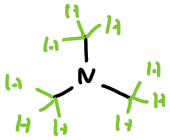
2/2

1. [Hore Section 2.2] The following compounds all exhibit a single line in their ^{1}H NMR spectra. Deduce their structures. *See also: Jigsaws 2B.3, 2C.2, 2D.1, and 2E.1.*

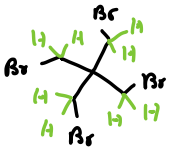
a. $C_6H_4I_2$



b. C_3H_9N

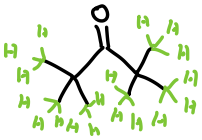


c. $C_5H_8Br_4$



d. CH_2F_2

e. $C_9H_{18}O$



1.75/2

2. * ^{1}H has a gyromagnetic ratio of 2.68×10^8 rad·s^{-1}T^{-1}.

   a. What are the relative populations of the α and β spin states of a proton in a 11.7 T spectrometer, at both room temperature and -150°C? The equation for the Boltzmann distribution is given below, where k = 1.381×10^{-23} J/K. Hint: Use the Larmor frequency to determine the energy difference.

$\gamma = 2{,}68 \cdot 10^8$ rad·s^{-1}·T^{-1}

$$\frac{N_\beta}{N_\alpha} = \exp\left(-\frac{\Delta E}{kT}\right) \qquad \Delta E = h\nu = h\frac{|\gamma| B}{2\pi}$$

$$\frac{N_\beta}{N_\alpha} = \exp\left(-\frac{h\gamma B}{2\pi kT}\right) = \exp\left(-\frac{6{,}626\cdot10^{-34}\cdot 2{,}68\cdot10^{8}\cdot 11{,}7}{2\cdot\pi\cdot 1{,}381\cdot10^{-23}\cdot(-150+273)}\right) = 0{,}99981 \text{ at } -150^\circ C$$

$$\frac{N_\beta}{N_\alpha} = \exp\left(-\frac{6{,}626\cdot10^{-34}\cdot 2{,}68\cdot10^{8}\cdot 11{,}7}{2\cdot\pi\cdot 1{,}381\cdot10^{-23}\cdot(25+273)}\right) = 0{,}99992 \text{ at } 25^\circ C$$

   b. Based only on the answers to the previous question (i.e., ignoring changes in state of the sample, equipment logistics, etc.), which of these two temperatures would you choose to run an experiment? Why?

We would choose -150°C to run an experiment because the relative population are smaller. So the population levels are more different and so we can see more change at this temperature of -150°C The NMR signal is proportional to the difference in population

1/2

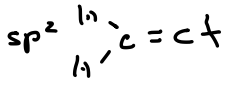
3. [Hore Section 2.2 and 2.3] The lowest energy electronic transitions in alkanes and alkenes are approximately 10 eV and 8 eV respectively. Predict whether saturated (sp^3) or unsaturated (sp^2) ^{13}C nuclei have larger chemical shifts. Assume the paramagnetic contribution is the dominant contribution. Justify the assumptions made in this exercise.

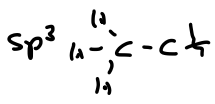
if bigger electronegativity, there is a greater electronic repulsion and therefore the chemical shift decreases.

the chemical shif of $sp^3 < sp^2$

Justify with equation (2.8) from Hore.

sp H-C≡C-H

sp^2 

sp^3 

Really good!

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Jigsaw 2A

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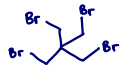
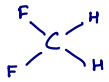


d. CH_2F_2



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$$\frac{N_\beta}{N_\alpha} = \exp\left(-\frac{\Delta E}{kT}\right)$$

$\nu_{Larmor} = \frac{\gamma \cdot B_0}{2\pi} = \frac{2.98 \times 10^8 \cdot 11,7}{2\pi} = 0,499 \times 10^9$ Hz

$\Delta E = \nu_{Larmor} \cdot h = 6.626 \times 10^{-34}$ J.Hz^{-1} $\times$ $3,135 \times 10^9$ Hz $= 3,307 \times 10^{-25}$ J

$\frac{N_\beta}{N_\alpha} = \exp\left(\frac{-\Delta E}{kT}\right) = \exp\left(\frac{-3,307 \times 10^{-25}}{1,381 \times 10^{-23} \times 123}\right) \simeq 0,9998$ at 123 K

$= \exp\left(\frac{-3,307 \times 10^{-25}}{1,381 \times 10^{-23} \times 298}\right) \simeq 0,99991$ at 298 K

   b. Based only on the answers to the previous question (i.e., ignoring changes in state of the sample, equipment logistics, etc.), which of these two temperatures would you choose to run an experiment? Why?

In order to get a bigger signal, we want a higher polarizat° which is correlated to the difference in population.
⇒ At 123K, the difference is slightly bigger so we would rather use this temperature to run the experiment.

3. [Hore Section 2.2 and 2.3] The lowest energy electronic transitions in alkanes and alkenes are approximately 10 eV and 8 eV respectively. Predict whether saturated (sp^3) or unsaturated (sp^2) ^{13}C nuclei have larger chemical shifts. Assume the paramagnetic contribution is the dominant contribution. Justify the assumptions made in this exercise. 2/2

we know that $\sigma_p \propto \frac{-1}{\Delta}\langle\frac{1}{r^3}\rangle$ ← distance between the nucleus & electrons; ← average excitat° energy

- Given that the excitation energy of alkenes (8 eV) < than alkanes, it's safe to say that the absolute value of σ_p is higher for alkenes, σ_p is more negative
- Assuming paramagnetic contribution is dominant $\sigma = \sigma_d + \sigma_p \simeq \sigma_p$.
- we know that more shielding yields a smaller chemical shift ⇒ since alkenes' shielding is more negative then an unsaturated nuclei (sp^2) would have a smaller chem shift.

- Both alkenes & alkanes have electron density around the carbon that isn't very different. In order for a diamagnetic contribut° to be higher, a more electronegative element should be present.