Great work!

CH-314 Structural Analysis
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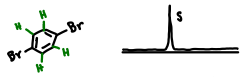
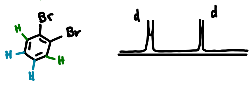
Jigsaw 2E

1. [Hore Section 2.2] How many distinct chemical shifts would you expect to find in the ^{1}H spectra of the three isomers of dibromobenzene? *See also: Jigsaws 2A.1, 2B.3 2C.2, and 2D.1.*

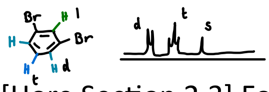
The 3 isomers :



→ We expect to see 1 pick

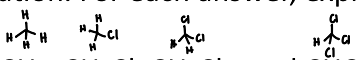


→ We expect to see 2 peaks w/ ratio 1:1



→ We expect to see 3 peaks w/ ratio 1:2:1

2. [Hore Section 2.3] For each of the following sets, rank the options from highest to lowest ^{1}H chemical shift. Assume the diamagnetic contribution is the dominant contribution. For each answer, explain why.

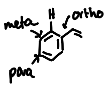


a. CH_4, CH_3Cl, CH_2Cl_2, and $CHCl_3$.

$CHCl_3 > CH_2Cl_2 > CH_3Cl > CH_4$

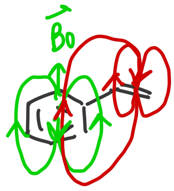
→ chemical shift gets higher with the increase of electronegativity from neighbouring atoms. The most Cl atom → the biggest chemical shift

b. The ortho, meta, and para protons in styrene.



ortho > meta > para

there's a bigger shielding for para position, bcs there's more shielding with a higher current



c. The protons in $CH_2BrCH_2CH_3$.

$CH_2Br > CH_2 > CH_3$

by lowering the electron density, there's less shielding which means a bigger shift

3. * [Hore Section 2.1, Week 2 Slide 25, and Keeler Section 4.2] The B_0 field induces precession of magnetization around the z-axis at the Larmor frequency, $\omega_0 = -\gamma B_0$. Here we neglect the effect of relaxation.

a. Starting with the magnetization along the **z**-axis, what is the direction of the magnetization of a ^{13}C site after one second in a 9.4 T magnetic field? The $\underbrace{\text{gyromagnetic ratio}}_{\gamma}$ for ^{13}C is 1.071×10^{7} rad·s^{-1}T^{-1}.

$\omega_0 = -(1.071 \cdot 10^7) \cdot (9.4) = -100674000$ rad/s, (w/ $\theta = \omega_0 \cdot t$ & $t = 1s$)

precession around the z-axis ⇒ no change in the direction; it starts along the z-axis and precesses around it

⇒ the direction of magnetization remains along the z-axis

b. Starting with the magnetization along the **x**-axis, what is the direction of the magnetization of a ^{13}C site after one second in a 9.4 T magnetic field?

as for (a), $\theta = -100\,674\,000$ rad

$-\dfrac{100\,674\,000}{2\pi} = -16\,022\,764.74$ ⇒ the magnetization completes 16 022 764 full turns

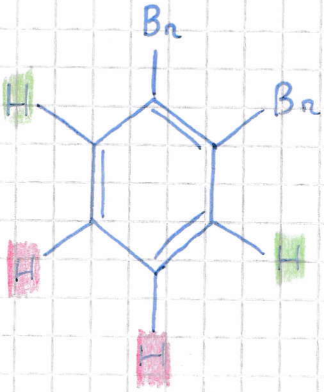
in addition to these, it completes an extra $-0.74 \times$ of one turn

so, the final direction is that of $(-0.74 \times 2\pi) = -4.65$ rad

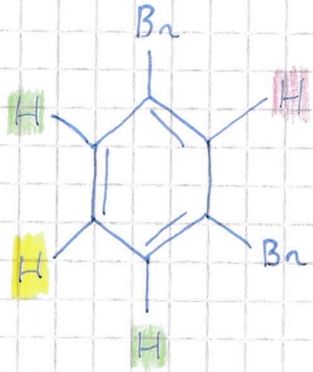
Nice job!

1) Equivalent H have the same chemical shift

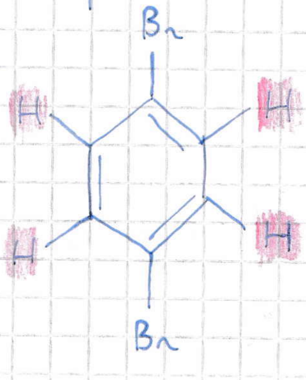
ortho



meta



para



2 peaks

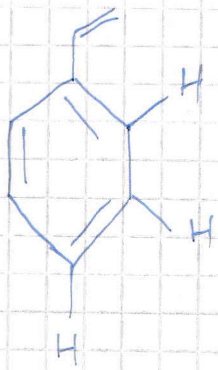
3 peaks

1 peak

2) electronegative atoms and electron attractor groups deshield nearby H atoms. The closer the group to the hydrogen, the stronger the effect.

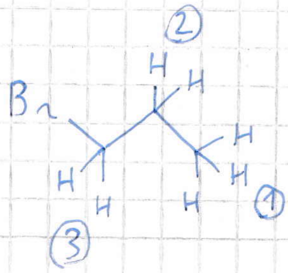
a) $CH_4 < CH_3Cl < CH_2Cl_2 < CHCl_3$

b)



$H_{para} < H_{meta} < H_{ortho}$

c)



$H_{①} < H_{②} < H_{③}$

3) $B_0 = 9,4\ T$

$\gamma = 1,071 \cdot 10^7\ rad/_{s \cdot T}$

$t = 1s$

$\omega_0 = -9,4 \cdot 1,071 \cdot 10^7 \cong -1,007 \cdot 10^8\ rad/_s$

$\theta(1s) = -1,007 \cdot 10^8 \cdot 1 = -1,007 \cdot 10^8\ rad$

Reduce this to a number between 0 and 2π

a) The magnetization starts on the z-axis. Since the rotation happens around the z-axis, the direction does not change.

final direction: $\begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$

b) The magnetization starts on the x-axis. In one second it will rotate $-1,007 \cdot 10^8$ rad.

final direction: $\begin{bmatrix} \cos(-1,007 \cdot 10^8) \\ \sin(-1,007 \cdot 10^8) \\ 0 \end{bmatrix} \cong \begin{bmatrix} 0,1217 \\ 0,9926 \\ 0 \end{bmatrix}$