

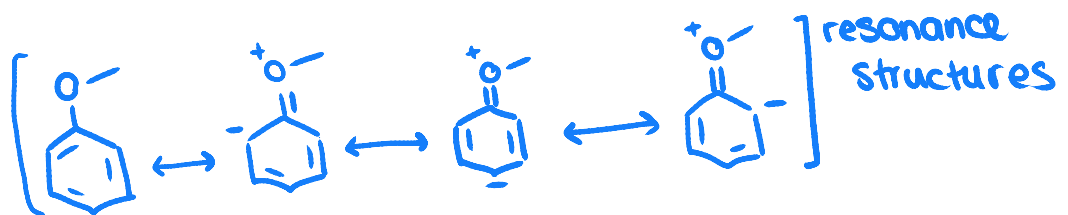
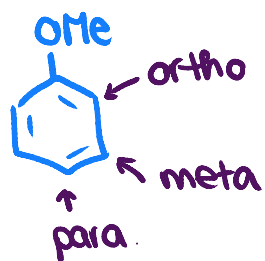
Jigsaw 2C

Home Section 2.4. Contributions to nuclear shielding

- Two students prepared each an NMR tube of ethanol in deuterated chloroform. The first one used 1 mM of ethanol, the second student used 100 times that concentration. Apart from the difference in intensity, will they obtain the same proton spectrum? Why or why not?

Yes, the spectrum will change. As the concentration increases the interactions between the molecules of ethanol also do. The -OH form hydrogen bonds which heavily change the chemical shift. The peaks corresponding to -CH₂ and -CH₃ will however not change too much.

- Predict which of the ortho, meta, and para protons in methoxybenzene has the highest and which the lowest ¹H chemical shift.



Methoxy is an electron donating group, with the resonance structures shown above, the shielding is increased on the positions where the electron pair can be delocalized.

Meta is the less shielded, thus the most shifted to the left. Ortho and para are more shielded thanks to the resonance structures. Between the two positions, ortho is more shielded than para because it is closer to the group.

Jigsaw 2C

Question 1:

The difference in concentration does yield a different proton spectrum. For a high concentration, intermolecular interactions happen due to the OH group of the ethanol. This bonding could cause shielding or un-shielding leading to shifts in the chemical shifts. In addition, apart from the changes in the intensity peaks, border peaks could be seen. For low concentration, the ethanol is diluted hence these interactions are negligible, the only effect could be the lower intensity signals.

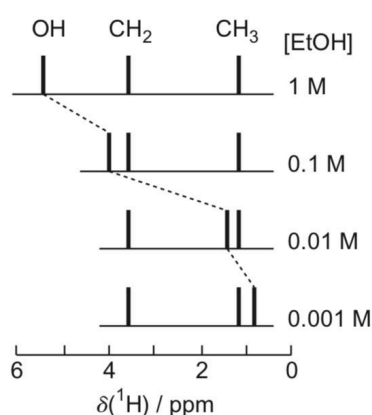


Fig. 2.27 Hydrogen bonding shifts in ethanol, as a function of concentration in CCl₄.

Question 2:

We know that electron donating groups tend to shield the protons whereas the electron withdrawing groups have an un-shielding effect. As the OMe group is an electron donating group it has a shielding effect. Furthermore, the electron density is increased at position ortho and para via resonance. Hence the ortho protons will have the highest shielding due to resonance and the proximity to the methoxy group, and the meta ones will have the lowest chemical shift.

Meta- will have less shielding that means higher chemical shift