

5.9: Chemical Shifts

The chemical shift feature of NMR makes it a powerful analytical tool. Identical nuclei (e.g. protons) undergo precession at somewhat different frequencies if they are in a **different electronic environment**. Electron currents in the electronic charge distribution give rise to an induced magnetic field that has a magnitude, $-\delta H_0$, where δ is a shielding constant. The magnetic field active in on the i^{th} nucleus is then

$$H_i = (1 - \delta)H_0$$

Only if the nuclei are in chemically indistinguishable positions (i.e. related by symmetry operations), will their δ 's be the same. The δ 's are dimensionless and for protons on at most an order of magnitude of 10^{-7} MHz. Thus the Larmor frequencies of protons only differ by ~ 10 ppm. For 300 MHz NMR, this is 3000 Hz, but since the linewidths < 1 Hz are common, very small chemical shift differences can be resolved in a 300 MHz instrument.

The Fourier Transform of a sample containing two differently shielded nuclei, σ_1 and σ_2 will contain two Lorentzians separated by $H_0 (\sigma_1 - \sigma_2) \gamma / 2\pi$ Hz etc.

Δf increases linearly with H_0 , which is characteristic of chemically shifted nuclei. There are charts that correlate the range of various types of protons commonly found in organic molecules. There are given as function of a standard, TMS: $(\text{CH}_3)_4\text{Si}$. δ is defined as the shift, Δ , in Hz relative to TMS taken at 0 (arbitrary standard). Since Δ is proportional to H_0 , this is compensated by dividing by the fixed frequency of the probe, f_0 .

The origin of the chemical shift for a nucleus is very complicated. We can derive it initially into local and remote effects. Local effects are from electrons on the atoms; remote effects from electrons on neighboring atoms.

Local Shift: Two types of contributions are found: **diamagnetic** and **paramagnetic**.

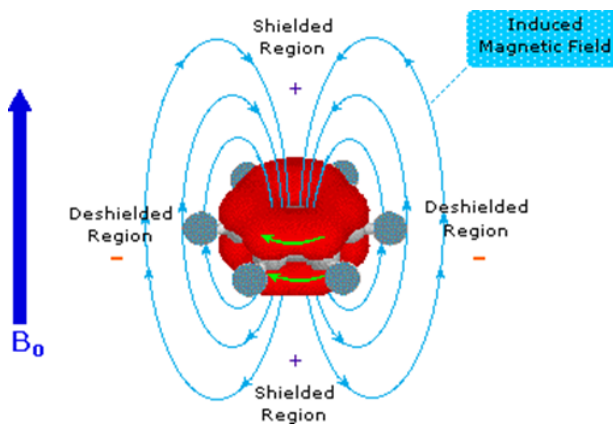
- Diamagnetic is an induced circulation of charge in the ground state wavefunction that **opposes** the field.
- Paramagnetic is field-induced mixing of the excited state wavefunction that leads to a contribution of opposite sign that **reinforces** the applied field.

Remote Shifts:

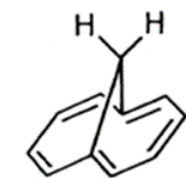
- The shielding at an atom like H that has little electron density can be influenced by field-induced moment on electron-rich neighboring atom. Take H-X, for example: the induced moment on X is the opposite to the field (only considering the diamagnetic part of the local effect). The induced (shielding) field of H depends on the orientation of H_0 relative to the HX axis.

Ring Currents in conjugated systems

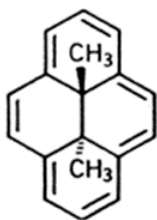
The π electrons in aromatic ring systems contribute to large currents in the presence of an external magnetic field. These currents induce fields at the positions of the protons that deshield them. The currents are produced when the H_0 is perpendicular to the aromatic plane.



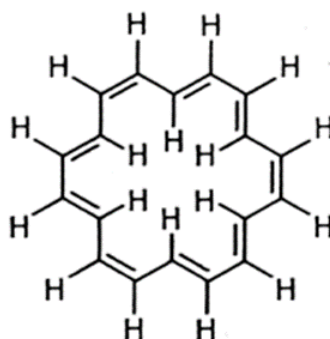
At the position of the H atoms, the direction of the induced fields along H_0 reinforces the applied field. This is massive deshielding (downfield shift of resonance)



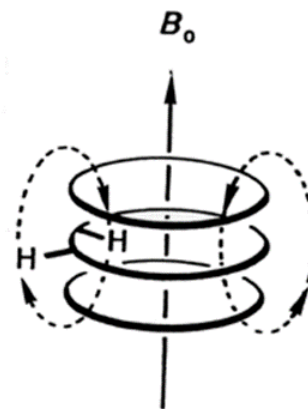
δ (Ring) 7.27; 6.95
 δ (CH₂) -0.51



δ (Ring) 8.14 - 8.64
 δ (CH₃) -4.25



δ (H outer) 9.28
 δ (H inner) -2.99



Aromatic compounds show a characteristic deshielding of ring protons (d 6 - 9 ppm vs. d 3 - 4 ppm for alkenes)

Upshot: The interpretation of chemical shift is very complicated; NMR can be used empirically for structural analysis with great success, without having to fully interpret the origin of the chemical shifts. A characteristic useful feature of NMR is the spin-spin splitting that is very useful in structural analysis.

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