5.4A: Diamagnetic shielding and deshielding

We come now to the question of why nonequivalent protons have different chemical shifts. The chemical shift of a given proton is determined primarily by its immediate electronic environment. Consider the methane molecule (CH\textsubscript{4}), in which the protons have a chemical shift of 0.23 ppm. The valence electrons around the methyl carbon, when subjected to B\textsubscript{0}, are induced to circulate and thus generate their own very small magnetic field that opposes B\textsubscript{0}. This induced field, to a small but significant degree, shields the nearby protons from experiencing the full force of B\textsubscript{0}, an effect known as local diamagnetic shielding. The methane protons therefore do not experience the full force of B\textsubscript{0} - what they experience is called B\textsubscript{eff}, or the effective field, which is slightly weaker than B\textsubscript{0}.

Therefore, their resonance frequency is slightly lower than what it would be if they did not have electrons nearby to shield them.

Now consider methyl fluoride, CH\textsubscript{3}F, in which the protons have a chemical shift of 4.26 ppm, significantly higher than that of methane. This is caused by something called the deshielding effect. Because fluorine is more electronegative than carbon, it pulls valence electrons away from the carbon, effectively decreasing the electron density around each of the protons. For the protons, lower electron density means less diamagnetic shielding, which in turn means a greater overall exposure to B\textsubscript{0}, a stronger B\textsubscript{eff}, and a higher resonance frequency. Put another way, the fluorine, by pulling electron density away from the protons, is deshielding them, leaving them more exposed to B\textsubscript{0}. As the electronegativity of the substituent increases, so does the extent of deshielding, and so does the chemical shift. This is evident when we look at the chemical shifts of methane and three halomethane compounds (remember that electronegativity increases as we move up a column in the periodic table).

\[
\begin{array}{cccc}
\text{H} & \text{C} & \text{H} & \text{H} \\
\text{H} & \text{C} & \text{Br} & \text{H} \\
0.23 \text{ ppm} & 2.68 \text{ ppm} & 3.05 \text{ ppm} & 4.26 \text{ ppm}
\end{array}
\]

To a large extent, then, we can predict trends in chemical shift by considering how much deshielding is taking place near a proton. The chemical shift of trichloromethane is, as expected, higher than that of dichloromethane, which is in turn higher than that of chloromethane.
The deshielding effect of an electronegative substituent diminishes sharply with increasing distance:

\[
\begin{array}{ccc}
\text{Cl} & \text{Cl} & \text{Cl} \\
\text{H} - \text{C} - \text{H} & \text{H} - \text{C} - \text{Cl} & \text{H} - \text{C} - \text{Cl} \\
3.05 \text{ ppm} & 5.30 \text{ ppm} & 7.27 \text{ ppm}
\end{array}
\]

The presence of an electronegative oxygen, nitrogen, sulfur, or \(sp^2\)-hybridized carbon also tends to shift the NMR signals of nearby protons slightly downfield:

\[
\begin{array}{ccc}
H_d & H_c & H_b & H_a \\
0.92 \text{ ppm} & 1.42 \text{ ppm} & 1.68 \text{ ppm} & \leftarrow 3.42 \text{ ppm}
\end{array}
\]

Table 2 lists typical chemical shift values for protons in different chemical environments.

Armed with this information, we can finally assign the two peaks in the the \(^1\text{H-NMR}\) spectrum of methyl acetate that we saw a few pages back. The signal at 3.65 ppm corresponds to the methyl ester protons (H\(_b\)), which are deshielded by the adjacent oxygen atom. The upfield signal at 2.05 ppm corresponds to the acetate protons (H\(_a\)), which is deshielded - but to a lesser extent - by the adjacent carbonyl group.

Finally, a note on the use of TMS as a standard in NMR spectroscopy: one of the main reasons why the TMS proton
signal was chosen as a zero-point is that the TMS protons are highly shielded: silicon is slightly less electronegative than carbon, and therefore donates some additional shielding electron density. Very few organic molecules contain protons with chemical shifts that are negative relative to TMS.

\[
\text{CH}_3 \\
\text{H}_3\text{C} - \text{Si} - \text{CH}_3 \\
\text{CH}_3
\]

5.4B: The chemical shifts of aromatic and vinylic protons

Some protons resonate much further downfield than can be accounted for simply by the deshielding effect of nearby electronegative atoms. Vinylic protons (those directly bonded to an alkene carbon) and aromatic (benzylic) protons are dramatic examples.

We’ll consider the aromatic proton first. Recall that in benzene and many other aromatic structures, a sextet of p-electrons is delocalized around the ring. When the molecule is exposed to B\(_0\), these p-electrons begin to circulate in a ring current, generating their own induced magnetic field that opposes B\(_0\). In this case, however, the induced field of the p-electrons does not shield the benzylic protons from B\(_0\) as you might expect—rather, it causes the protons to experience a stronger magnetic field in the direction of B\(_0\) — in other words, it adds to B\(_0\) rather than subtracting from it.

To understand how this happens, we need to understand the concept of diamagnetic anisotropy (anisotropy means ‘non-uniformity’). So far, we have been picturing magnetic fields as being oriented in a uniform direction. This is only true over a small area. If we step back and take a wider view, however, we see that the lines of force in a magnetic field are actually anisotropic. They start in the ‘north’ direction, then loop around like a snake biting its own tail.
If we are at point A in the figure above, we feel a magnetic field pointing in a northerly direction. If we are at point B, however, we feel a field pointing to the south.

In the induced field generated by the aromatic ring current, the benzylic protons are at the equivalent of ‘point B’ – this means that the induced current in this region of space is oriented in the same direction as $B_0$.

In total, the benzylic protons are subjected to three magnetic fields: the applied field ($B_0$) and the induced field from the p-electrons pointing in one direction, and the induced field of the non-aromatic electrons pointing in the opposite (shielding) direction. The end result is that benzylic protons, due to the anisotropy of the induced field generated by the pring current, appear to be highly deshielded. Their chemical shift is far downfield, in the 6.5-8 ppm region.

Example 5.5

The $^1$H-NMR spectrum of [18] annulene has two peaks, at 8.9 ppm and -1.8 ppm (upfield of TMS!) with an integration ratio of 2:1. Explain the unusual chemical shift of the latter peak.
Solution

Diamagnetic anisotropy is also responsible for the downfield chemical shifts of vinylic protons and aldehyde protons (4.5-6.5 ppm and 9-10 ppm, respectively). These groups are not aromatic and thus do not generate ring currents as does benzene, but the p-electrons circulate in such a way as to generate a magnetic field that adds to $B_0$ in the regions of space occupied by the protons.

5.4C: Hydrogen-bonded protons

Protons that are directly bonded to oxygen and nitrogen have chemical shifts that can vary widely depending on solvent and concentration. This is because these protons can participate to varying degrees in hydrogen-bonding interactions, and hydrogen bonding greatly influences the electron density around the proton. Signals for hydrogen-bonding protons also tend to be broader than those of hydrogens bonded to carbon, a phenomenon that is also due to hydrogen bonding.

Contributors


Additional Reading

Carey 4th Edition On-Line Activity

Chemical Shift

Khan Academy

Chemical shift

Electronegativity and chemical shift
Web Pages

Wikipedia page on chemical shift
Information on Chemical Shifts
Chemical Shifts of protons
Description of the chemical shift
Overview of Chemical shifts
Signals of OH and NH

**Physics based description of chemical shifts**

**Technical info on chemical shift**

Videos

Chemical Shifts and regions of the spectrum
Video on chemical Shift
NMR shift video

Tutorial

Position of Signals: Chemical Shift

Sources with Common Shift Values

Carey 4th Edition On-Line Activity

Table of NMR Shifts

Web Pages

NMR (and IR) shift values
Chemical Shift Table

Detailed Table of NMR shifts

Shifts of Aromatic Molecules

Predicting NMR Shifts

Advanced Article on predicting shifts

Organic Spectra Database

Chart of NMR shifts