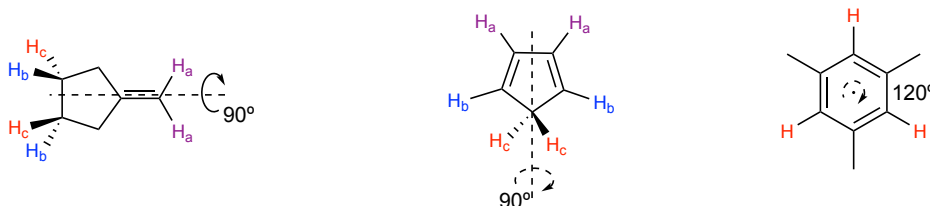# A Brief Overview of
Chemical Shift Equivalence & Magnetic Equivalence

Topicity and Chemical Shift Equivalence

A group of hydrogens are *homotopic* when a simple molecular rotation results in these hydrogens exchanging places. Homotopic hydrogens are always chemical shift equivalent.

The name comes from the *substitution method*. If you take two copies of the molecule and replace one of the H's with a D in each copy, the hydrogens are *homotopic* if you end up with a pair of *homomers* (i.e., identical molecules that are related by a simple rotation).

Hydrogens are *enantiotopic* when the hydrogens exchange places after an *improper rotation* (S_n). The most common examples are S_1, which is a plane of symmetry (σ_v, σ_h), and S_2, which is a point of inversion (**i**). Typical NMR solvents are achiral, so enantiotopic hydrogens can always be considered chemical shift equivalent.
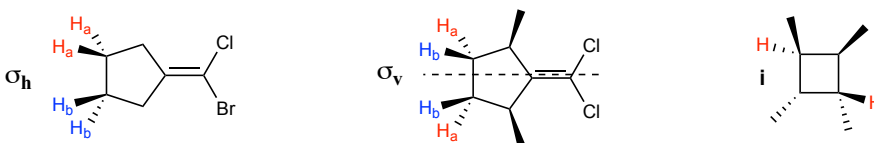
The name comes from the *substitution method*. If you take two copies of the molecule and replace one of the H's with a D in each copy, the hydrogens are *enantiotopic* if you end up with a pair of *enantiomers* (i.e., molecules related by a reflection, inversion, or higher-order improper-rotation).
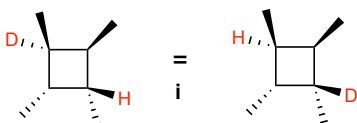
Note: inversion is the same as rotating the molecule 180° around an axis and then reflecting the molecule through a mirror-plane perpendicular to that axis. This is an improper-rotation of order 2, S_2.

Note that the four hydrogens on the following example molecule are all *chemical shift equivalent*. The pairs 1&3 and 2&4 are *homotopic* (by rotation), but the pairs 1&2 and 3&4 as well as 1&4 and 2&3 are *enantiotopic* (by reflection through the page and then perpendicular to the page, respectively), so all four end up being *chemical shift equivalent*.
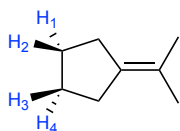
Hydrogens are *diastereotopic* if they are *not* homotopic or enantiotopic (i.e., no symmetry operation exists that can exchange the two hydrogens). *Diastereotopic* hydrogens are chemical shift non-equivalent. They might have *accidental* chemical shift equivalence, but changing the solvent or temperature will typical resolve such accidental overlap. The name comes from the *substitution method*, where the D replacement gives rise to *diastereomers*.
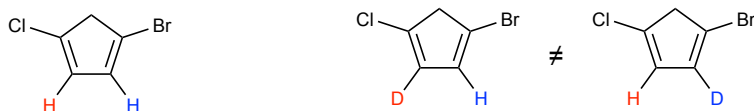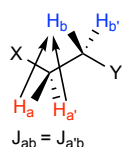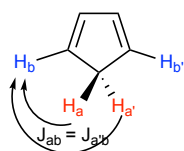
Magnetic Equivalence

After determining which hydrogens in a molecule are *chemical shift equivalent* (or *non-equivalent*), you can then move on to determining the expected multiplicity of each signal. Typically, J-coupling multiplets only appear between hydrogens that are chemical shift non-equivalent and the multiplet structure behaves as though chemical shift equivalent hydrogens don't couple with themselves. However, certain arrangements of hydrogens give rise to the phenomenon of *magnetic non-equivalence* and this leads to rather complicated multiplets that cannot be simplified by higher magnetic field strengths. This effect depends on the *J-coupling topology* and it turns out that the (usually invisible) J-coupling between chemical shift equivalent spins plays an important role.

1) *Magnetic equivalence* or *non-equivalence* only applies to a pair of hydrogens that are *chemical shift equivalent*.
2) A pair of chemically equivalent hydrogens is *magnetically equivalent* only if each hydrogen in the pair has the *exact same* J-values to any nearby hydrogen that couples to *both* hydrogens in the chemically equivalent pair.

Open chains that can rotate freely typically have vicinal J-couplings of ~7 Hz. The hydrogens in each chemical shift equivalent pair below would be *magnetically equivalent* because each hydrogen in a pair couples to any given vicinal hydrogen with J=7 Hz. Similarly, a pair of hydrogens that have the same number of bonds and identical dihedral angles to any adjacent hydrogen will be magnetically equivalent because the Karplus relationship ensures that the J-values are identical.

$J_{ab} = J_{a'b} = 7$ Hz and $J_{ab'} = J_{a'b'} = 7$ Hz, so H_a & $H_{a'}$ are *magnetically equivalent*. The same argument can be used to show H_b & $H_{b'}$ are *magnetically equivalent*.

$J_{ab} = J_{a'b}$ and $J_{ab'} = J_{a'b'}$ (Karplus: identical ^3J, same dihedral angle) so H_a & $H_{a'}$ are *magnetically equivalent*. H_b & $H_{b'}$ are *magnetically equivalent* by the same argument.

The following molecule also has two pairs of chemical shift equivalent spins that couple to each other. One might expect to see a doublet of doublets (one larger doublet from the geminal coupling and one smaller doublet from the vicinal coupling), but instead we see very complicated multiplets. This system is *magnetically non-equivalent* because H_a couples to H_b with a different value than $H_{a'}$ couples to H_b. Specifically, J_{ab} is a geminal coupling, ~15 Hz, whereas $J_{a'b}$ is a vicinal coupling, ~7 Hz. One can imagine H_b flipping between the up and down spin states and, due to this difference in J-values, H_a and $H_{a'}$ will *feel* this spin-flip differently; hence they are *magnetically non-equivalent* despite being chemical shift equivalent.

$J_{ab} = {}^2J \approx 15Hz$
$J_{a'b} = {}^3J \approx 7Hz$
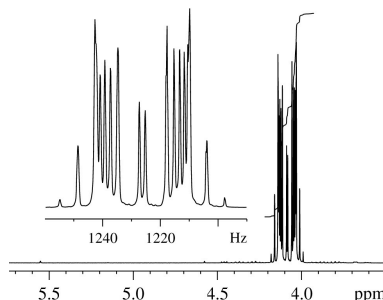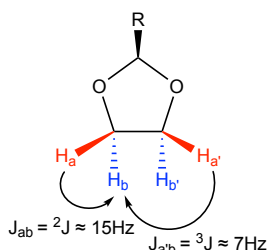
Similar things happen in conjugated systems where ^4J coupling is common because ^3J and ^4J values are always quite different. Furan provides a nice example. Again, one might expect a simple doublet of doublets (one large from the ortho coupling and one small from the meta coupling); instead, we see the bizarre multiplets that arise from magnetic non-equivalence. This is because J_{ab} has a different value than $J_{a'b}$, making H_a and $H_{a'}$ magnetically non-equivalent. H_b and $H_{b'}$ are similarly magnetically non-equivalent, because they each couple to H_a (or $H_{a'}$) with different J-values.

$J_{ab} = {}^3J \approx 7.5Hz$
$J_{a'b} = {}^4J \approx 1.5Hz$
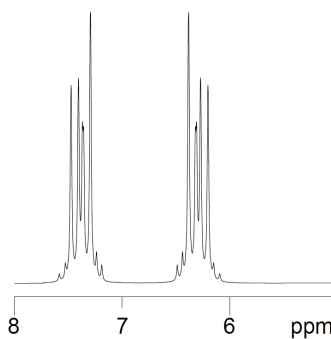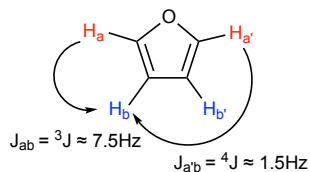
Simulated spectra let us explore the relative importance of different J-coupling values with regard to the appearance of magnetic non-equivalence. We'll use ortho-dichlorobenzene (ODCB) for our example. Electron-structure calculations or detailed analysis of the complex multiplets reveal the following J-values. The shorthand diagram will be used to help us visualize which J-values we change for the simulated spectra.
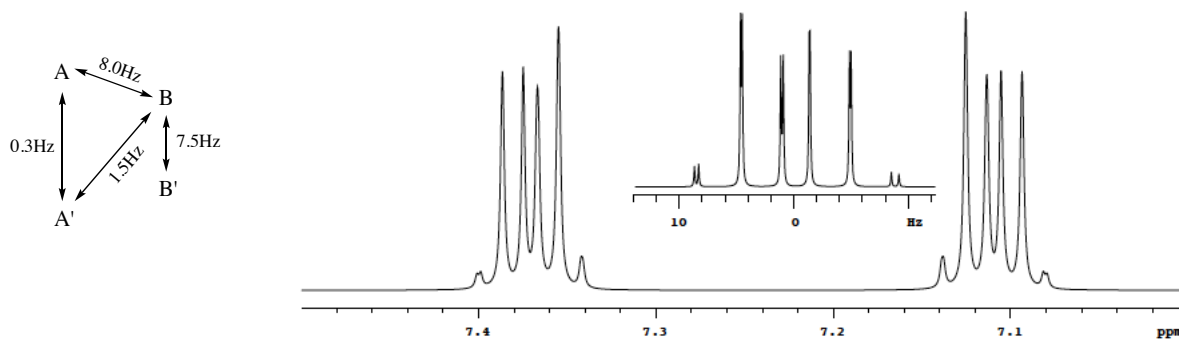
$J_{ab} = J_{a'b'} = 8.0$ Hz
$J_{a'b} = J_{ab'} = 1.5$ Hz
$J_{aa'} = 0.3$ Hz
$J_{bb'} = 7.5$ Hz
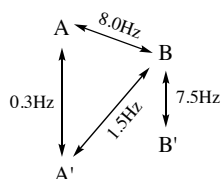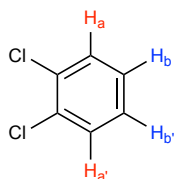
Students are often surprised to learn that chemical shift equivalent spins have non-zero J-couplings between themselves (e.g., $J_{aa'}$ and $J_{bb'}$) as they have generally been told that *"chemical shift equivalent hydrogens don't couple to each other."* It's true that we don't usually observe these couplings, but they certainly exist. In fact, we can simulate what the spectrum of ODCB would look like if we set $J_{aa'}$ and $J_{bb'} = 0$ Hz. We get the simple doublet of doublets that one might naively expect.
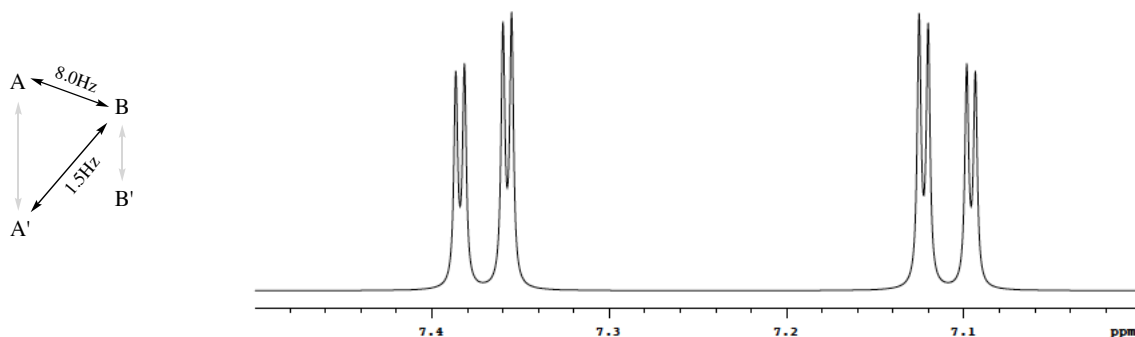
If we set $J_{aa'} = 0.3$ Hz and $J_{bb'} = 7.5$ Hz. We get *exactly* the same spectrum observed in real life.

On the other hand, if we set $J_{ab} = J_{a'b} = 8.0$ Hz (and $J_{ab'} = J_{a'b'} = 8.0$ Hz). We get triplets, as expected. However, there is still some unexpected splitting and leaning because the chemical shifts are close enough that we're seeing 2nd-order effects ($\Delta\upsilon/J < 10$).