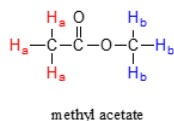


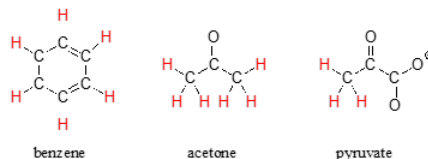
5.3: Chemical Equivalence

The frequency of radiation absorbed by a proton (or any other nucleus) during a spin transition in an NMR experiment is called its 'resonance frequency'. If all protons in all organic molecules had the same resonance frequency, NMR spectroscopy but would not be terribly useful for chemists. Fortunately for us, however, resonance frequencies are not uniform for different protons in a molecule - rather, the resonance frequency varies according to the electronic environment that a given proton inhabits. In methyl acetate, for example, there are two distinct 'sets' of protons.

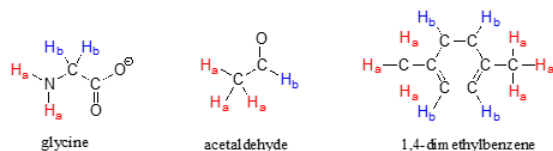


The three methyl acetate protons labeled H_a above have a different resonance frequency compared to the three H_b protons, because the two sets of protons are in non-identical electronic environments: the H_a protons are on a carbon next to a carbonyl carbon, while the H_b protons are on a carbon next to an oxygen. In the terminology of NMR, all three H_a protons are chemically equivalent to each other, as are all three H_b protons. The H_a protons are, however, chemically nonequivalent to the H_b protons. As a consequence, the resonance frequency of the H_a protons is different from that of the H_b protons. For now, do not worry about why the different electronic environment gives rise to different resonance frequencies - we will get to that soon.

The ability to recognize chemical equivalency and nonequivalency among atoms in a molecule will be central to understanding NMR. Each of the molecules below contains only one set of chemically equivalent protons: all six protons on benzene, for example, are equivalent to each other and have the same resonance frequency in an NMR experiment. Notice that any description of the bonding and position of one proton in benzene applies to all five other protons as well.

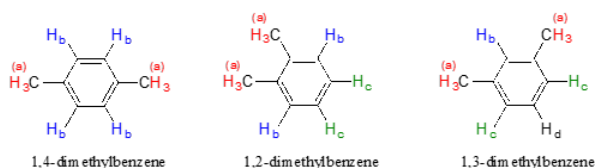


Each of the molecules in the next figure contains two sets of chemically equivalent protons, just like our previous example of methyl acetate, and again in each case the resonance frequency of the H_a protons will be different from that of the H_b protons.



Take acetaldehyde as an example: a description of the bonding and position of the H_b proton does not apply to the three H_a protons: H_b is bonded to an sp^2 -hybridized carbonyl carbon while the H_a protons are bonded to an sp^3 -hybridized methyl carbon.

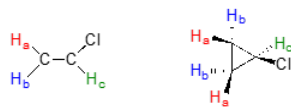
Note that while all four aromatic protons in 1,4-dimethylbenzene are chemically equivalent, its constitutional isomer 1,2-dimethylbenzene has two sets of aromatic protons in addition to the six methyl (H_a) protons. The 1,3-substituted isomer, on the other hand, has three sets of aromatic protons.



In 1,2-dimethylbenzene, both H_b protons are adjacent to a methyl substituent, while both H_c protons are two carbons away. In 1,3-dimethylbenzene, H_b is situated between two methyl groups, the two H_c protons are one carbon away from a methyl group, and H_d is two carbons away from a methyl group.

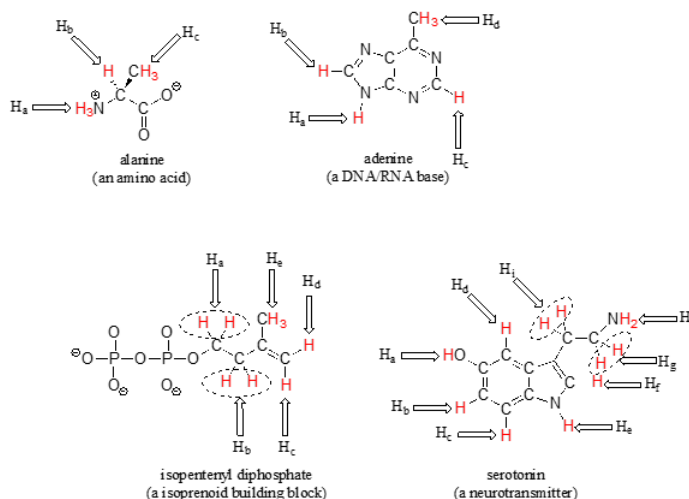
As you have probably already realized, chemical equivalence or non-equivalence in NMR is closely related to symmetry. Different planes of symmetry in the three isomers of dimethylbenzene lead to different patterns of equivalence.

Stereochemistry can play a part in determining equivalence or nonequivalence of nuclei in NMR. In the chloroethene (commonly known as vinyl chloride, the compound used to make polyvinyl chloride or PVC), H_a and H_b are in nonequivalent electronic environments, because H_a is *cis* to the chlorine atom while H_b is *trans*. Likewise, H_a and H_b in chlorocyclopropane are nonequivalent due to their positions either on the same or opposite side of the ring relative to chlorine.



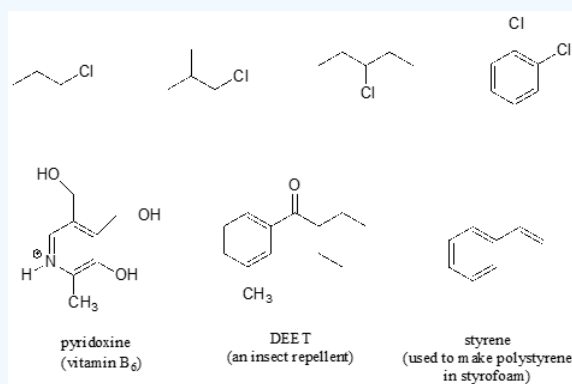
If you think back to our discussion of prochirality in section 3.11, you should recognize that the H_a and H_b protons in the examples above are diastereotopic pairs.

Most organic molecules have several sets of protons in different chemical environments, and each set will have a different resonance frequency in 1H -NMR spectroscopy. Below we see some examples of multiple sets of protons in biological molecules.



? Exercise 5.3.1

How many sets of equivalent protons do the following molecules contain?



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