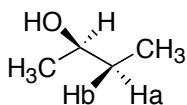


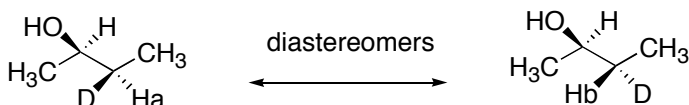
Diastereotopic Protons

2-butanol

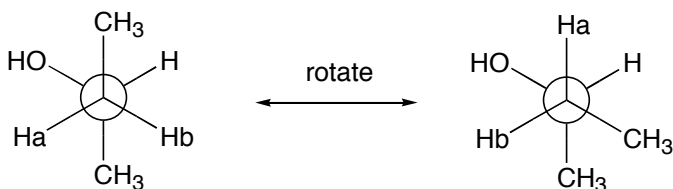
Ha and Hb protons at C-3 of 2-butanol are said to be diastereotopic and are at different chemical shift positions in the NMR spectrum because of the nearby stereogenic center at C-2. Hb and Ha cannot be put in the same chemical environment.

The methyl group is only one signal because the C-C bond can freely rotate and NMR cannot distinguish between the H's. The barrier to bond rotation is only a few kilocalories per mole and about 15 to 20 kilocalories per mole of energy are available at room temperature. Hence rotation is very rapid.

If you substitute Ha or Hb with deuterium (labeled as D), which is the isotope of hydrogen with one proton and one neutron, you get diastereomers.

Newman Projection

Round circle in structure below is back carbon (carbon 2 of 2-butanol) – carbon 3 is directly attached to it and is represented as the dot (point) where the bonds meet in front.

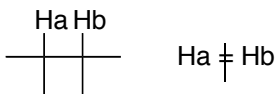


Anti Staggered conformation
(most stable)

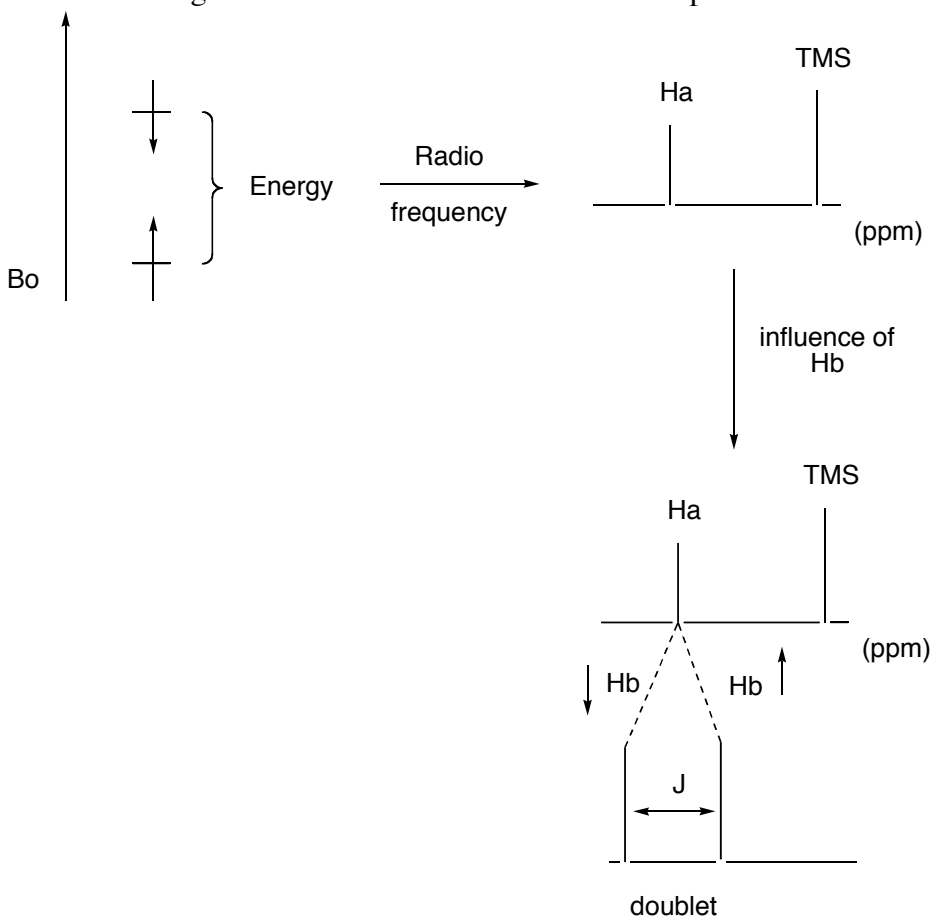
Gauche conformation

When there is stereogenic center present, the two hydrogens, Ha and Hb, of the methylene (CH₂) group cannot be brought into the same chemical environment. Bond rotation can bring Hb to the position where Ha was before, as represented by the above Newman projections of the two conformations, but the CH₃'s are occupying different positions and therefore the two methylene H's are not in the same chemical environment.

Spin-Spin Splitting (Coupling) – consider the structure below



Ha is not a singlet due to the influence of Hb on it's spin and vice versa.

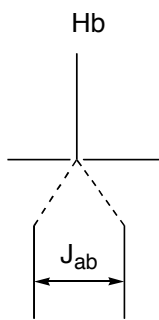
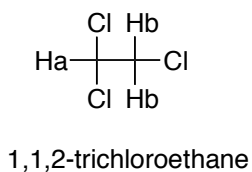


J = coupling constant

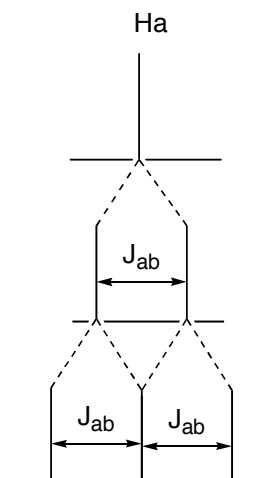
The Ha coupling constant corresponds to the energy difference caused by the Hb proton in alignment with the field and against the field.

Limitations of Coupling

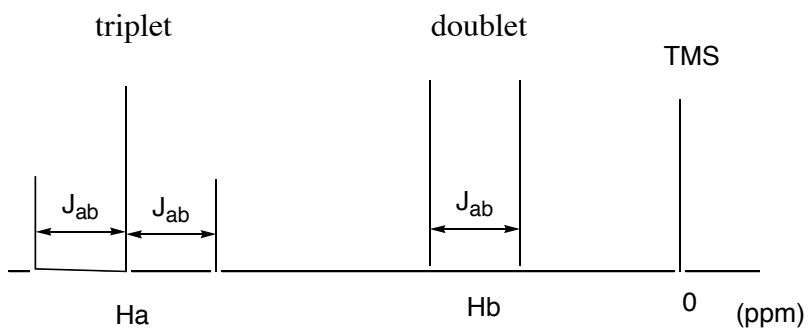
1. < 3 bonds separating nuclei
2. no coupling across O, N, S, C=O



doublet



triplet

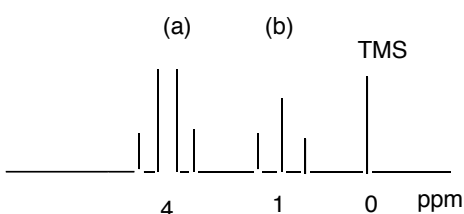
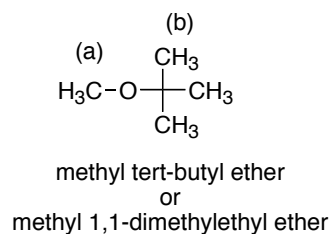
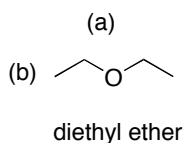


Pascal's Triangle

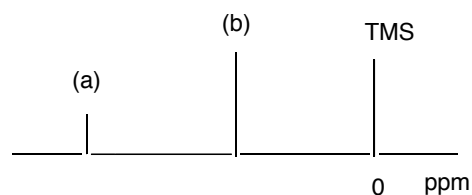
1
 1 1
 1 2 1
 1 3 3 1
 1 4 6 4 1

above represents intensities of singlet, doublet (1 to 1), triplet (1 to 2 to 1), quartet (1 to 3 to 3 to 1), pentuplet (1 to 4 to 6 to 4 to 1)

Consider examples below and the types hydrogens (a and b)



Intensity would be 6:4 or 3:2



Intensity would be 3:9 or 1:3

No stereogenic centers present. No coupling across oxygen.
Both molecules should have 2 signals. Both have ether functional groups.

Carbon NMR

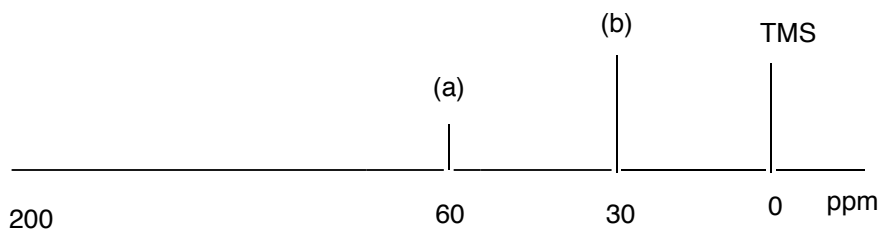
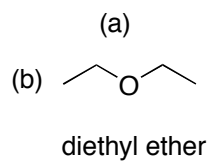
^{12}C has 6 protons and 6 neutrons no nuclear spin, invisible in NMR

^{13}C has 6 protons and 7 neutrons stable isotope, occurs naturally in 1.1% abundance

^{14}C has 6 protons and 8 neutrons radioactive, half life is $t_{1/2} = 5730$ years

^{13}C has an odd number of neutrons, therefore it has nuclear spin and is NMR active. ^{12}C and ^{14}C both have an even number neutrons and even number of protons and are not NMR active (they have no nuclear spin and cannot be seen by NMR)

A ^{13}C NMR spectrum is run decoupled (this means to irradiate all protons so that there is no ^1H spin-spin coupling to ^{13}C) so that all the ^{13}C signals are singlets.



There are two different carbon's in diethyl ether therefore one would expect to see two different signals. Each appears as a singlet in the proton (¹H) decoupled (that is irradiated) carbon-13 spectrum.

There is no ¹³C-¹³C spin-spin coupling because the chance of there being two ¹³C's next to each other is $0.01 \times 0.01 = 0.0001$ or one part in 10,000.