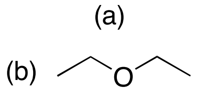
Chem 263 Jan 12, 2006

Carbon NMR

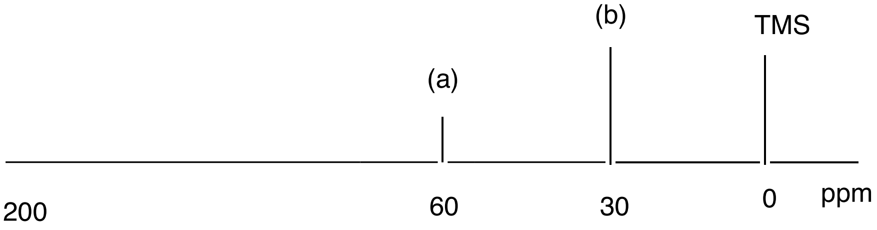
^{12}C has 6 protons and 6 neutrons	no nuclear spin, invisible in NMR
^{13}C has 6 protons and 7 neutrons	stable isotope, occurs naturally in 1.1% abundance
^{14}C has 6 protons and 8 neutrons	radioactive, half life is $t_{1/2}$ = 5730 years

^{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 ^{1}H spin-spin coupling to ^{13}C) so that all the ^{13}C signals are singlets.

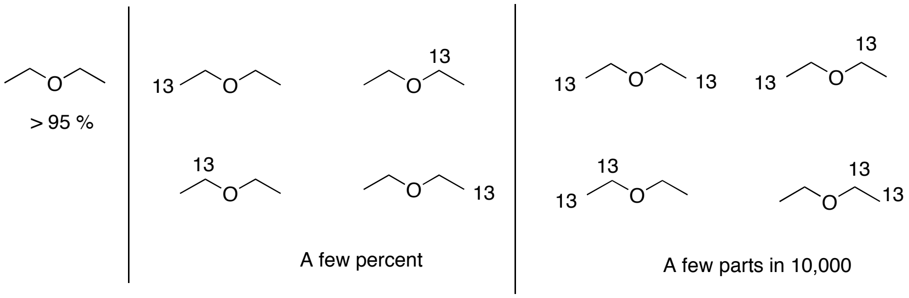


diethyl ether



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 (^{1}H) decoupled (that is irradiated) carbon-13 spectrum.

There is no ^{13}C-^{13}C spin-spin coupling because the chance of there being two ^{13}C's next to each other is 0.01 x 0.01 = 0.0001 or one part in 10,000, which is too small to detect.



In ^{1}H NMR spectra, the relative area of the peaks indicates how many H's are present.
In ^{13}C NMR spectra, the intensity or area of the peak cannot be used to calculate the relative number of carbons because of relaxation effects and transfer of energy from decoupled hydrogens.

2-D NMR

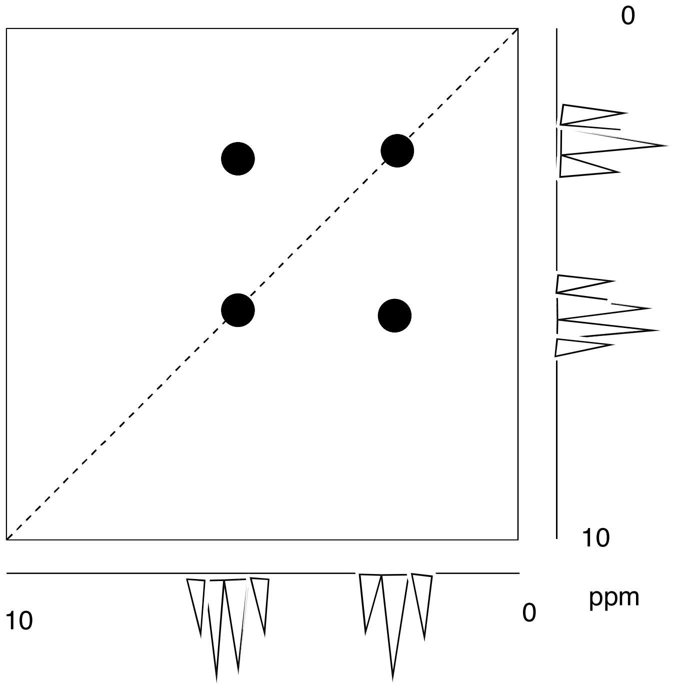
Two major types of experiments:

1. Through bonds energy transfer (dependent on coupling constants, J)
2. Through space energy transfer (see NOE below)

Correlation Spectroscopy (COSY)

Shown below is a COSY spectrum of diethyl ether.

The off diagonal cross peaks show that the triplet and the quartet correlate to each other and the hydrogens that are responsible for those signals are on adjacent atoms (i.e coupled) in the molecule. For a simple molecule like diethyl ether, this is trivial and can be seen from the one dimensional spectrum. However, in complex molecules with many triplets and quartets etc., the connectivity of coupled hydrogens can be determined.



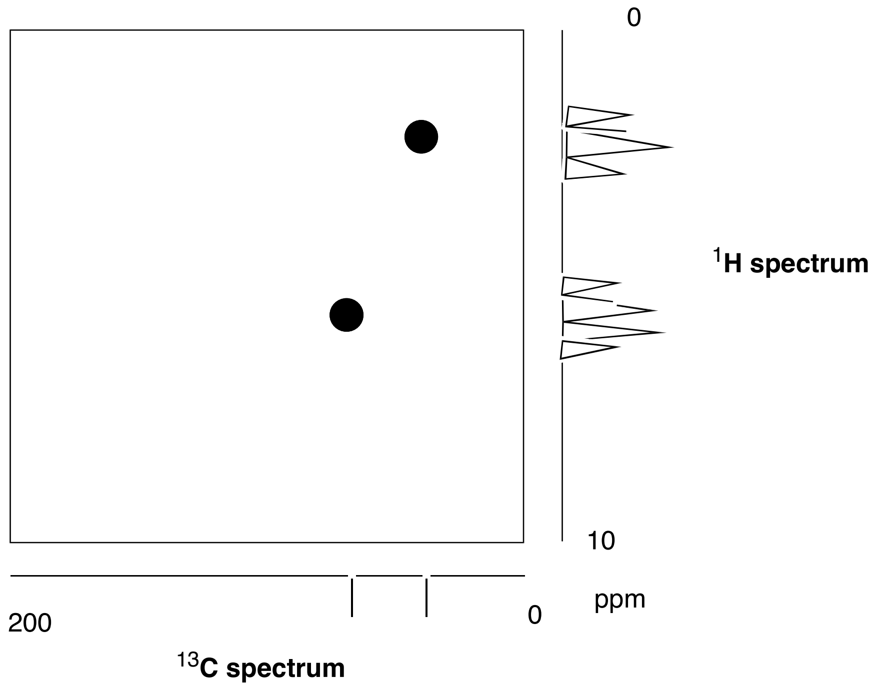
Heteronuclear Correlation Spectroscopy (HETCOR)

Heteronuclear Multiple Quantum Coherence (HMQC)

Shown below is the HETCOR spectra of diethyl ether ($CH_3CH_2OCH_2CH_3$).

HETCOR shows which hydrogens are bonded to which carbons.

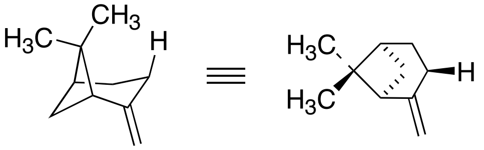
This technique correlates the ^{1}H NMR spectrum with the ^{13}C NMR spectrum. It allows connectivity patterns to be established in conjunction with COSY. In other words, COSY tells which hydrogens are adjacent to each other and HETCOR allows the connection to their respective carbons.



Nuclear Overhauser Effect (NOE)

An NOE effect is an energy transfer between two nuclei (e.g. protons) through space.

The effect drops off proportionally to $1/R^6$ where R = internuclear distance



β-pinene: two drawings of the same molecule

For better understanding of this structure, please see additional graphics page on our web site (www.chem.ualberta.ca/~vederas then click on basic organic chemistry) or use models available from first floor chemistry storeroom

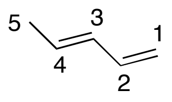
This technique allows you to distinguish between the two methyl groups in β-pinene (major constituent of turpentine). If the single diastereotopic H shown on the methylene is irradiated, it will transfer energy via the NOE effect to the closest methyl group and produce an enhanced signal. This will be shown by that one methyl group peak in the NMR spectrum becoming more intense. Irradiation of that same methyl will analogously enhance the methylene hydrogen shown. The more distant methyl will not show this NOE effect. This technique is useful for determining the 3-D orientation (structure) of molecules, including proteins. Three dimensional structures of proteins with 50,000 molecular weight and thousands of atoms have been determined by advanced versions of the NOE method.

Conjugated Molecules

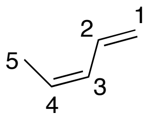
"Separated by a single bond from double bond"

Double bond, cation, anion, radical

Review of nomenclature and examples
The two molecules below are stereoisomers, and both are conjugated.

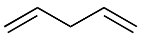


E-1,3-pentadiene



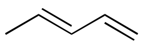
Z-1,3-pentadiene

The two molecules below are constitutional (structural) isomers.



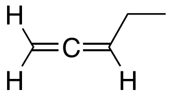
1,4-pentadiene

NOT conjugated

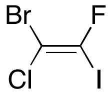


E-1,3-pentadiene

The 1,2-pentadiene shown below is not conjugated. It has cumulated double bonds. This molecule is an allene and is a structural isomer with respect to the above 1,3-pentadienes.



Another example for nomenclature below: Is this an E or Z alkene (olefin)?



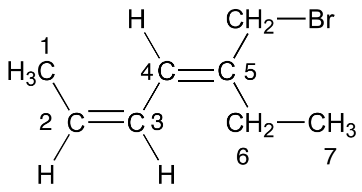
First of all, look at the highest priority (that is the highest atomic number of the atom directly attached) on either side of the double bond.

I is highest priority relative to F.
Br is highest priority relative to Cl

Therefore it is an E double bond as the high priority groups are on opposite sides of the double bond

The name is (E)-1-bromo-1-chloro-2-fluoro-2-iodoethylene.

One more example:



(2*Z*,4*E*)-5-(bromomethyl)-2,4-heptadiene

To assign the first double bond between C2 and C3, methyl group is the larger group compares to H on C2, carbon chain (C4 to C7) is the larger group compares to H on C3, two larger groups on the same side of double bond, and then it is Z conformation.

To assign the second double bond between C4 and C5, carbon chain (C1 to C3) is the larger group compares to H on C4, bromomethyl group is the larger group compares to ethyl group on C5, two larger groups on the opposite side of double bond, and then it is E conformation.