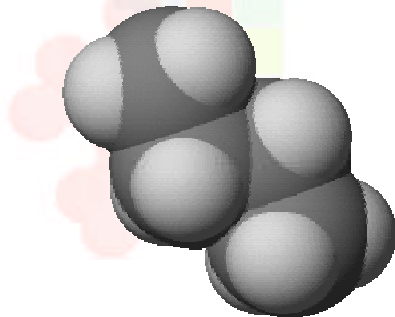


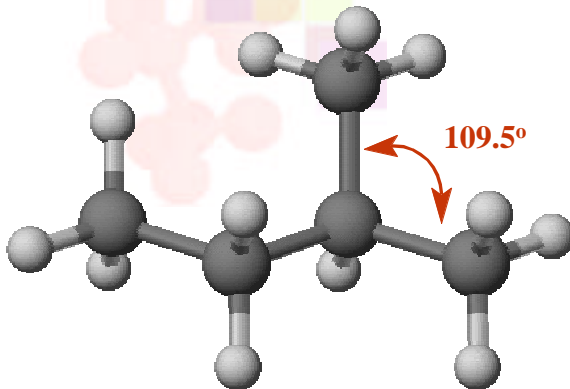
Alkanes & Cycloalkanes



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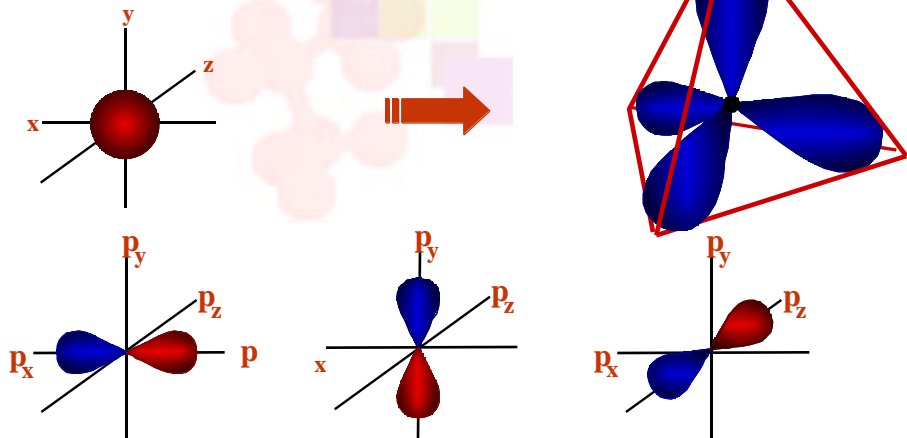
Alkanes

Alkanes represent the most basic functional group within organic chemistry. They contain only **carbon and hydrogen**; all carbons are sp^3 and all bond angles are 109.5° .



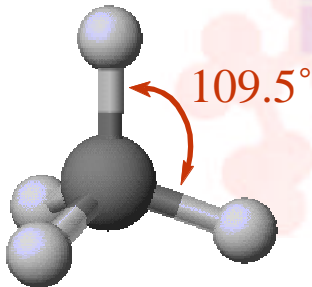
Orbital hybridization in alkanes

Recall that an sp^3 hybrid arises from the combination of four atomic orbitals to form a **molecular orbital** with tetrahedral geometry.

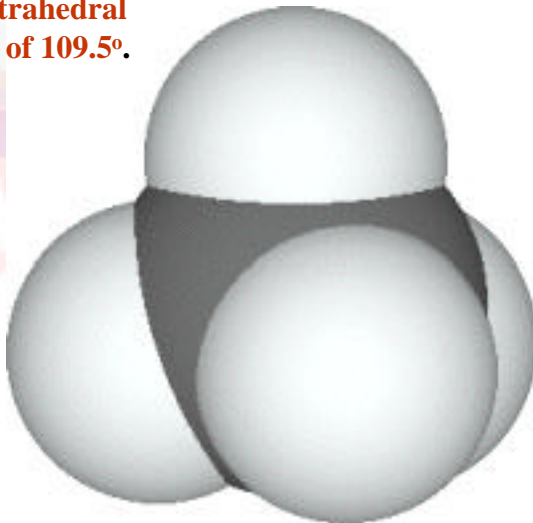


Methane (CH_4) the simplest alkane

Again, methane is **tetrahedral**
with **dihedral angles of 109.5°** .

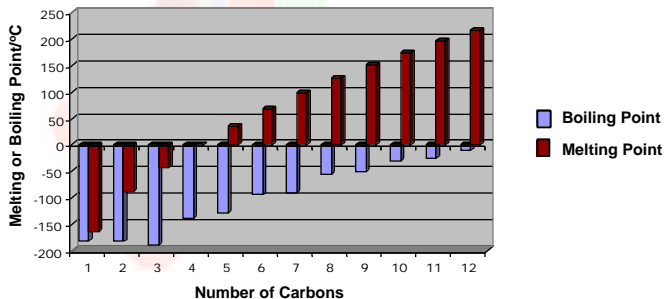


**“Ball and
Stick” Model**



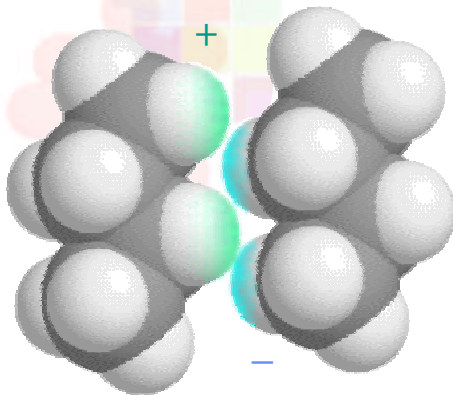
“Space Filling” Model

Physical properties of simple alkanes



For simple straight-chain alkanes, boiling and melting points generally increase with increasing chain length.

The dependence of the boiling and melting points on chain length can be explained in terms of increasing *attractive van der Waals interactions* as the chain length increases.



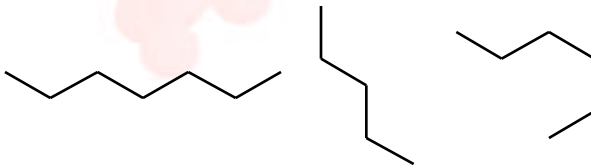
Nomenclature of simple alkanes

According to **IUPAC** convention, the chemical name of an alkane is based on the length of the *parent chain*. The name is composed of a **prefix** to indicate the number of carbons in the parent chain, followed by the **suffix**, *ane* to indicate the functional group is an alkane.

<u>Prefix</u>	<u>Number of Carbons</u>
meth...	1
eth...	2
prop...	3
but...	4
pent...	5
hex...	6
hept...	7
oct...	8
non...	9
dec...	10

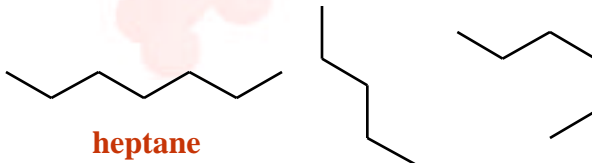
IUPAC rules for the nomenclature of simple (unbranched) alkanes

The name is composed of a **prefix** to indicate the number of carbons in the parent chain, followed by the **suffix, *ane*** to indicate the functional group is an alkane



IUPAC rules for the nomenclature of simple (unbranched) alkanes

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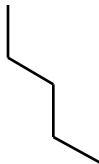


IUPAC rules for the nomenclature of simple (unbranched) alkanes

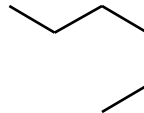
The name is composed of a **prefix** to indicate the number of carbons in the parent chain, followed by the **suffix, *ane*** to indicate the functional group is an alkane



heptane



pentane

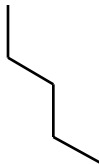


IUPAC rules for the nomenclature of simple (unbranched) alkanes

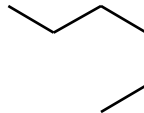
The name is composed of a **prefix** to indicate the number of carbons in the parent chain, followed by the **suffix, *ane*** to indicate the functional group is an alkane



heptane

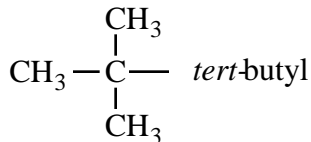
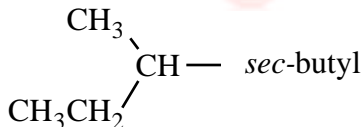
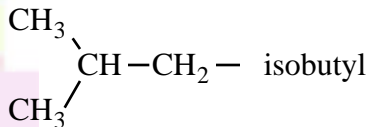
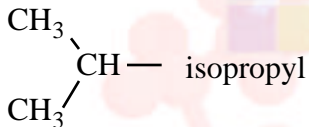


pentane

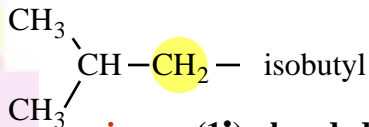
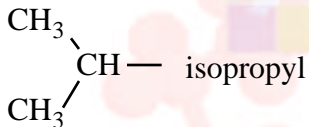


hexane

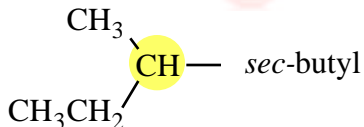
Branched alkanes also have widely used common names.



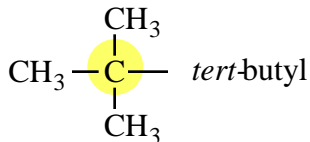
In branched alkanes, carbons are often classified by their degree of branching...



primary (1°): bonded to one other carbon



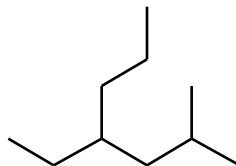
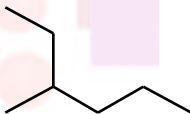
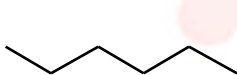
secondary (2°): bonded to two other carbons



tertiary (3°): bonded to three other carbons

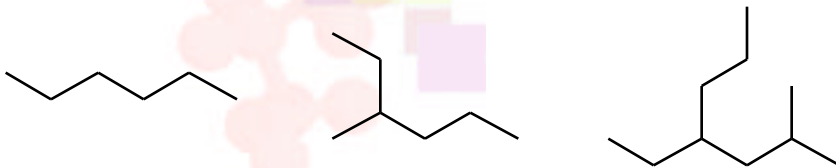
IUPAC rules for the *systematic* nomenclature of branched alkanes

1. For branched alkanes: the longest continuous chain determines the base name for the alkane.



IUPAC rules for the *systematic* nomenclature of branched alkanes

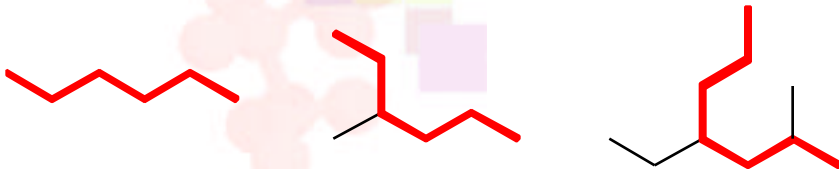
1. For branched alkanes: the longest continuous chain determines the base name for the alkane.



Indicate the longest continuous carbon chains in the molecules shown above.

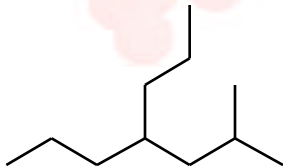
IUPAC rules for the *systematic* nomenclature of branched alkanes

1. For branched alkanes: the longest continuous chain determines the base name for the alkane.

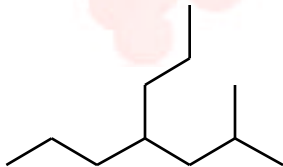


Indicate the longest continuous carbon chains in the molecules shown above.

2. Number the atoms in the chain, beginning at the end nearer the **first substituent** on the chain. If there are substituents occurring at equal distances from both ends of the chain, begin numbering at the end providing the **lowest number sequence at the first point of difference**. When two equal chains compete for selection as base chain, choose the one with the **greatest number of substituents**.

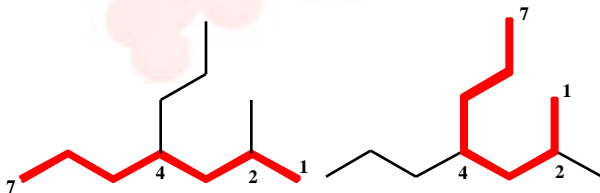


2. Number the atoms in the chain, beginning at the end nearer the **first substituent** on the chain. If there are substituents occurring at equal distances from both ends of the chain, begin numbering at the end providing the **lowest number sequence at the first point of difference**. When two equal chains compete for selection as base chain, choose the one with the **greatest number of substituents**.



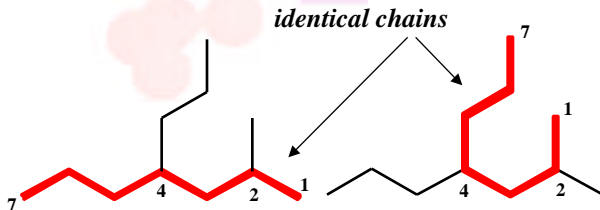
Indicate and number the longest continuous carbon chain in the molecule shown above.

2. Number the atoms in the chain, beginning at the end nearer the **first substituent** on the chain. If there are substituents occurring at equal distances from both ends of the chain, begin numbering at the end providing the **lowest number sequence at the first point of difference**. When two equal chains compete for selection as base chain, choose the one with the **greatest number of substituents**.



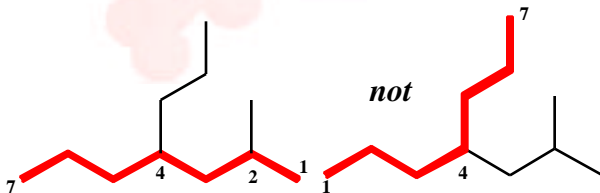
Indicate and number the longest continuous carbon chain in the molecule shown above.

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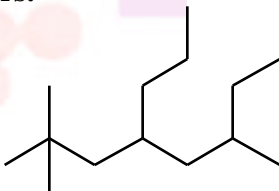
Indicate and number the longest continuous carbon chain in the molecule shown above.

2. Number the atoms in the chain, beginning at the end nearer the **first substituent** on the chain. If there are substituents occurring at equal distances from both ends of the chain, begin numbering at the end providing the **lowest number sequence at the first point of difference**. When two equal chains compete for selection as base chain, choose the one with the **greatest number of substituents**.

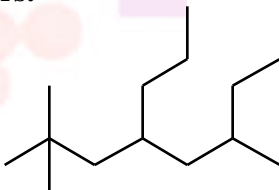


The chain shown on the right is not selected because it has fewer substituents.

3. Substituents on the chain are named as **alkyl radicals** and are numbered using the numbering system from (2). When two or more substituents are identical, use the multipliers: **di-, tri-, tetra-**, etc. **Names are to be arranged alphabetically without regard for these multiplier prefixes.** Write the name as a single word, using hyphens to separate prefixes and commas to separate numbers.

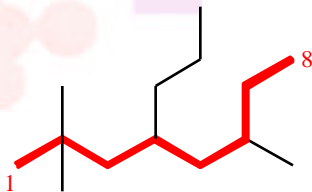


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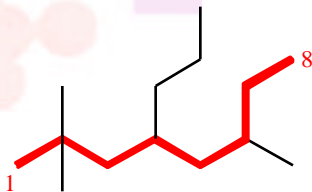


Indicate and number the longest continuous carbon chain in the molecule shown above.

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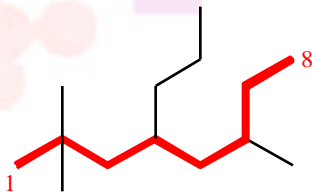


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Number and name the substituents...

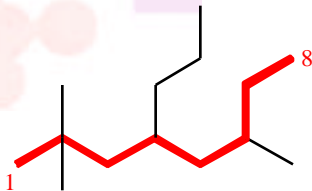
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2,2,6-trimethyl
4-propyl

Number and name the substituents...

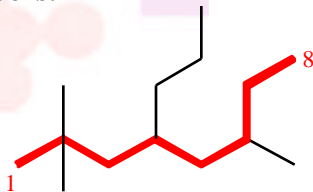
3. Substituents on the chain are named as **alkyl radicals** and are numbered using the numbering system from (2). When two or more substituents are identical, use the multipliers: **di-, tri-, tetra-,** etc. **Names are to be arranged alphabetically without regard for these multiplier prefixes.** Write the name as a single word, using hyphens to separate prefixes and commas to separate numbers.



**2,2,6-trimethyl
4-propyl**

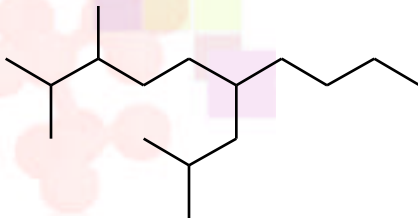
**Number and name the substituents...
...arrange these alphabetically and write the name.**

3. Substituents on the chain are named as **alkyl radicals** and are numbered using the numbering system from (2). When two or more substituents are identical, use the multipliers: **di-, tri-, tetra-**, etc. **Names are to be arranged alphabetically without regard for these multiplier prefixes.** Write the name as a single word, using hyphens to separate prefixes and commas to separate numbers.

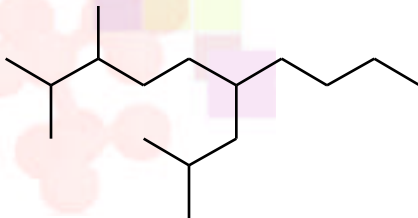


2,2,6-trimethyl-4-propyloctane
not 3,7,7-trimethyl-5-propyloctane

4. Complex substituents are numbered **from the point of attachment** to the main chain and are included in parenthesis.

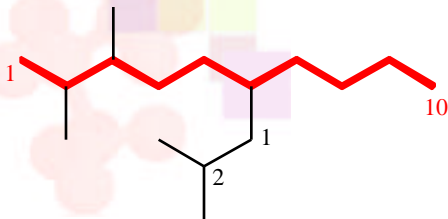


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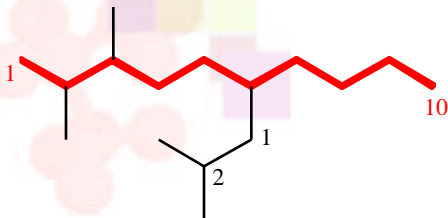


Indicate and number the longest continuous carbon chain in the molecule shown above.

4. Complex substituents are numbered **from the point of attachment** to the main chain and are included in parenthesis.

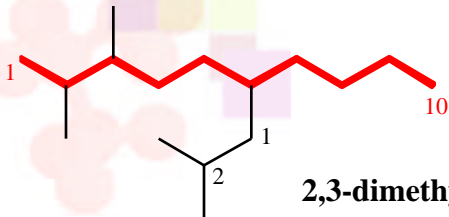


4. Complex substituents are numbered **from the point of attachment** to the main chain and are included in parenthesis.



Number and name the substituents...

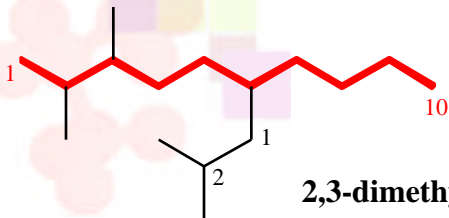
4. Complex substituents are numbered **from the point of attachment** to the main chain and are included in parenthesis.



**2,3-dimethyl
6-(2-methylpropyl)**

Number and name the substituents...

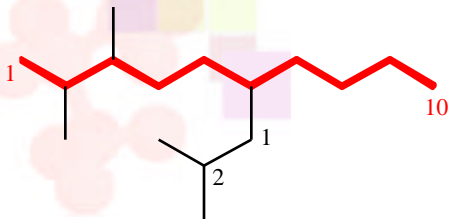
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**2,3-dimethyl
6-(2-methylpropyl)**

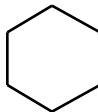
**Number and name the substituents...
...arrange these alphabetically and write the name.**

4. Complex substituents are numbered **from the point of attachment** to the main chain and are included in parenthesis.



2,3-dimethyl-6-(2-methylpropyl)decane
or **6-isobutyl-2,3-dimethyldecane**

5. Cycloalkanes are named by adding the prefix *cyclo*.



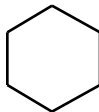
5. Cycloalkanes are named by adding the prefix *cyclo*.



cyclopentane

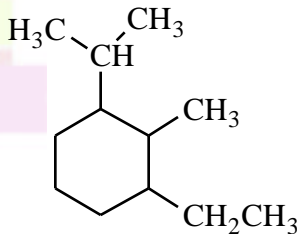
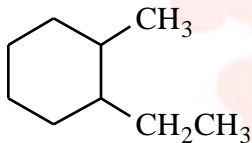


cyclopropane



cyclohexane

6. Substituents are numbered to give the **lowest possible numbers**, or **lowest possible number at the first point of difference**. If more than one type of substituent is present, begin numbering **alphabetically**.

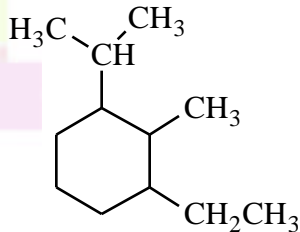
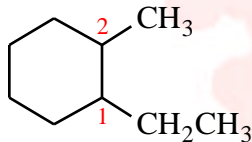


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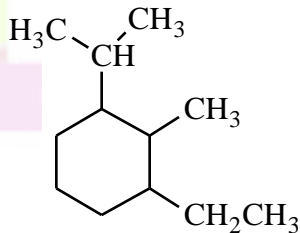
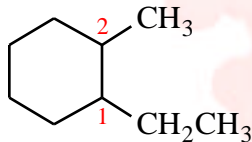


Number the ring carbons in the molecules shown above.

6. Substituents are numbered to give the **lowest possible numbers**, or **lowest possible number at the first point of difference**. If more than one type of substituent is present, begin numbering **alphabetically**.

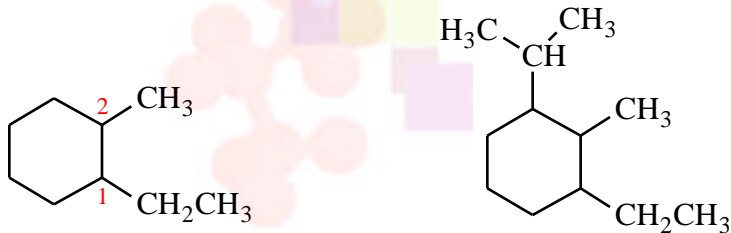


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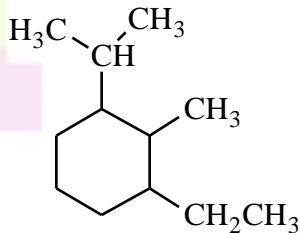
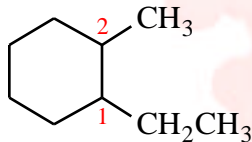
Name the substituents...

6. Substituents are numbered to give the **lowest possible numbers**, or **lowest possible number at the first point of difference**. If more than one type of substituent is present, begin numbering **alphabetically**.



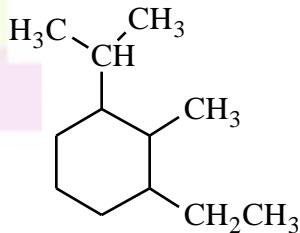
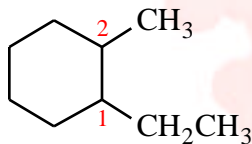
Name the substituents...
1-ethyl *and* 2-methyl

6. Substituents are numbered to give the **lowest possible numbers**, or **lowest possible number at the first point of difference**. If more than one type of substituent is present, begin numbering **alphabetically**.



Name the substituents...
1-ethyl *and* 2-methyl
...arrange alphabetically and write the name.

6. Substituents are numbered to give the **lowest possible numbers**, or **lowest possible number at the first point of difference**. If more than one type of substituent is present, begin numbering **alphabetically**.



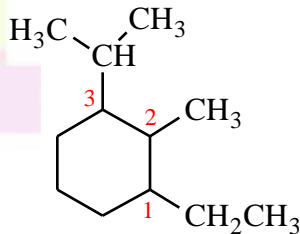
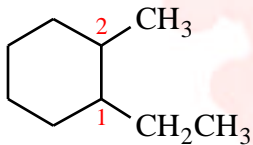
1-ethyl-2-methylcyclohexane

Name the substituents...

1-ethyl *and* 2-methyl

...arrange alphabetically and write the name.

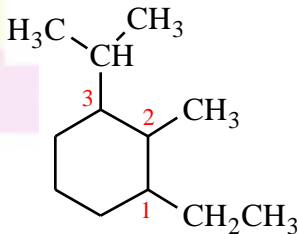
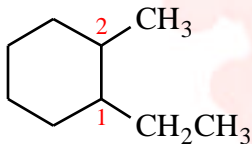
6. Substituents are numbered to give the **lowest possible numbers**, or **lowest possible number at the first point of difference**. If more than one type of substituent is present, begin numbering **alphabetically**.



1-ethyl-2-methylcyclohexane

Name the substituents...

6. Substituents are numbered to give the **lowest possible numbers**, or **lowest possible number at the first point of difference**. If more than one type of substituent is present, begin numbering **alphabetically**.

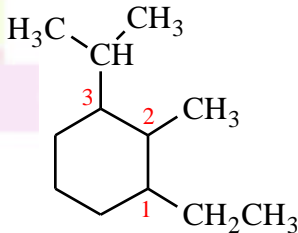
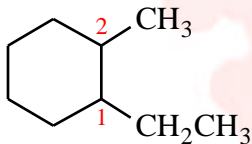


1-ethyl-2-methylcyclohexane

Name the substituents...

1-ethyl, 2-methyl *and* 3-isopropyl (or 3-methylethyl)

6. Substituents are numbered to give the **lowest possible numbers**, or **lowest possible number at the first point of difference**. If more than one type of substituent is present, begin numbering **alphabetically**.



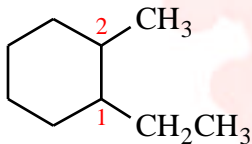
1-ethyl-2-methylcyclohexane

Name the substituents...

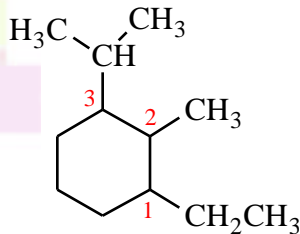
1-ethyl, 2-methyl *and* 3-isopropyl (or 3-methylethyl)

...arrange alphabetically and write the name.

6. Substituents are numbered to give the **lowest possible numbers**, or **lowest possible number at the first point of difference**. If more than one type of substituent is present, begin numbering **alphabetically**.



1-ethyl-2-methylcyclohexane



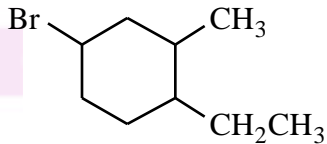
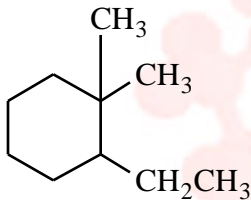
1-ethyl-3-isopropyl-2-methylcyclohexane

Name the substituents...

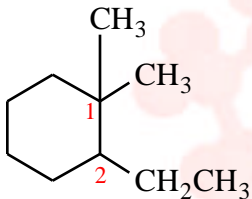
1-ethyl, 2-methyl *and* 3-isopropyl (or 3-methylethyl)

...arrange alphabetically and write the name.

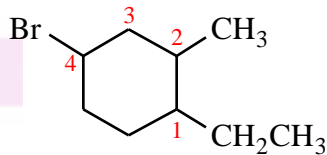
Provide an acceptable IUPAC name for the following:



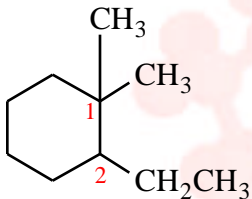
Provide an acceptable IUPAC name for the following:



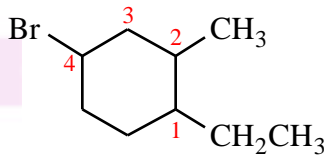
2-ethyl-1,1-
dimethylcyclohexane



Provide an acceptable IUPAC name for the following:

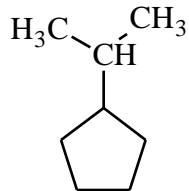
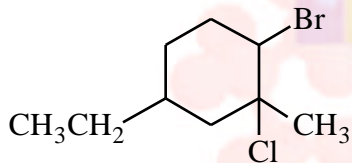


2-ethyl-1,1-
dimethylcyclohexane

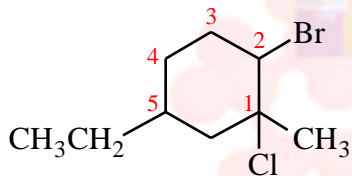


4-bromo-1-ethyl-2-
methylcyclohexane

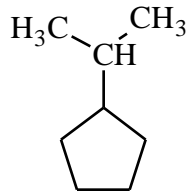
Provide an acceptable IUPAC name for the following:



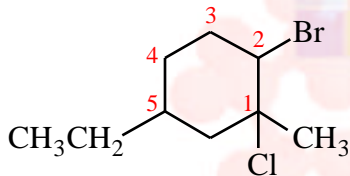
Provide an acceptable IUPAC name for the following:



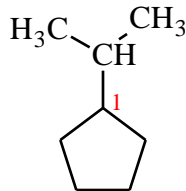
2-bromo-1-chloro-5-ethyl-1-methylcyclohexane



Provide an acceptable IUPAC name for the following:

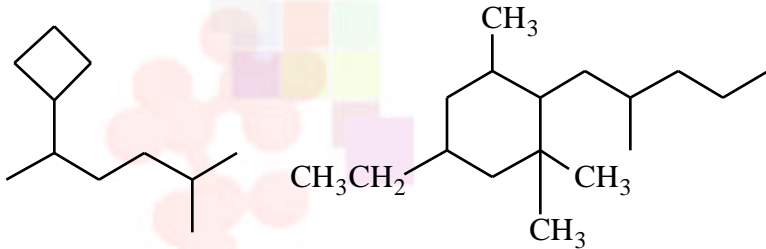


2-bromo-1-chloro-5-ethyl-1-methylcyclohexane

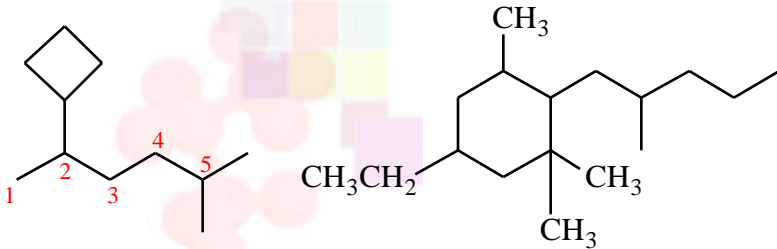


**isopropylcyclopentane
or
(methylethyl)cyclopentane**

Provide an acceptable IUPAC name for the following:



Provide an acceptable IUPAC name for the following:



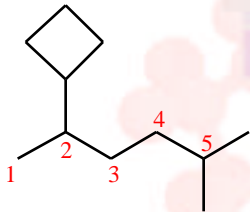
2-cyclobutyl-5-methylhexane

not

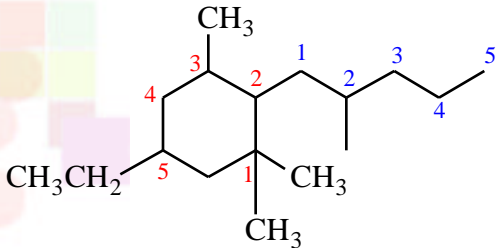
(1,4-dimethylpentyl)cyclobutane

**...if the “side chain” has more carbons
than the cycloalkane, it is the main chain**

Provide an acceptable IUPAC name for the following:

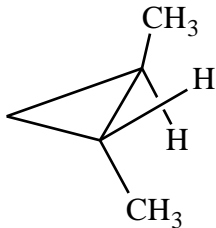
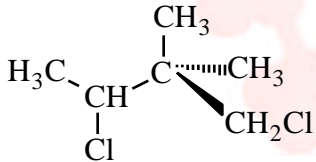
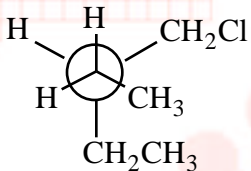


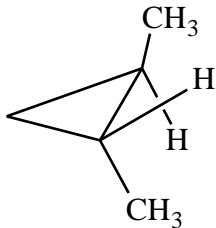
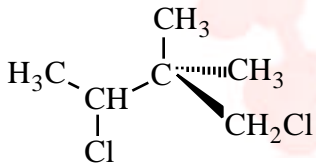
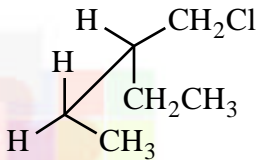
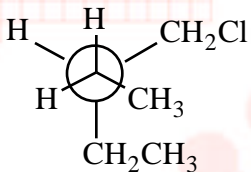
2-cyclobutyl-5-methylhexane
not
(1,4-dimethylpentyl)cyclobutane

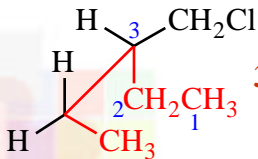
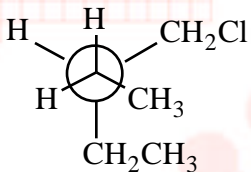


5-ethyl-1,1,3-trimethyl-2-
(2-methylpentyl)cyclohexane

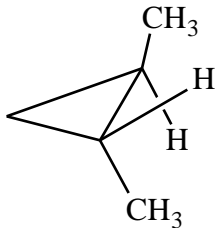
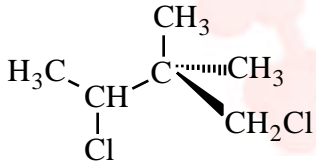
Provide an acceptable IUPAC name for the following:

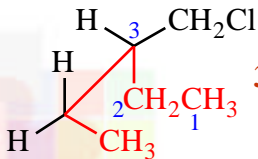
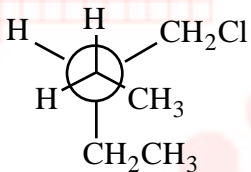




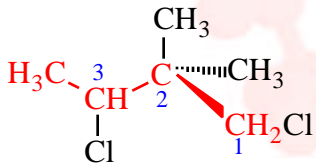


3-chloromethylpentane

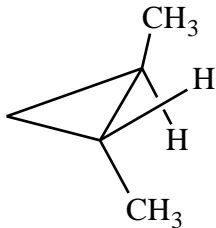


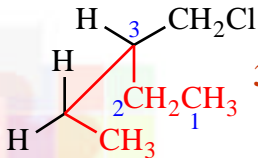
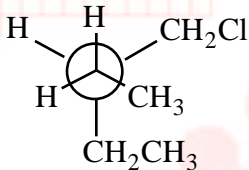


3-chloromethylpentane

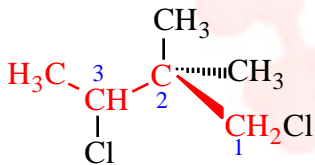


1,3-dichloro-2,2-dimethylbutane

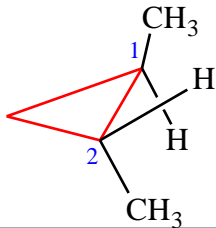




3-chloromethylpentane

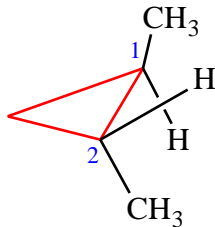


1,3-dichloro-2,2-dimethylbutane

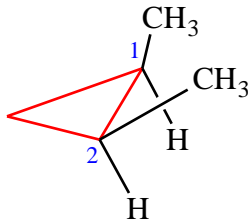


1,2-dimethylcyclopropane

But this name is ambiguous
since we can draw **two isomers**
of 1,2-dimethylcyclopropane.



1,2-dimethylcyclopropane

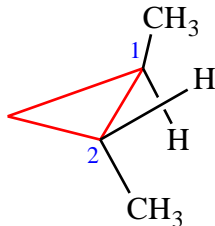


1,2-dimethylcyclopropane

In order to differentiate the stereochemistry of the two isomers, we use *cis-* and *trans-* in the name.

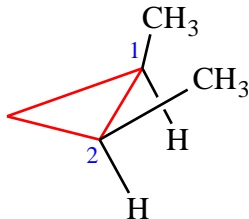
trans- ...opposite sides

trans-1,2-dimethylcyclopropane



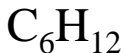
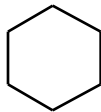
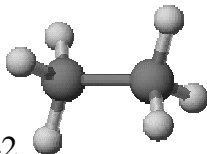
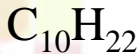
cis- ...same side

cis-1,2-dimethylcyclopropane



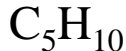
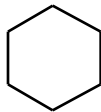
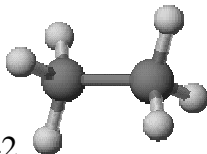
Calculating “Degrees of Unsaturation”

General Formula for an Alkane:



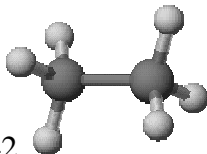
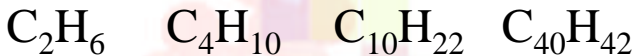
Calculating “Degrees of Unsaturation”

General Formula for an Alkane:

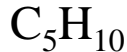
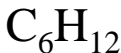
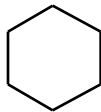


Calculating “Degrees of Unsaturation”

General Formula for an Alkane:

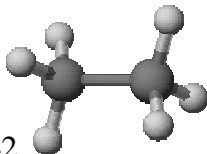
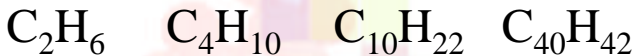


For a Cycloalkane:

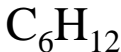
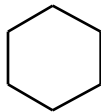


Calculating “Degrees of Unsaturation”

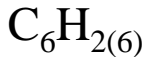
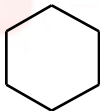
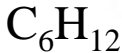
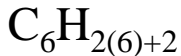
General Formula for an Alkane:



For a Cycloalkane:

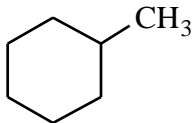


For cycloalkanes, every two “missing” hydrogens are referred to as one **“degree of unsaturation”**.

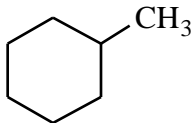


...one degree of unsaturation

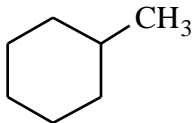
Calculate the degrees of unsaturation in the following compounds:



Calculate the degrees of unsaturation in the following compounds:

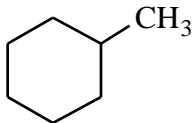


Calculate the degrees of unsaturation in the following compounds:



$$2(7) + 2 = 16$$

Calculate the degrees of unsaturation in the following compounds:



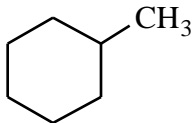
...**two** degrees of unsaturation

$$2(7) + 2 = 16$$

Calculate the degrees of unsaturation in the following compounds:



...**two** degrees of
unsaturation



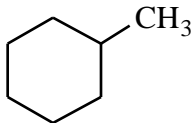
...**one** degree of
unsaturation

$$2(7) + 2 = 16$$

Calculate the degrees of unsaturation in the following compounds:



...**two** degrees of
unsaturation



...**one** degree of
unsaturation

$$2(7) + 2 = 16$$

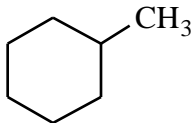
One degree of unsaturation for every ring.

Calculate the degrees of unsaturation in the following compounds:

One degree of unsaturation for every ring.



...**two** degrees of
unsaturation



...**one** degree of
unsaturation

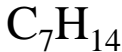
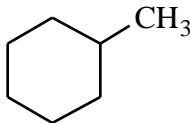
When counting rings in a polycyclic compound, you are **not allowed to retrace any path**, only to connect atoms following **new paths**.

Calculate the degrees of unsaturation in the following compounds:

One degree of unsaturation for every ring.



...**two** degrees of
unsaturation

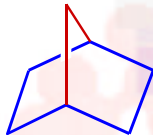


...**one** degree of
unsaturation

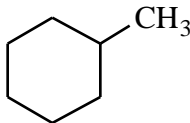
When counting rings in a polycyclic compound, you are **not allowed to retrace any path**, only to connect atoms following **new paths**.

Calculate the degrees of unsaturation in the following compounds:

One degree of unsaturation for every ring.



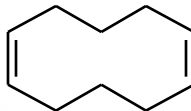
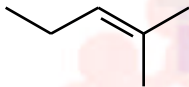
...**two** degrees of unsaturation



...**one** degree of unsaturation

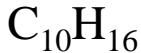
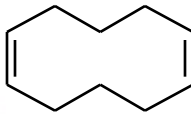
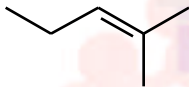
When counting rings in a polycyclic compound, you are **not allowed to retrace any path**, only to connect atoms following **new paths**.

Calculate the degrees of unsaturation in the following compounds:

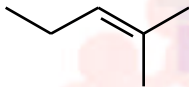


The concept of degrees of unsaturation can also be applied to **alkenes**, **alkynes** and carbon compounds containing **heteroatoms**.

Calculate the degrees of unsaturation in the following compounds:

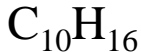
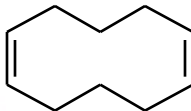


Calculate the degrees of unsaturation in the following compounds:



...one double bond; **one**
degree of unsaturation

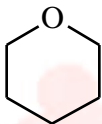
$$2(6) + 2 = 14$$



...one ring and two
double bonds; **three**
degrees of unsaturation

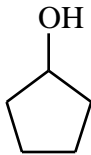
$$2(10) + 2 = 22$$

For compounds containing oxygen, simply **ignore the oxygen** and calculate based on carbons and hydrogens:



...one ring; **one** degree
of unsaturation

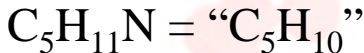
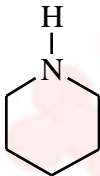
$$2(5) + 2 = 12$$



...one ring; **one** degree
of unsaturation

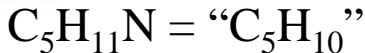
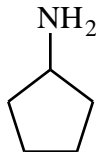
$$2(5) + 2 = 12$$

For compounds containing nitrogen, **subtract one hydrogen for each nitrogen**, and calculate based on remaining carbons and hydrogens:



...one ring; **one** degree
of unsaturation

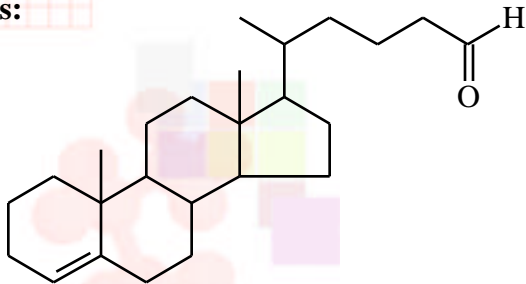
$$2(5) + 2 = 12$$



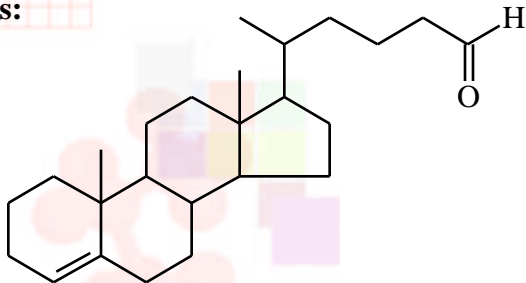
...one ring; **one** degree
of unsaturation

$$2(5) + 2 = 12$$

Calculate the degrees of unsaturation in the following compounds:



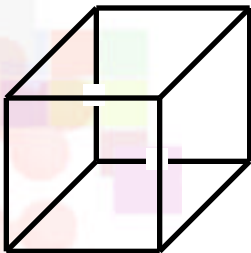
Calculate the degrees of unsaturation in the following compounds:



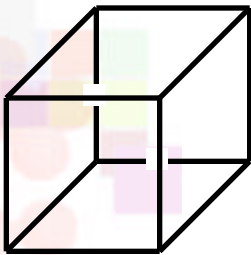
...4 rings and two double bonds; **six** degree of unsaturation

$$2(25) + 2 = 52$$

Calculate the degrees of unsaturation in the following compounds:



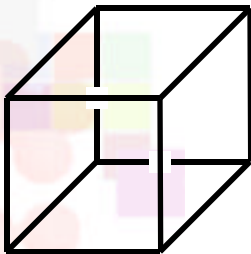
Calculate the degrees of unsaturation in the following compounds:



Five degree of unsaturation, therefore **five rings**.

$$2(8) + 2 = 18$$

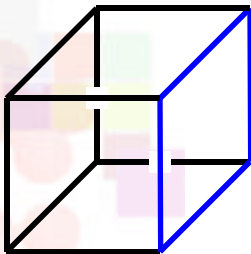
Calculate the degrees of unsaturation in the following compounds:



Five degree of unsaturation, therefore **five rings**.

When counting rings in a polycyclic compound, you are **not allowed to retrace any path**, only to connect atoms following **new paths**.

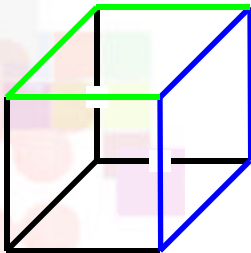
Calculate the degrees of unsaturation in the following compounds:



Five degree of unsaturation, therefore **five rings**.

When counting rings in a polycyclic compound, you are **not allowed to retrace any path**, only to connect atoms following **new paths**.

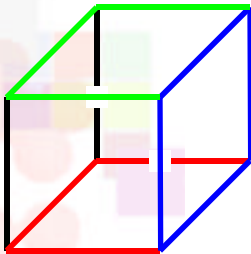
Calculate the degrees of unsaturation in the following compounds:



Five degree of unsaturation, therefore **five rings**.

When counting rings in a polycyclic compound, you are **not allowed to retrace any path**, only to connect atoms following **new paths**.

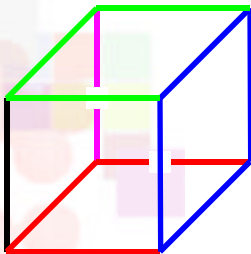
Calculate the degrees of unsaturation in the following compounds:



Five degree of unsaturation, therefore **five rings**.

When counting rings in a polycyclic compound, you are **not allowed to retrace any path**, only to connect atoms following **new paths**.

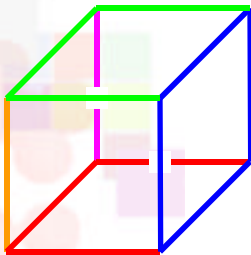
Calculate the degrees of unsaturation in the following compounds:



Five degree of unsaturation, therefore **five rings**.

When counting rings in a polycyclic compound, you are **not allowed to retrace any path**, only to connect atoms following **new paths**.

Calculate the degrees of unsaturation in the following compounds:



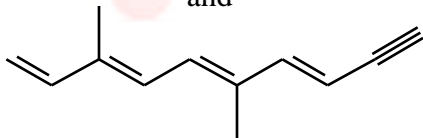
Five degree of unsaturation, therefore **five rings**.

When counting rings in a polycyclic compound, you are **not allowed to retrace any path**, only to connect atoms following **new paths**.

Calculate the degrees of unsaturation in the following compounds:



and

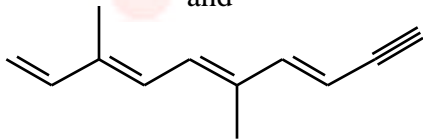


Calculate the degrees of unsaturation in the following compounds:

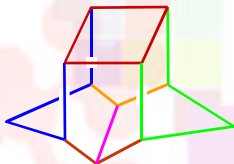


$C_{12}H_{14} = 6$ degrees of unsaturation

and

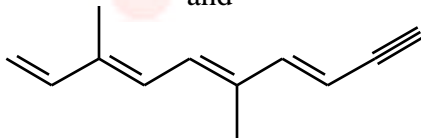


Calculate the degrees of unsaturation in the following compounds:

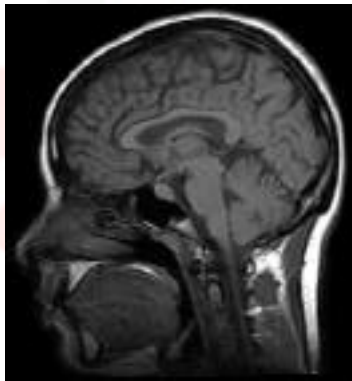


$C_{12}H_{14} = 6$ degrees of unsaturation

and



^{13}C NMR Spectroscopy



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Nuclear Magnetic Resonance

Nuclei of isotopes with an odd number of protons, an odd number of neutrons, or both, exhibit mechanical spin phenomena which are associated with angular momentum.

This angular momentum is characterized by a nuclear spin quantum number, I such that,

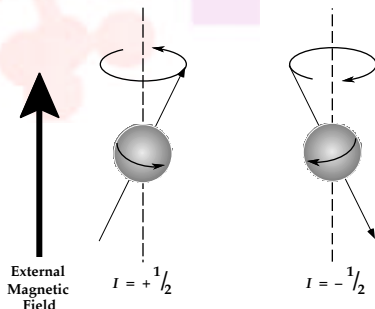
$$I = \frac{1}{2}n, \text{ where } n \text{ is an integer.}$$

When $I = 0$, nuclei do not possess spin angular momentum and are **NMR-silent**; ^{12}C , ^{16}O are examples of this.

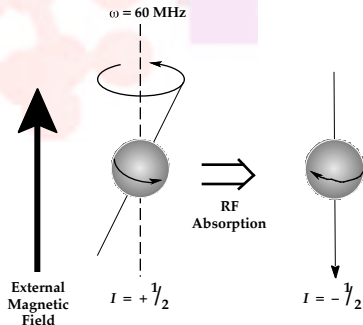
Nuclei with $I = \frac{1}{2}$ possess spin angular momentum and can be studied in the NMR; these include ^1H , ^{13}C , ^{19}F , ^{31}P , etc.

Atomic nuclei are charged, and nuclei with spin generate a small **electric** and **magnetic** field surrounding the nucleus.

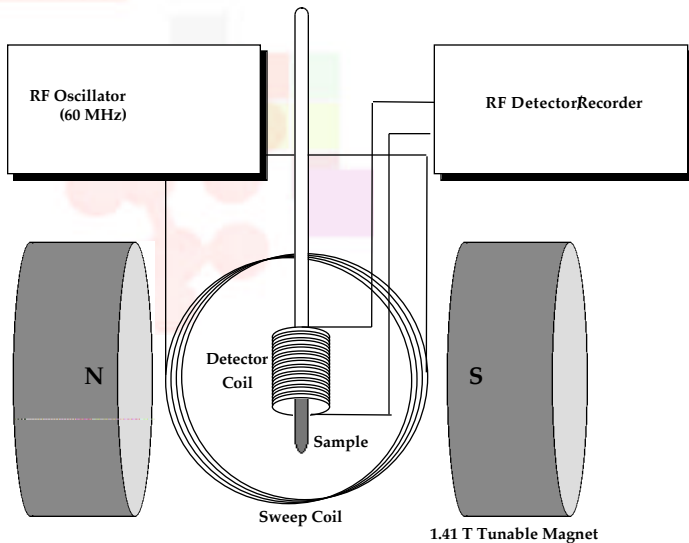
When a nucleus with spin of $1/2$ is placed in a magnetic field, the nuclei will tend to orient either **parallel** to the field (low energy) or **anti-parallel** the field (high energy). *The lower energy state is slightly more populated.*



If electromagnetic radiation of the appropriate energy interacts with the nucleus, the two electric fields can couple and energy from the radiation can be absorbed. When a nucleus absorbs energy in this manner, it undergoes a change in spin orientation (a *spin-flip*) and the nucleus is said to be in **resonance** with the incoming electromagnetic radiation.



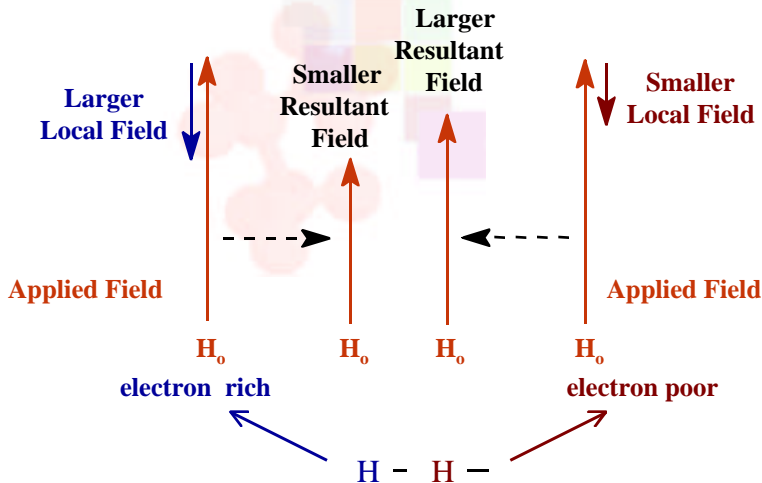
A schematic representation of a simple NMR spectrometer.



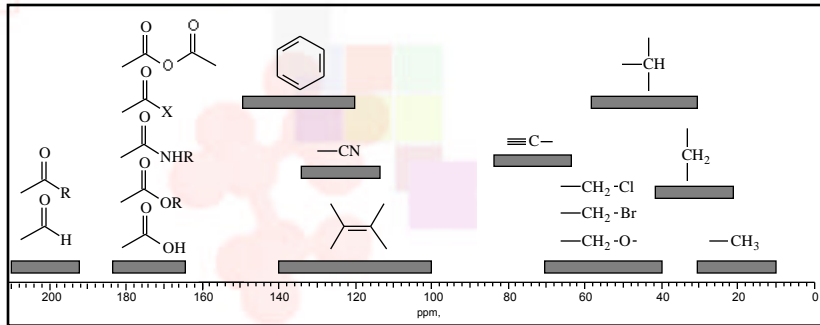
If all nuclei of a given type underwent the change in spin orientation at the same frequency, NMR spectroscopy would be of little value. In fact, **the frequency at which resonance occurs in a nucleus depends largely upon the electronic environment surrounding that nucleus.**

This is because the valence electrons around the nucleus are caused to *circulate* by the applied magnetic field. This circulation, termed a **local diamagnetic current**, induces a local magnetic field that is oriented to *oppose* the applied field. *The net result is that the nucleus feels a reduced magnetic field; that is, the applied field has been shielded by the local diamagnetic current.*

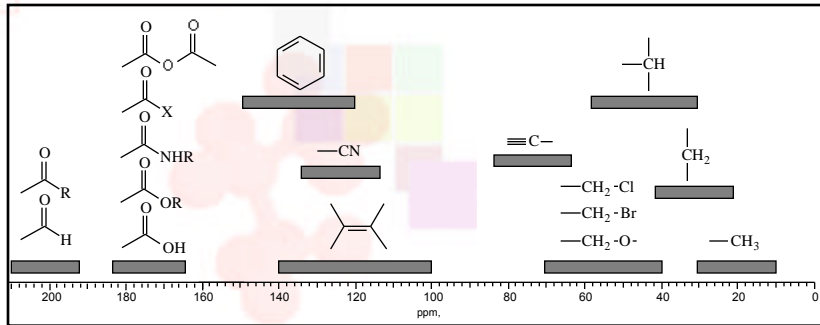
Nuclei which are in *electron rich* environments will undergo transition at a **higher applied field** than nuclei in *electron poor* environments.



Chemical shifts in ^{13}C NMR are sensitive to electronegative environment.

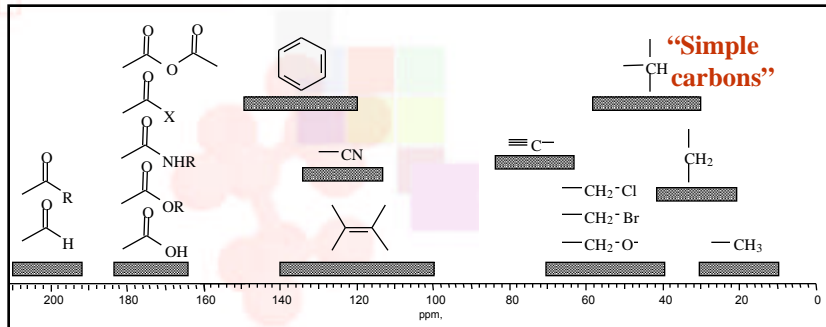


Chemical shifts in ^{13}C NMR are sensitive to electronegative environment.

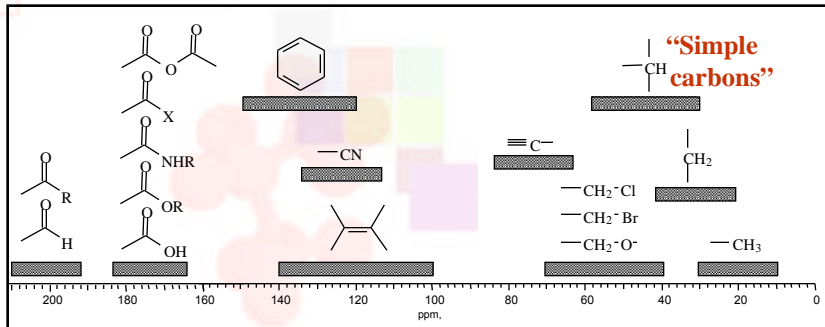


$$\text{Chemical shift } (\delta) = \frac{\text{observed shift}}{\text{oscillator frequency}} \times 10^6 \equiv \text{ppm} \quad (\text{parts per million})$$

Chemical shifts in ^{13}C NMR are sensitive to electronegative environment.

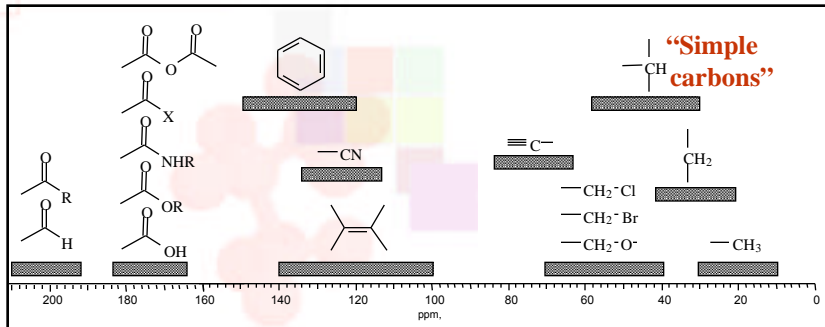


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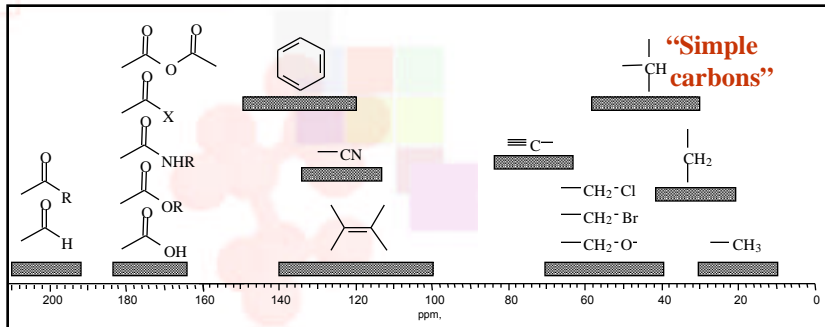
- **Electronegative groups** tend to move NMR signals from attached carbons to **higher ppm values**.

Chemical shifts in ^{13}C NMR are sensitive to electronegative environment.



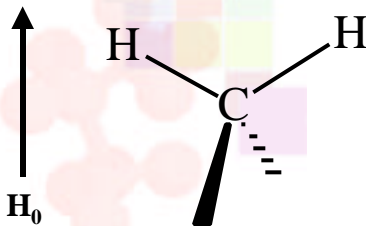
- **Electronegative groups** tend to move NMR signals from attached carbons to **higher ppm values**.
- The π -system of **alkenes and aromatic compounds** strongly deshield nuclei and move them to **higher ppm values**.

Chemical shifts in ^{13}C NMR are sensitive to electronegative environment.

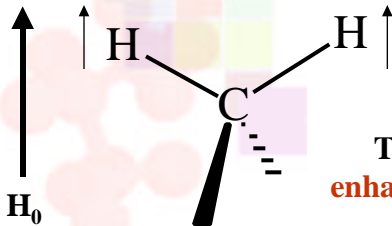


- **Electronegative groups** tend to move NMR signals from attached carbons to **higher ppm values**.
- The π -system of **alkenes and aromatic compounds** strongly deshield nuclei and move them to **higher ppm values**.
- **Carbonyl carbons** are strongly deshielded and occur at **very high ppm values**.

The **hydrogens** which are attached to a carbon also have a **spin of $1/2$** and will therefore generate **small, local magnetic fields** depending on their orientation.



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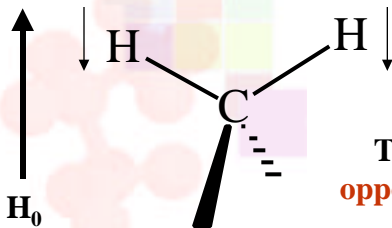


The local fields can **enhance** the applied field.

Increase the local field.



The **hydrogens** which are attached to a carbon also have a **spin of $1/2$** and will therefore generate **small, local magnetic fields** depending on their orientation.



The local fields can **oppose** the applied field.

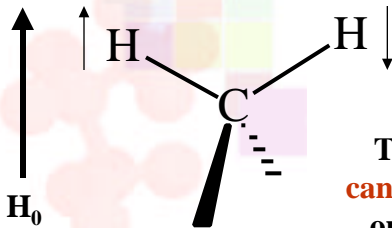
Decrease the local field.



Increase the local field.



The **hydrogens** which are attached to a carbon also have a **spin of $1/2$** and will therefore generate **small, local magnetic fields** depending on their orientation.



The local fields can **cancel**, having **no effect** on the applied field.

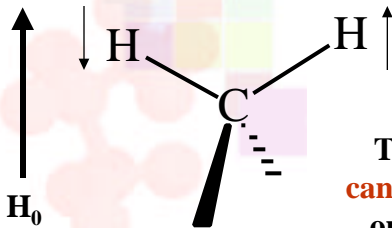
Decrease the local field.



Increase the local field.



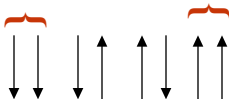
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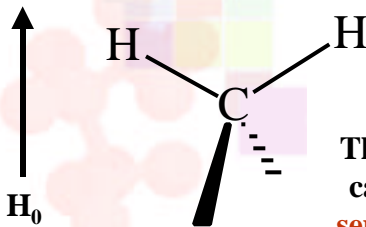
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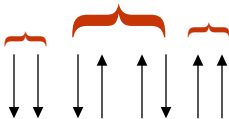


The net effect is that the carbon will sense **three separate magnetic fields**.

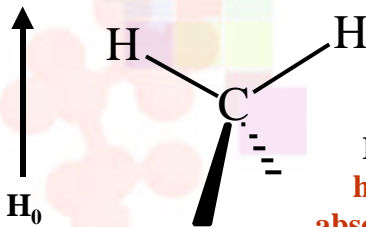
Decrease the local field.

No effect.

Increase the local field.



Therefore, the attached hydrogens will **split** the ^{13}C NMR signal into **three peaks**, in the ratio of 1:2:1 (a **triplet**).

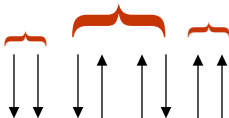


In general, n attached hydrogens will split the absorbance into $(n+1)$ peaks.

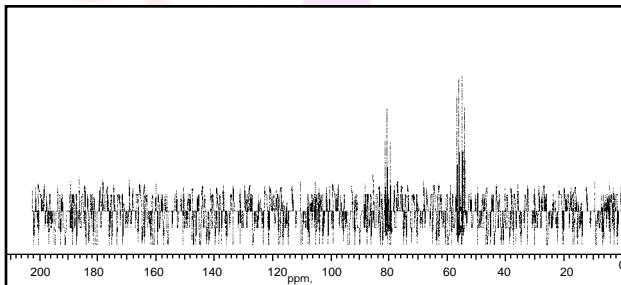
Decrease the local field.

No effect.

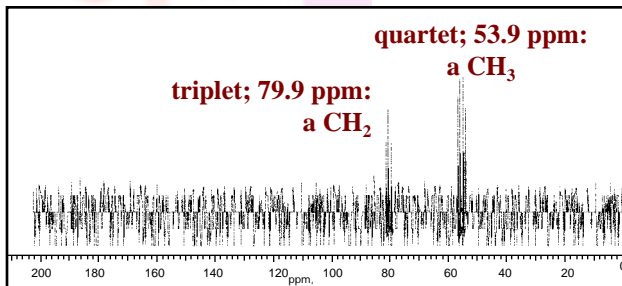
Increase the local field.



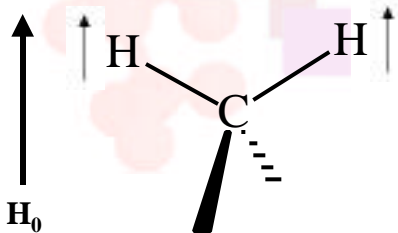
The low natural abundance of the ^{13}C isotope contributes to a **large noise-signal ratio** in ^{13}C NMR spectra. In spite of the noise, splitting between the carbon and the attached hydrogens can generally be observed. Again, according to the $(n + 1)$ rule, **n attached hydrogens will split a ^{13}C absorbance into $(n+1)$ peaks.**



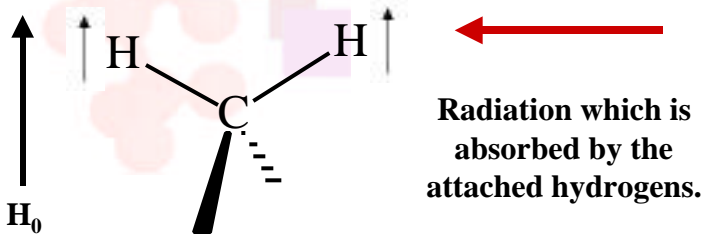
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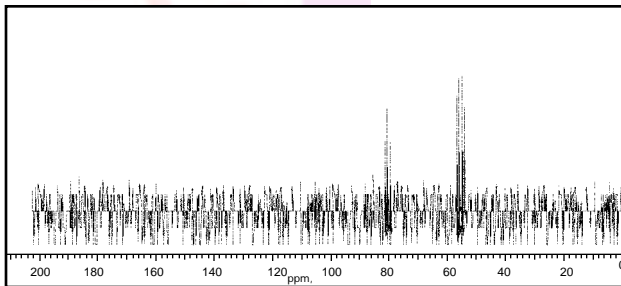
The ^{13}C NMR spectrum can be significantly improved utilizing a technique called **proton decoupling**, in which the attached protons are irradiated constantly, randomizing their local magnetic fields, destroying the coupling and making the peak into a **singlet**.



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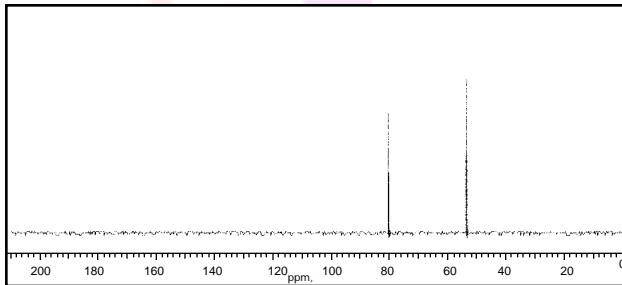


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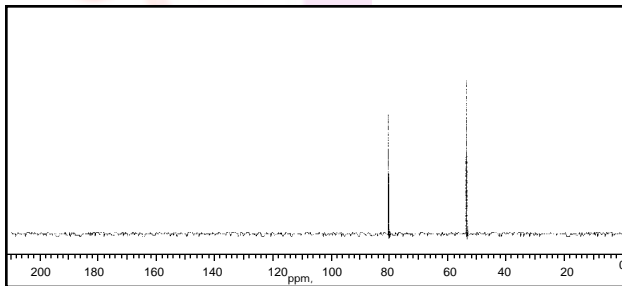
Proton decoupling off.

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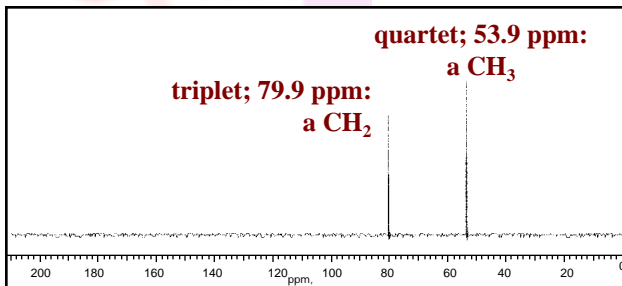


Proton decoupling on.

The enhancement in signal intensity which is observed is a result of the **Nuclear Overhauser Effect**, in which some of the energy from the attached proton is transferred to the ^{13}C nucleus. This effect, however, is uneven and **the observed peak intensities are not proportional to the number of carbons giving rise to the absorbance.**



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^{13}C NMR tells us two things...



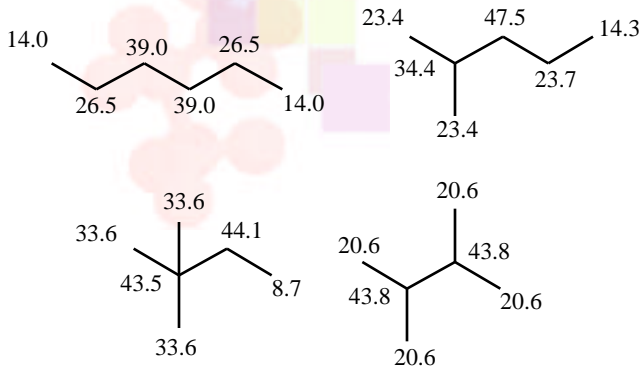
^{13}C NMR tells us two things...

- The **chemical shift** tells us the **electronic environment** (simple, aromatic, alkene, adjacent to electronegative groups, etc.)

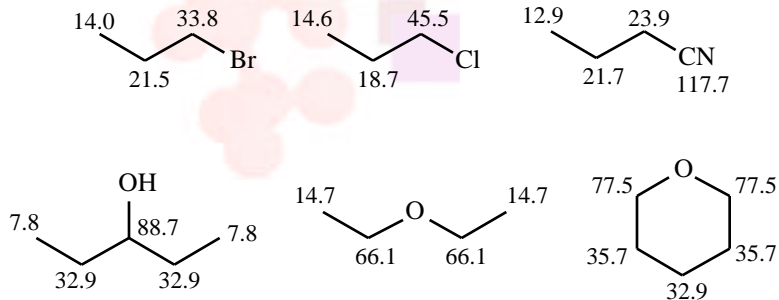
¹³C NMR tells us two things...

- The **chemical shift** tells us the **electronic environment** (simple, aromatic, alkene, adjacent to electronegative groups, etc.)
- The **splitting** tells us the **number of equivalent hydrogens attached to that carbon** (n hydrogens gives $n+1$ peaks).

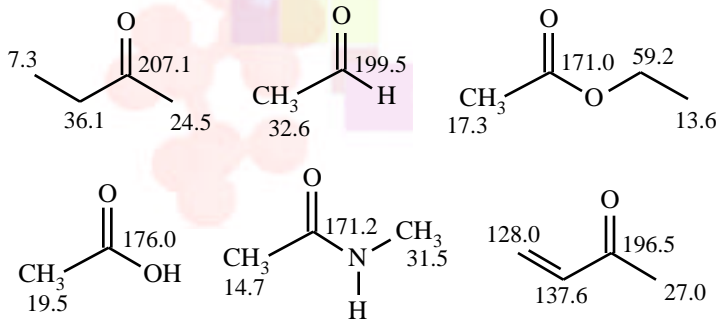
Simple alkanes appear in the region **20-50 ppm**; secondary and “interior” carbons are shifted to **higher values due to steric effects**.



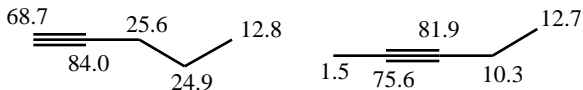
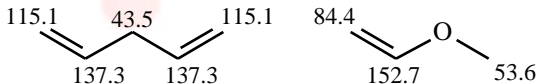
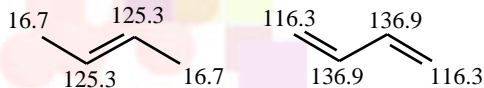
Carbons adjacent to electronegative atoms appear in the region **40-80 ppm**; again, steric effects can increase this value.



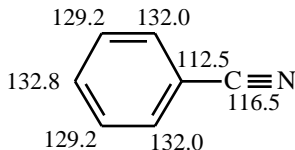
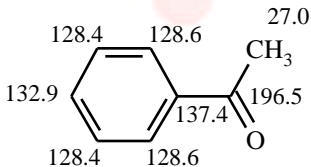
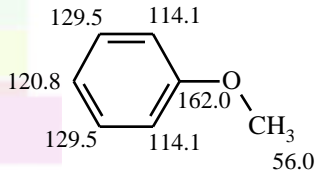
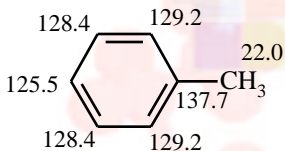
Carbonyls are **very highly shifted** and appear in the range **170-210 ppm**; **ketones** are the most deshielded (highest δ values; generally > 200) and **esters, amides and acids** are the lowest.



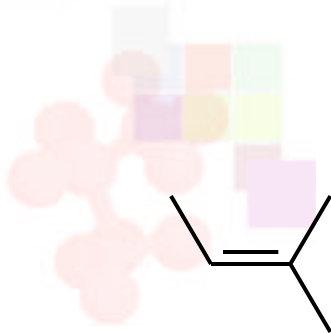
Simple **alkene** carbons appear in the region **110-150 ppm**; **alkyne** carbons are generally **70-90 ppm** and **carbons attached to alkynes are highly shielded**, appearing below **10 ppm**.



Arenes appear in the region 120-160 ppm; examining the number of singlets and doublets in the benzene region gives information regarding ring substitution.

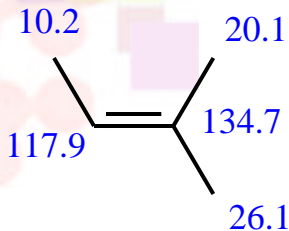


How many peaks will appear in the **proton-decoupled** ^{13}C NMR for the compound shown below?



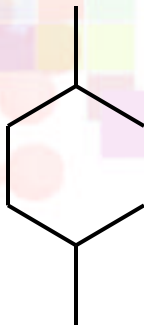
There will be **five peaks** in the proton-decoupled ^{13}C NMR.

How many peaks will appear in the **proton-decoupled** ^{13}C NMR for the compound shown below?



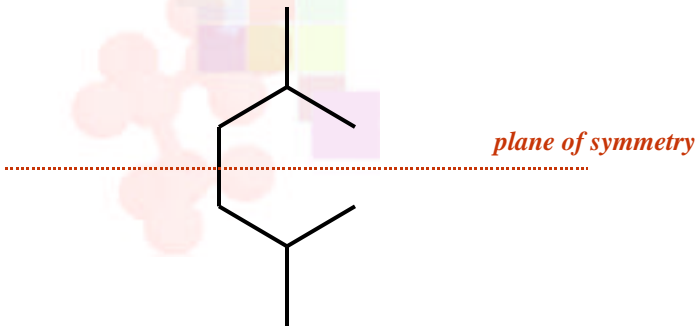
There will be **five peaks** in the proton-decoupled ^{13}C NMR.

How many peaks will appear in the **proton-decoupled** ^{13}C NMR for the compound shown below?



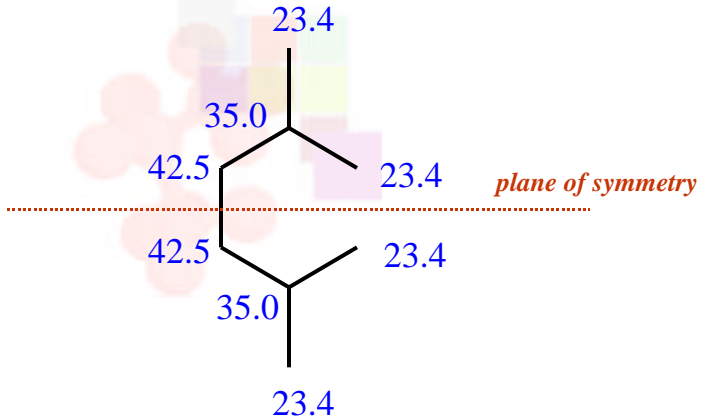
There will be **three peaks** in the proton-decoupled ^{13}C NMR.

How many peaks will appear in the **proton-decoupled** ^{13}C NMR for the compound shown below?



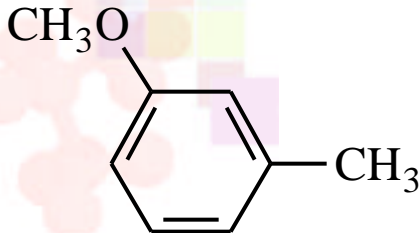
There will be **three peaks** in the proton-decoupled ^{13}C NMR.

How many peaks will appear in the **proton-decoupled** ^{13}C NMR for the compound shown below?



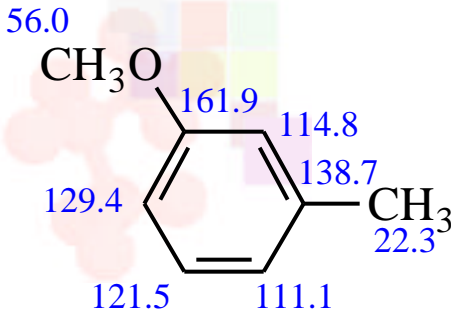
There will be **three peaks** in the proton-decoupled ^{13}C NMR.

How many peaks will appear in the **proton-decoupled** ^{13}C NMR for the compound shown below?



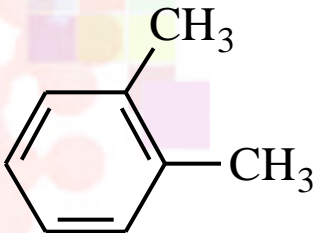
There will be **eight peaks** in the proton-decoupled ^{13}C NMR.

How many peaks will appear in the **proton-decoupled** ^{13}C NMR for the compound shown below?



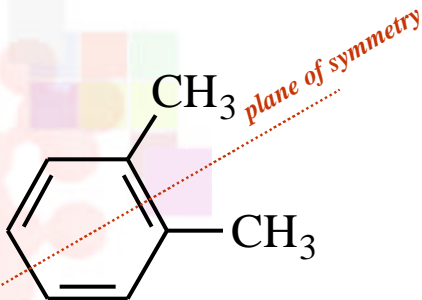
There will be **eight peaks** in the proton-decoupled ^{13}C NMR.

How many peaks will appear in the **aromatic region** of the **proton-decoupled** ^{13}C NMR for the compound shown below?



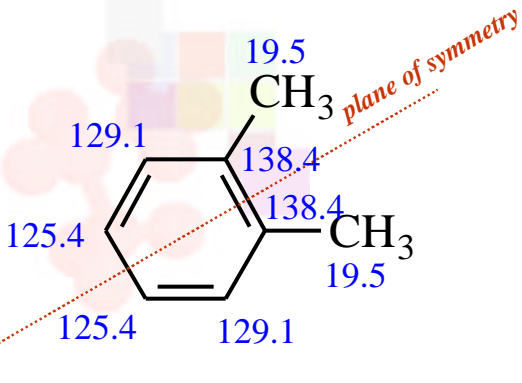
There will be **three peaks** in the proton-decoupled ^{13}C NMR.

How many peaks will appear in the **aromatic region** of the **proton-decoupled** ^{13}C NMR for the compound shown below?



There will be **three peaks** in the proton-decoupled ^{13}C NMR.

How many peaks will appear in the **aromatic region** of the **proton-decoupled** ^{13}C NMR for the compound shown below?



There will be **three peaks** in the proton-decoupled ^{13}C NMR.