

**Dr. Akbar Ali**

**Organic Chemistry**

**BS-3 Regular 2020**

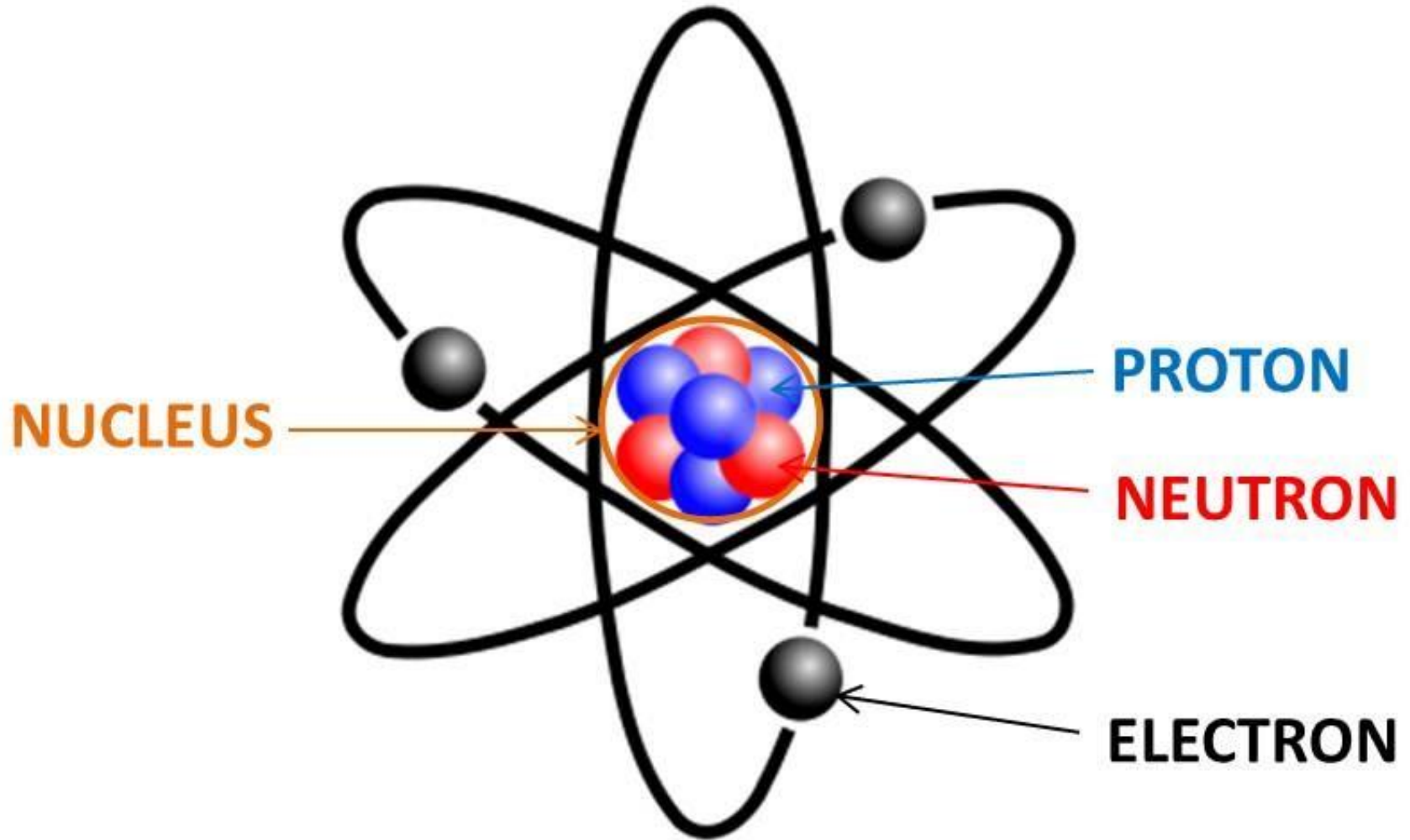
**CHEM-271**

# Atom:

- An **atom** is the smallest unit of ordinary matter that forms a chemical element.
- Every solid, liquid, gas, and plasma is composed of neutral or ionized atoms.
- Atoms are extremely small, typically around 100 picometers across.
- Every atom is composed of a nucleus and one or more electrons bound to the nucleus.
- The nucleus is made of one or more protons and a number of neutrons.

- More than 99.94% of an atom's mass is in the nucleus.
- The protons have a positive electric charge, the electrons have a negative electric charge, and the neutrons have no electric charge.
- If the number of protons and electrons are equal, then the atom is electrically neutral.
- If an atom has more or fewer electrons than protons, then it has an overall negative or positive charge, respectively – such atoms are called ions.

# Atom:



# Chemical Bond

- A **chemical bond** is a lasting attraction between atoms, ions or molecules that enables the formation of chemical compounds.
- The bond may result from the electrostatic force of attraction between oppositely charged ions as in ionic bonds or through the sharing of electrons as in covalent bonds.
- The strength of chemical bonds varies considerably; there are "strong bonds" or "primary bonds" such as covalent, ionic and metallic bonds, and "weak bonds" or "secondary bonds" such as dipole–dipole interactions, the London dispersion force and hydrogen bonding.

# Atomic Orbital:

- In atomic theory and quantum mechanics, an **atomic orbital** is a mathematical function describing the location and wave-like behavior of an electron in an atom.
- This function can be used to calculate the probability of finding any electron of an atom in any specific region around the atom's nucleus.
- The term *atomic orbital* may also refer to the physical region or space where the electron can be calculated to be present, as predicted by the particular mathematical form of the orbital.

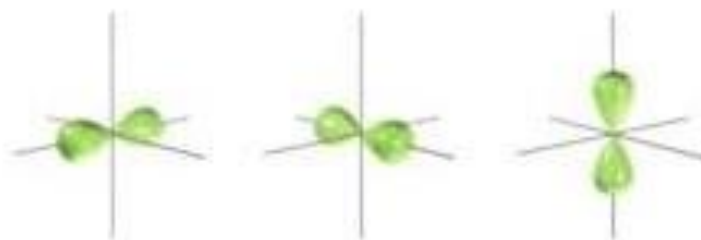
- Each orbital in an atom is characterized by a unique set of values of the three quantum numbers  $n$ ,  $\ell$ , and  $m$ , which respectively correspond to the electron's energy, angular momentum.
- Each such orbital can be occupied by a maximum of two electrons, each with its own spin quantum number  $s$ .
- The simple names **s orbital**, **p orbital**, **d orbital**, and **f orbital** refer to orbitals with angular momentum quantum number  $\ell = 0, 1, 2$ , and  $3$  respectively.
- These names, together with the value of  $n$ , are used to describe the electron configurations of atoms.

**Orbital Type****Spatial Orientations** $s$ 

The  $s$  orbital has only one shape, which is spherical.

 $p$ 

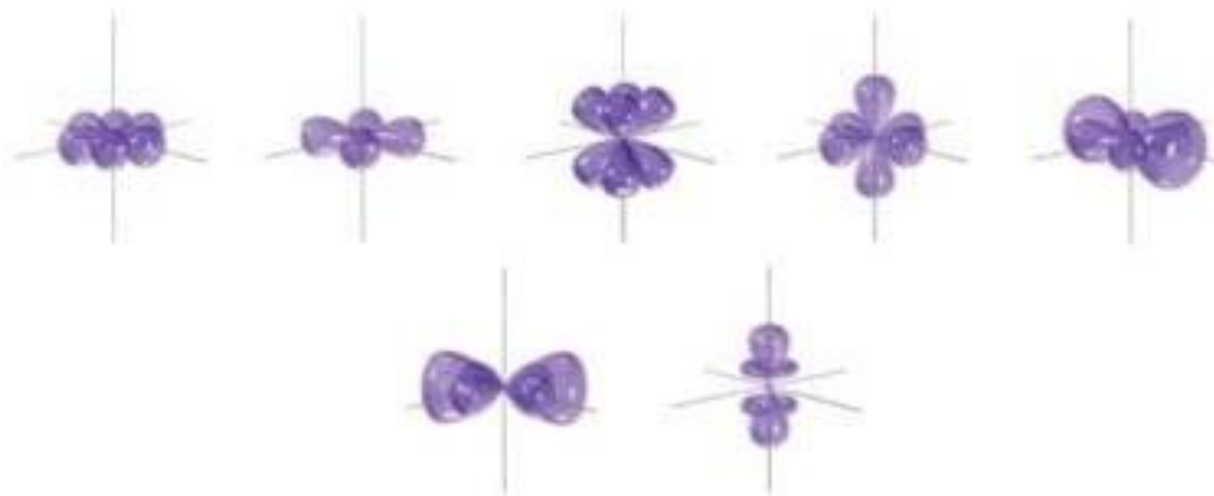
There are three  $p$  orbitals. They differ by orientation.

 $d$ 

There are five  $d$  orbitals.

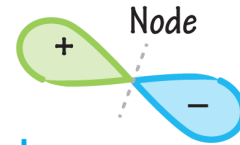
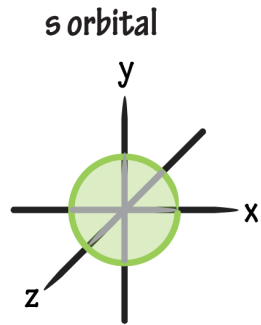
 $f$ 

There are seven  $f$  orbitals.



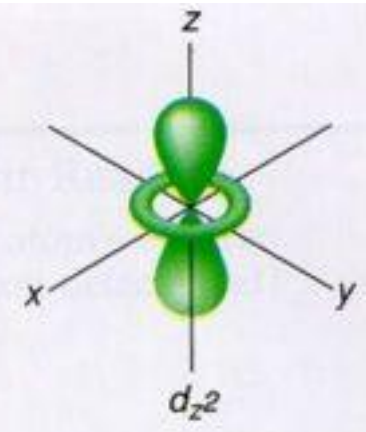
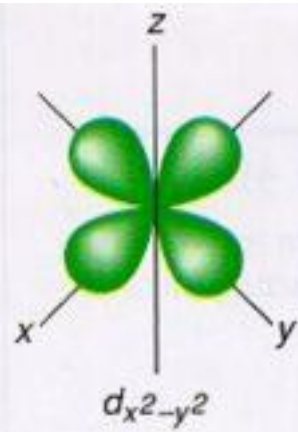
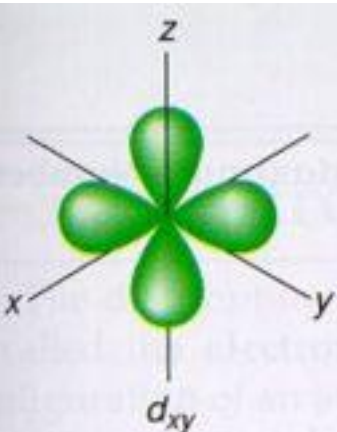
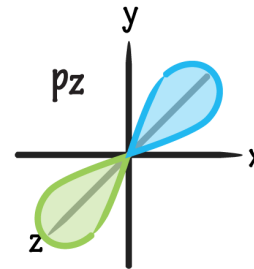
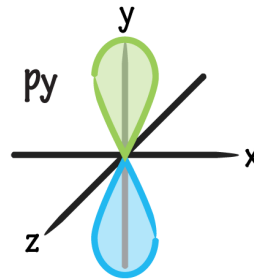
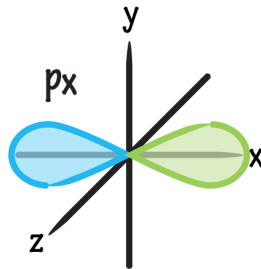


# SHAPE

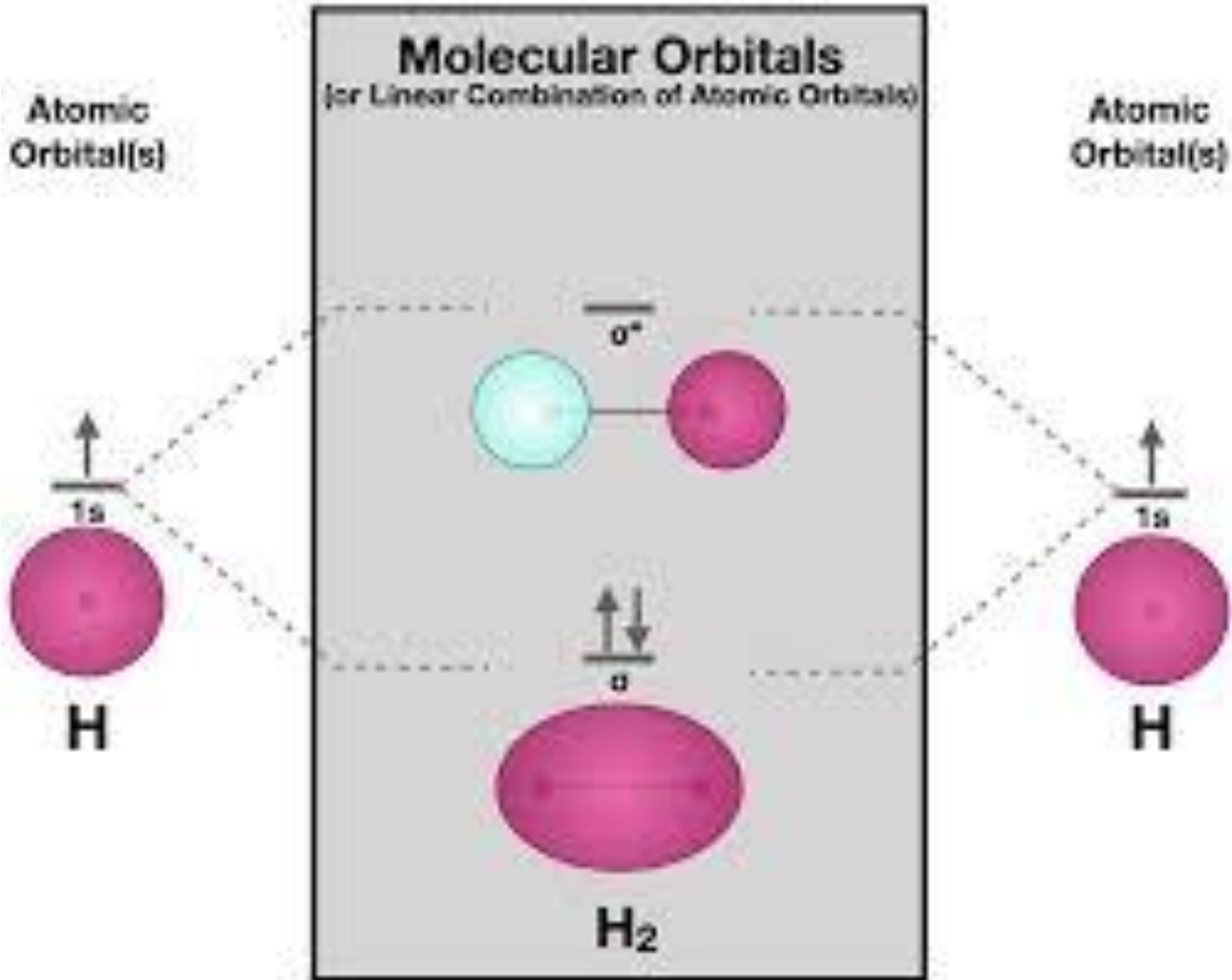


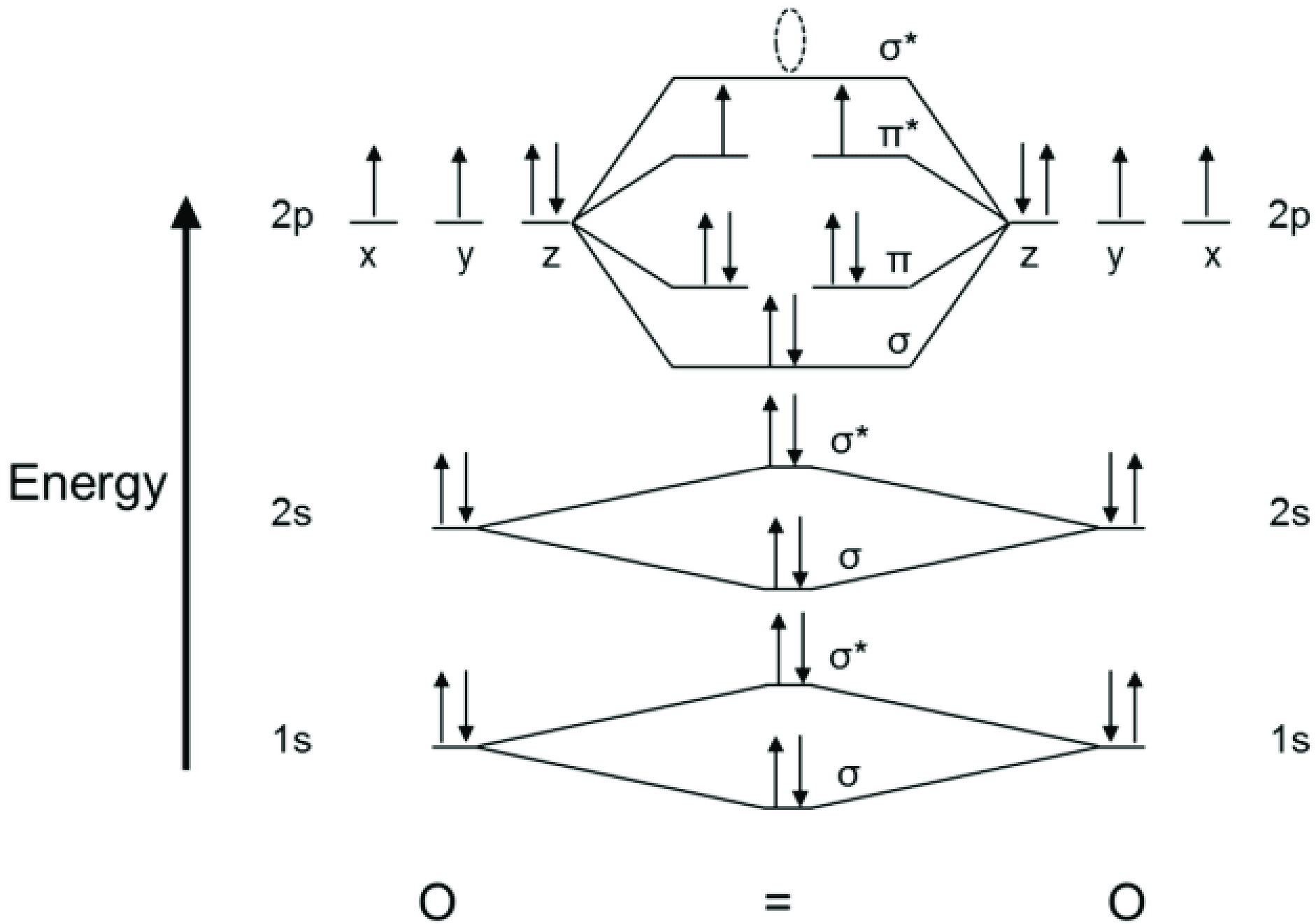
- Node**
- ✓ The point where an electron cannot be located.
  - ✓ More nodes, higher energy.

## p orbitals



# Molecular Orbitals





## Hybrid orbitals

The atomic orbitals obtained when two or more nonequivalent orbitals from the same atom combine in preparation for bond formation.

**Hybridization:** the concept of mixing two atomic orbitals with the same energy levels to give a degenerated new type of orbitals.

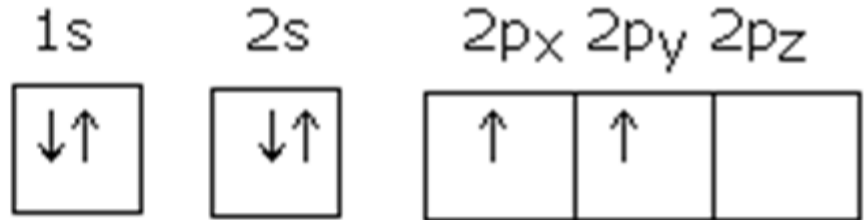
This intermixing is based on quantum mechanics. The atomic orbitals of the same energy level can only take part in hybridization and both full filled and half-filled orbitals can also take part in this process, provided they have equal energy.

## Types of Hybridization

Based on the [types of orbitals](#) involved in mixing, the hybridization can be classified as  $sp^3$ ,  $sp^2$ ,  $sp$ ,  $sp^3d$ ,  $sp^3d^2$ ,  $sp^3d^3$ . Let us now discuss the various types of hybridization, along with their examples.

## 6C : $1s^2, 2s^2, 2p^2$

Electronic configuration of C  
in ground state



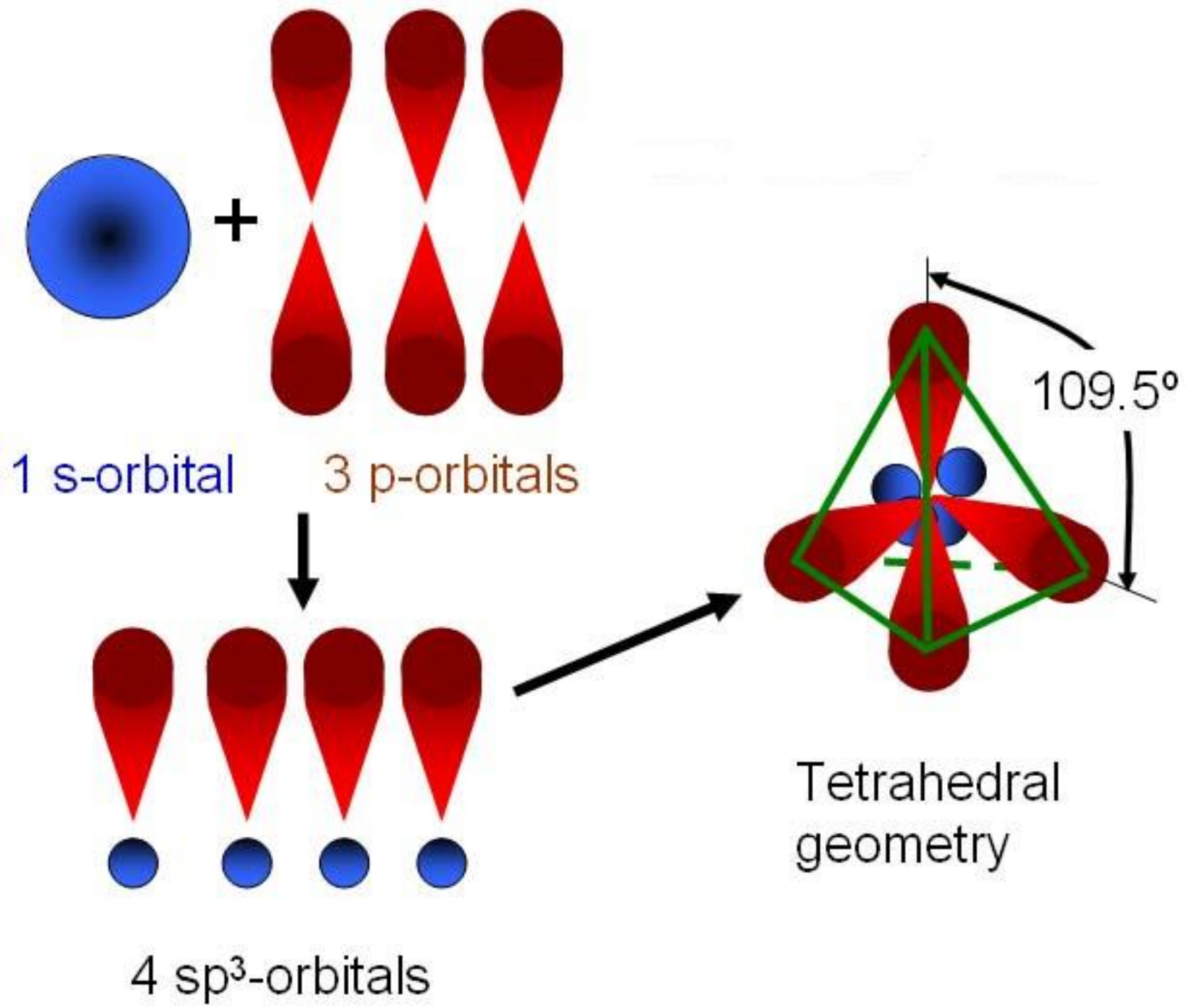
Electronic configuration of C  
in excited state.



## sp<sup>3</sup> Hybridization

When one 's' orbital and 3 'p' orbitals belonging to the same shell of an atom mix together to form four new equivalent orbital, the type of hybridization is called a **tetrahedral hybridization or sp<sup>3</sup>**. The new orbitals formed are called **sp<sup>3</sup> hybrid orbitals**.

- These are directed towards the four corners of a regular [tetrahedron](#) and make an angle of 109°28' with one another.
- The angle between the sp<sup>3</sup> hybrid orbitals is 109.28°
- Each sp<sup>3</sup> hybrid orbital has 25% s character and 75% p character.
- Example of sp<sup>3</sup> hybridization: [ethane](#) (C<sub>2</sub>H<sub>6</sub>), methane.

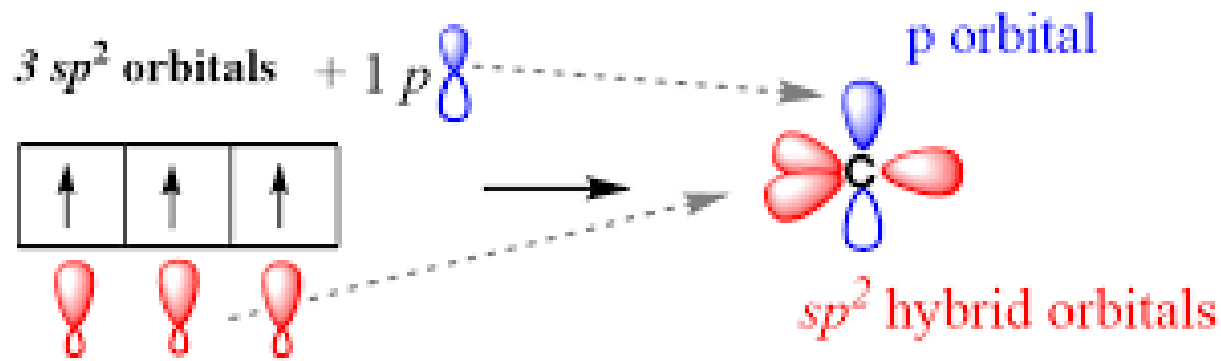


## **sp<sup>2</sup> Hybridization**

**sp<sup>2</sup> hybridisation** is observed when one s and two p orbitals of the same shell of an atom mix to form 3 equivalent orbital. The new orbitals formed are called **sp<sup>2</sup> hybrid orbitals**.

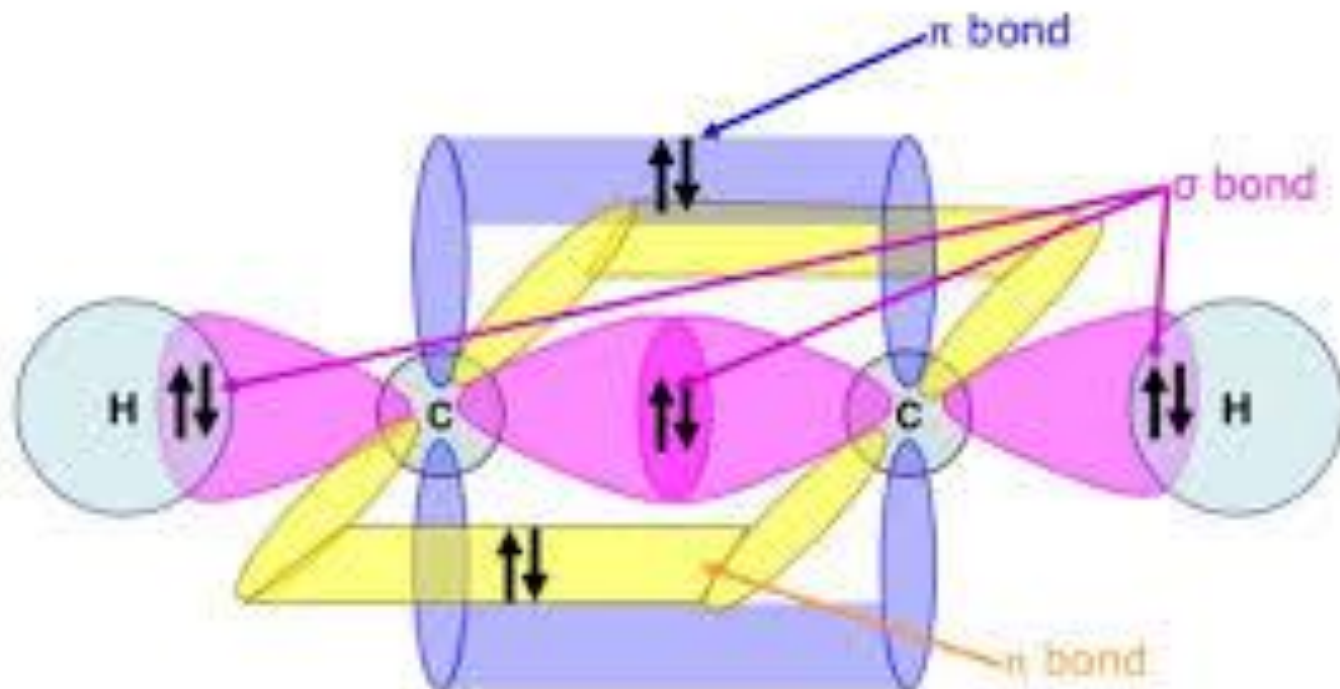
- sp<sup>2</sup> hybridization is also called trigonal hybridization as the trigonal symmetry is maintained at 120°.
- It involves mixing of one 's' orbital and two 'p' orbital's of equal energy to give a new hybrid orbital known as sp<sup>2</sup>.
- All the three hybrid orbitals remain in one plane and make an angle of 120° with one another. Each of the hybrid orbitals formed has 33.33% s character and 66.66% 'p' character.

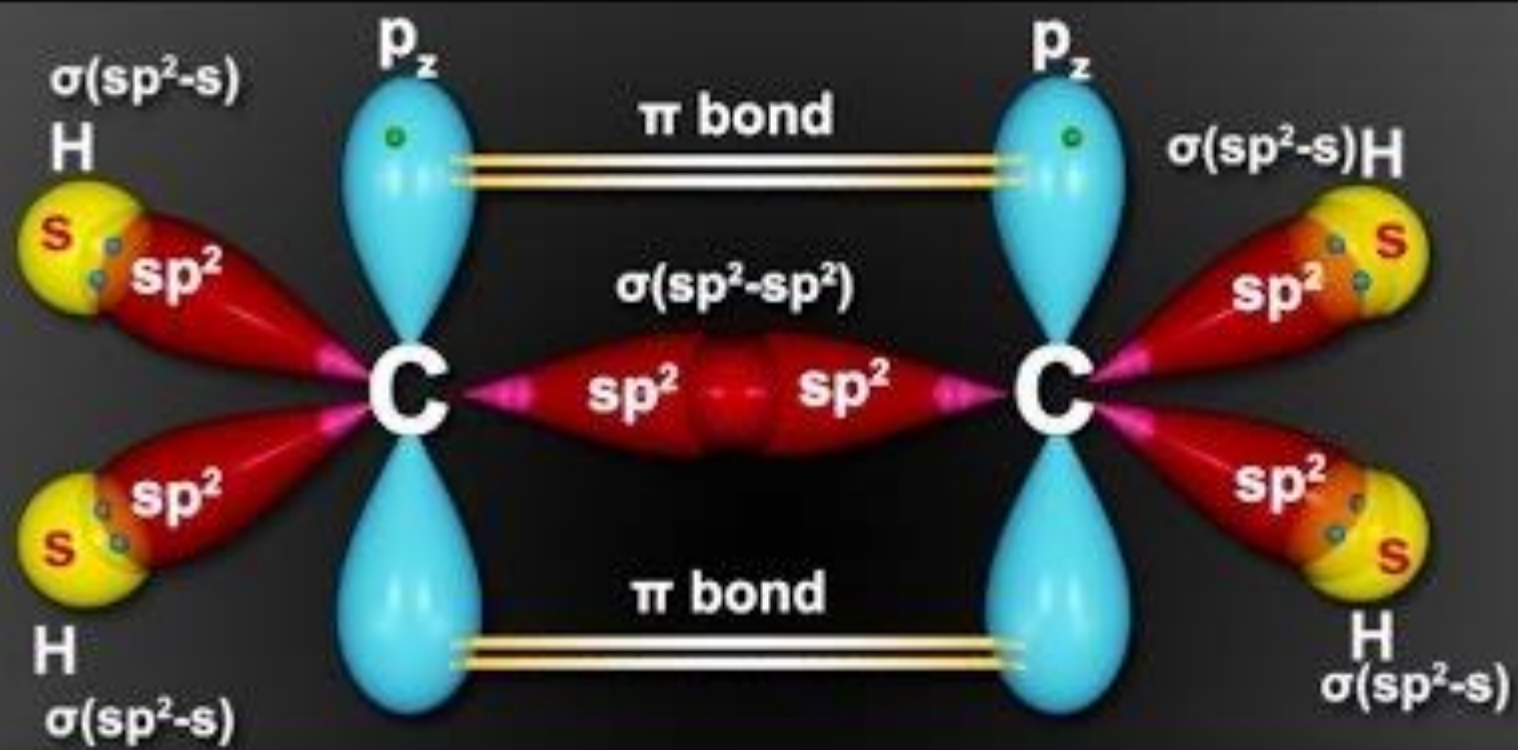




3 orbitals formed

Example: **Ethyne ( $C_2H_2$ )**





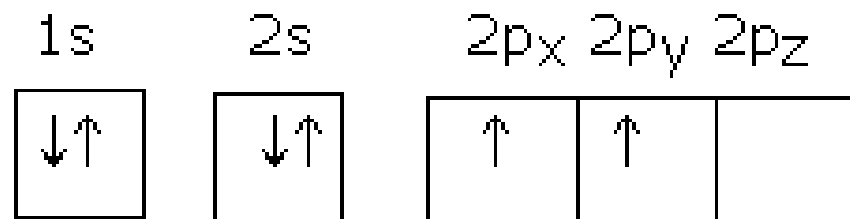
# SP2 HYBRIDIZATION

## sp Hybridization

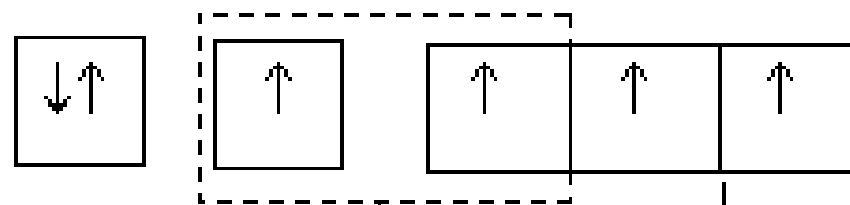
sp hybridization is observed when one s and one p orbital in the same main shell of an atom mix to form two new equivalent orbitals. The new orbitals formed are called **sp hybridized orbitals**.

- It forms linear molecules with an angle of  $180^\circ$
- This type of hybridization involves the mixing of one 's' orbital and one 'p' orbital of equal energy to give a new hybrid orbital known as an sp hybridized orbital.
- sp hybridization is also called diagonal hybridization.
- Each sp hybridized orbital has an equal amount of s and p character, i.e., 50% s and p character.

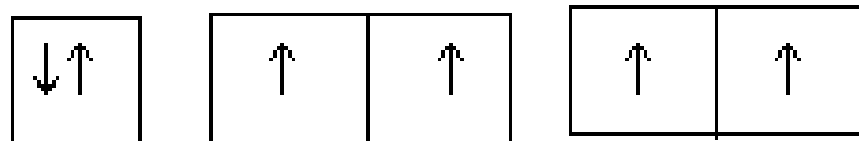
Electronic configuration of C in ground state



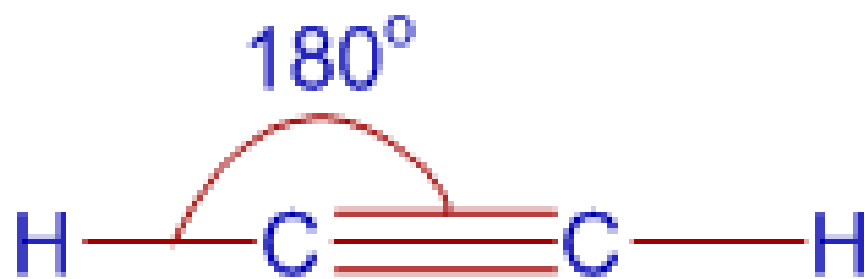
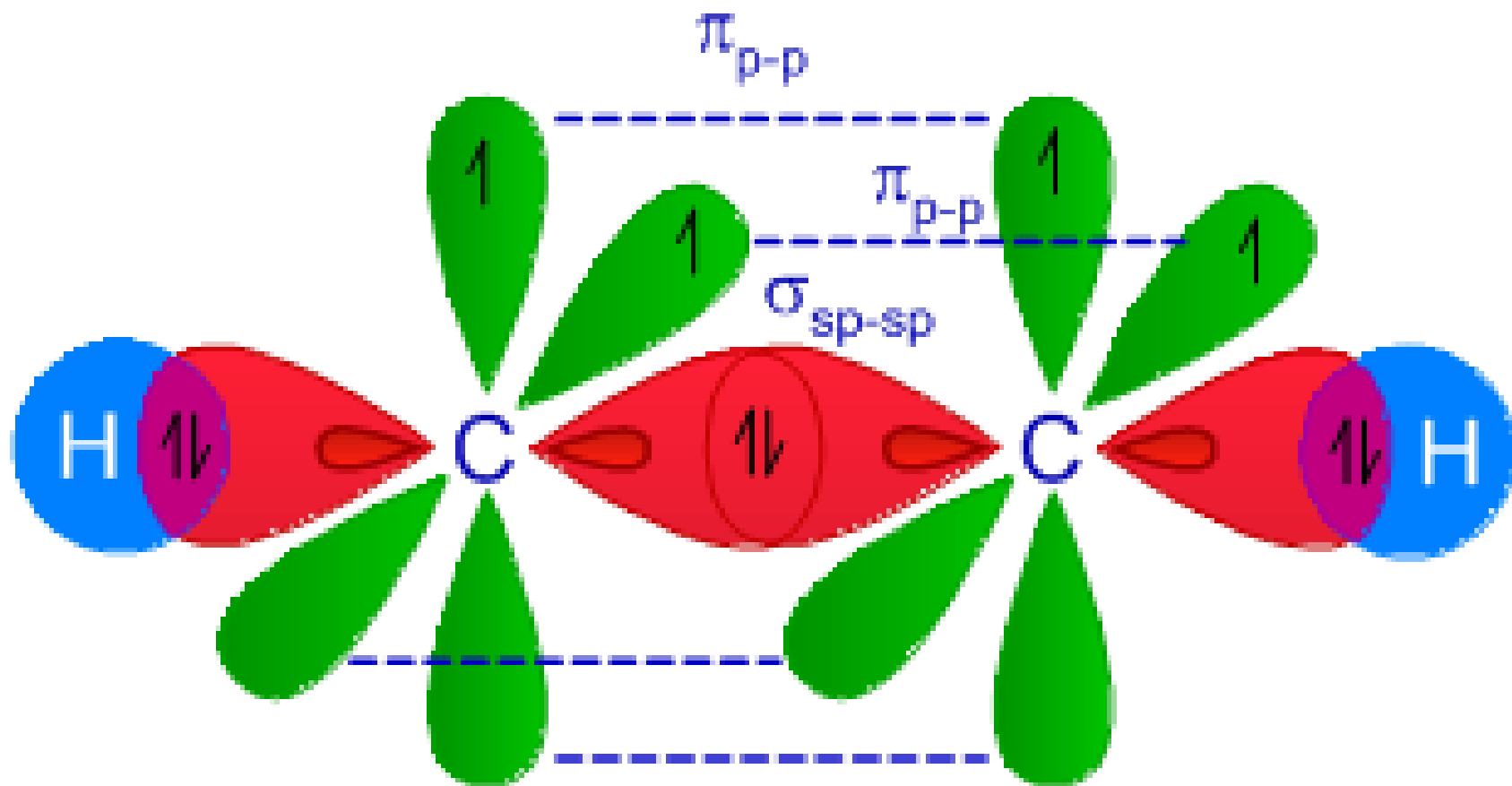
Electronic configuration of C in excited state.



sp hybridization in C

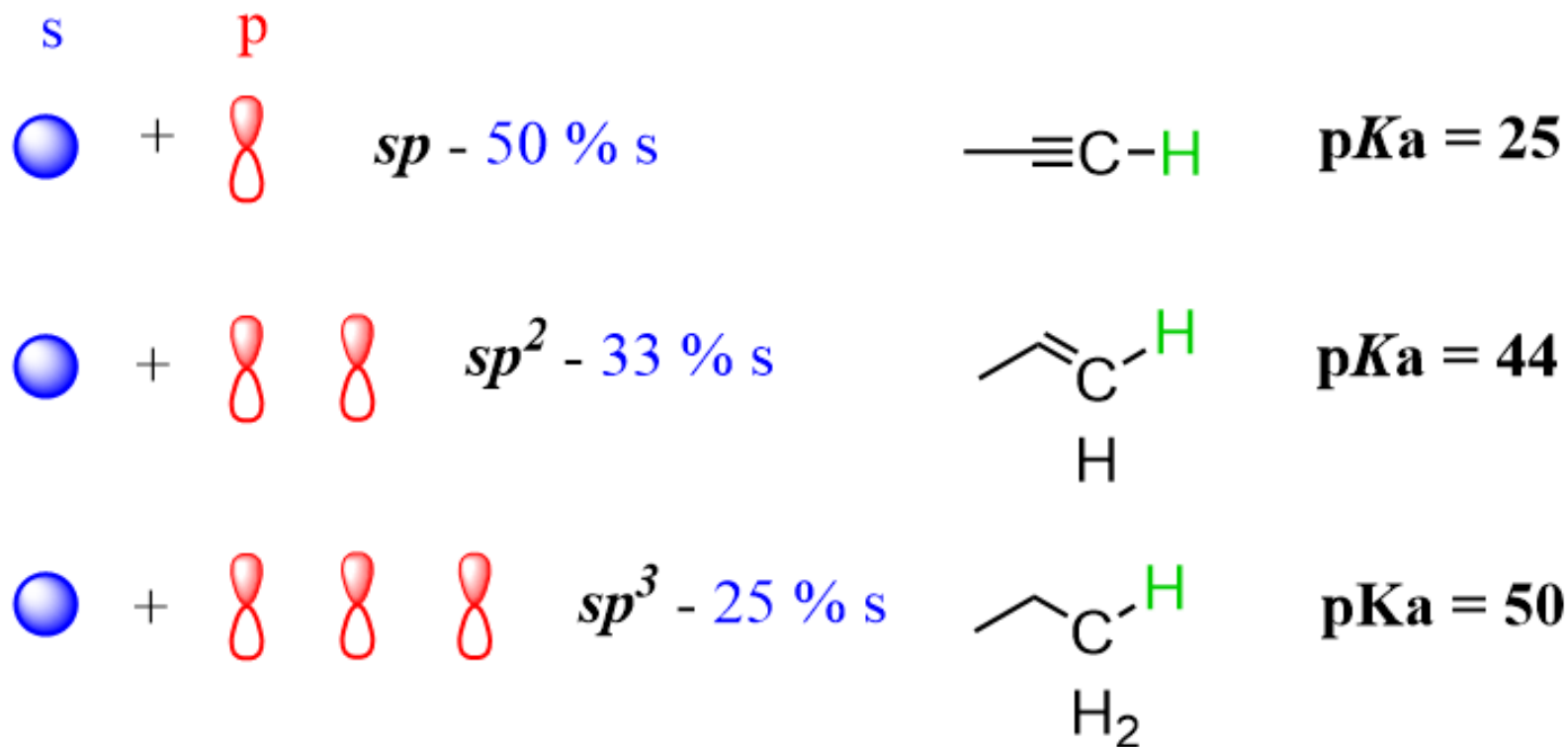


two sp hybridized orbitals      two unhybridized orbitals



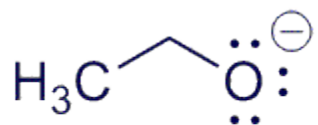
# Hybridization Effect on the Acidity of Hydrocarbons

More % s - stronger acid

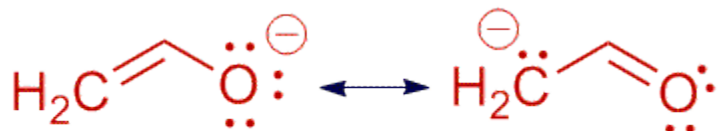


## Localized and delocalized Bond:

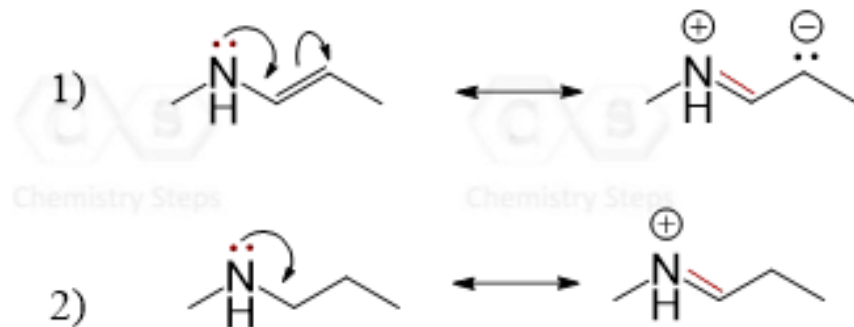
A localized bond pair travels between two atoms. A bond pair that moves between two different pairs of atoms is considered delocalized. You can identify delocalized bonds by checking the electron locations in two different resonance forms; if the pair changes location and form, it is delocalized.

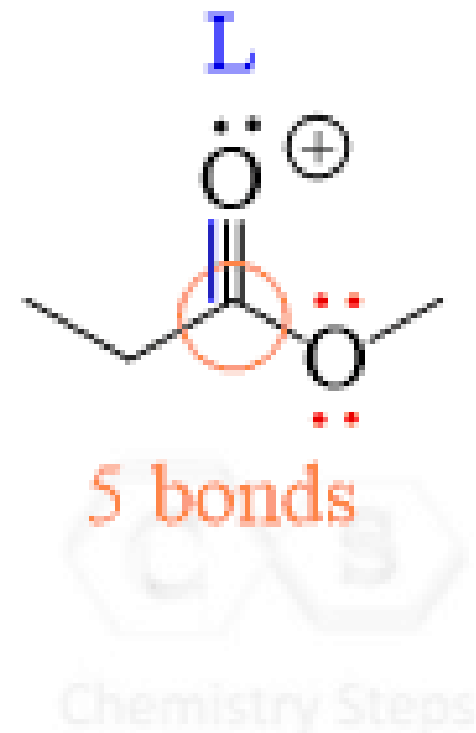
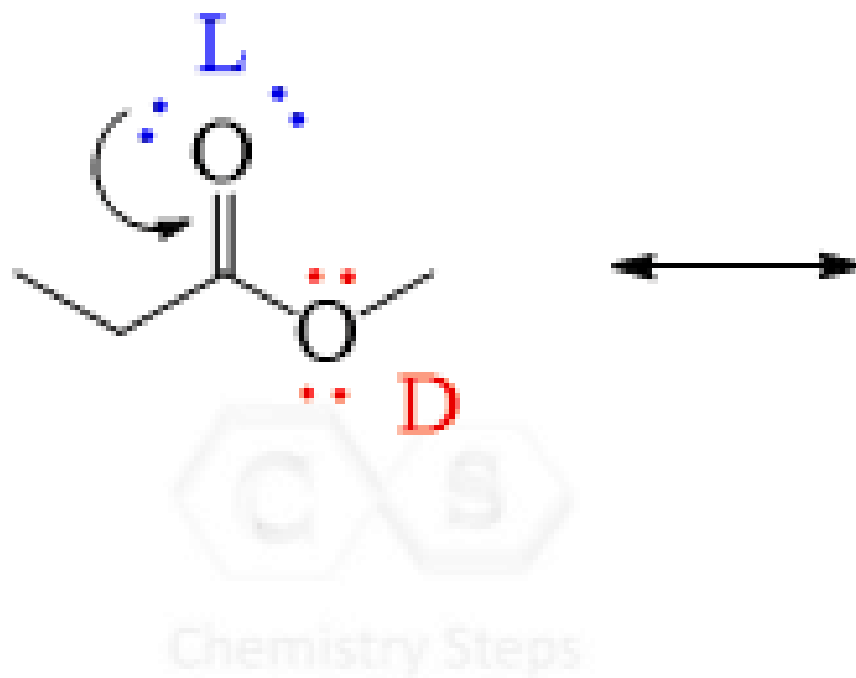
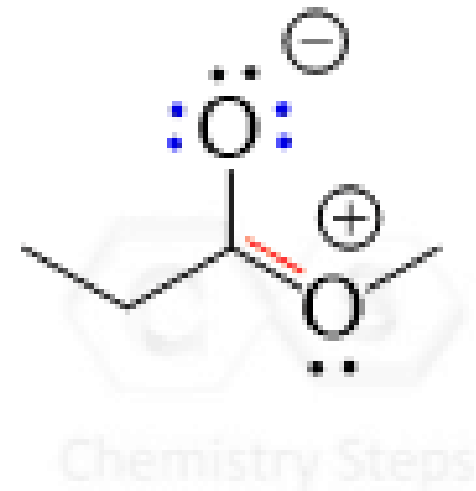
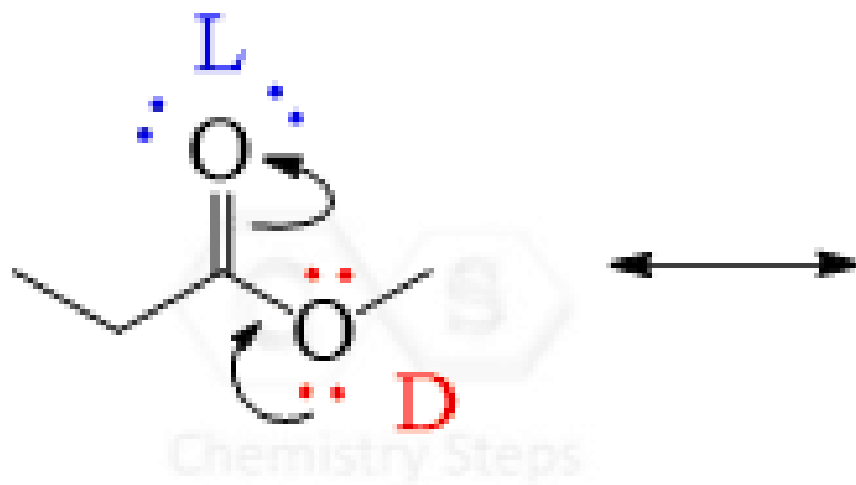


*localized*



*delocalized*

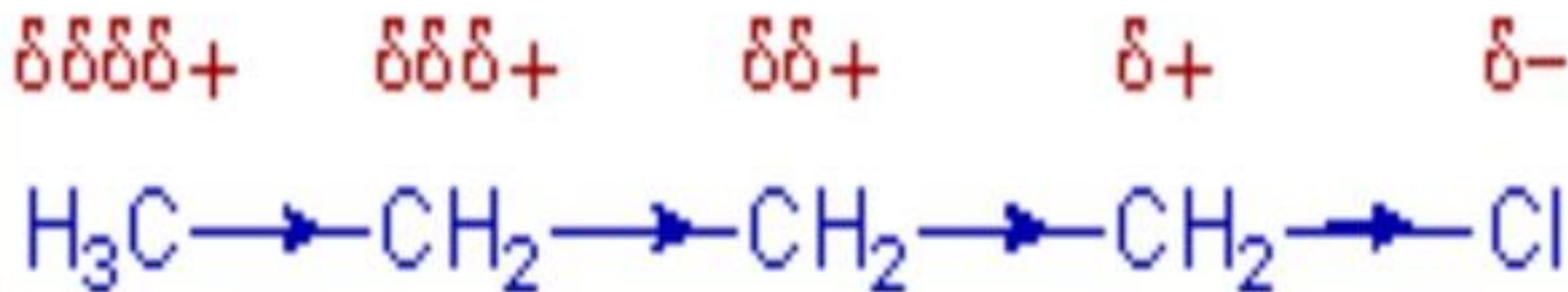






## INDUCTIVE EFFECT

*The polarization of a  $\sigma$  bond due to electron withdrawing or electron donating effect of adjacent groups or atoms is called inductive effect.*



# INDUCTIVE EFFECT

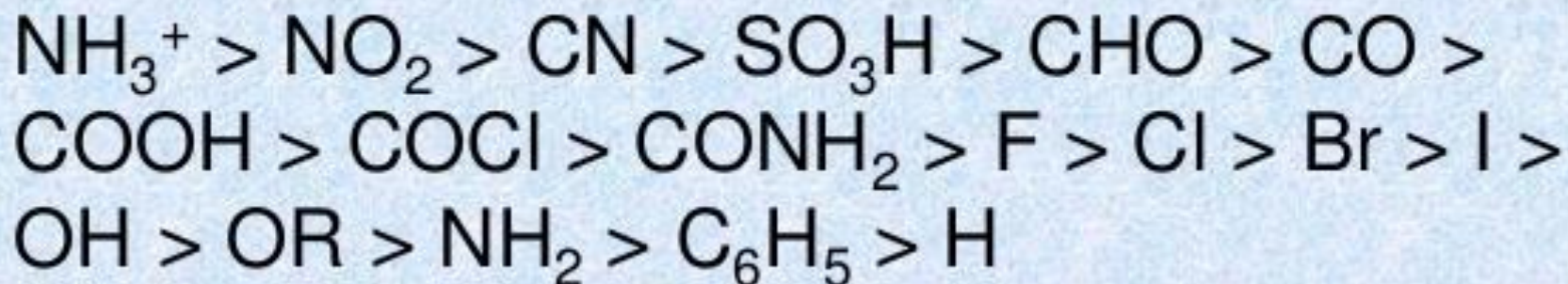


- In turn Carbon-1 draws some Positive charge ( $\delta^+$ ) towards it from the adjacent C-C bond .
- In this way the polar C-Cl bond induces polarity in the adjacent bond.
- Such polarization of  $\sigma$ -bond caused by the polarisation of the adjacent  $\sigma$ -bond is called **Inductive Effect**.
- This effect is passed on to the subsequent bonds also but the effect decreases rapidly as the no.of intervening bonds increases.

## TYPES OF INDUCTIVE EFFECT

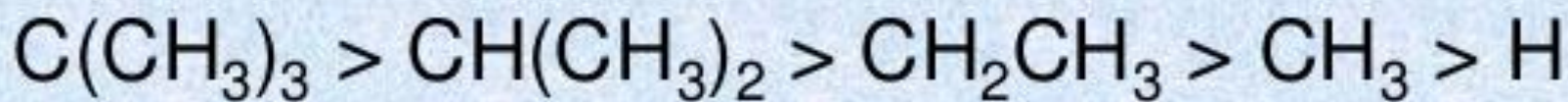
### 1) Negative inductive effect (-I):

The electron withdrawing nature of groups or atoms is called as negative inductive effect. It is indicated by -I. Following are the examples of groups in the decreasing order of their -I effect:

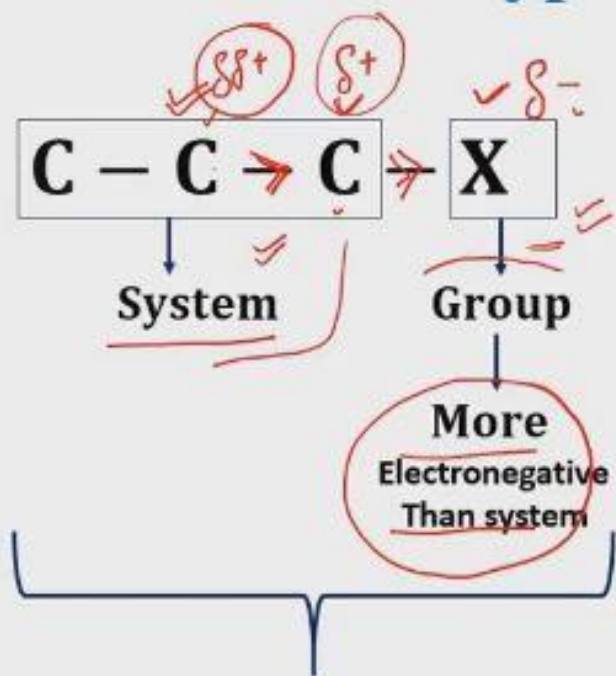


## 2) Positive inductive effect (+I):

It refers to the electron releasing nature of the groups or atoms and is denoted by +I. Following are the examples of groups in the decreasing order of their +I effect.

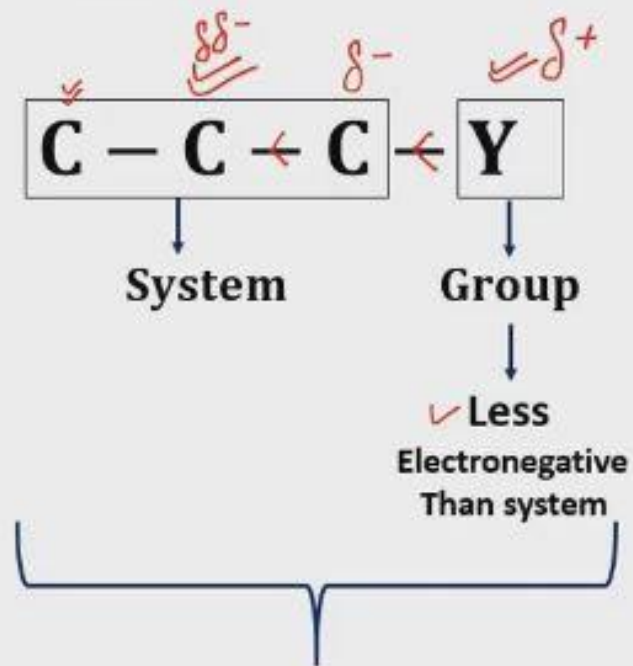


# Types of Inductive Effect



-I effect

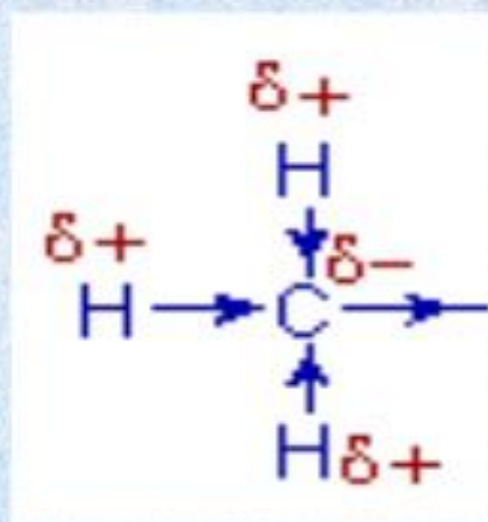
"X" is called -I effecting group



+I effect

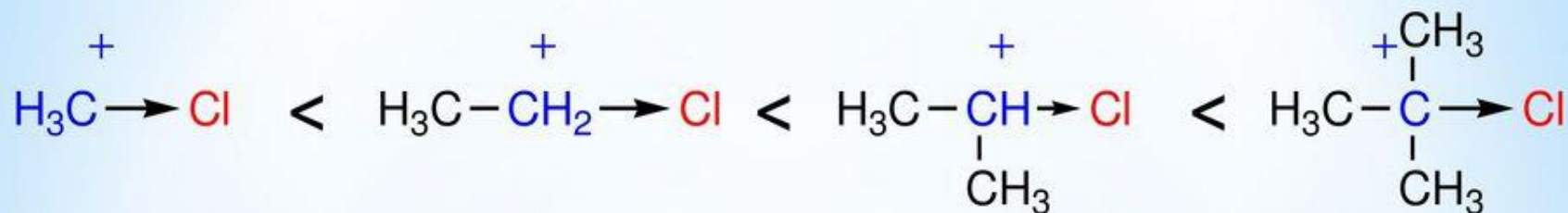
"Y" is called +I effecting group

- **Why alkyl groups are showing positive inductive effect?**
- Though the C-H bond is practically considered as non-polar, there is partial positive charge on hydrogen atom and partial negative charge on carbon atom. Therefore each hydrogen atom acts as electron donating group. This cumulative donation turns the alkyl moiety into an electron donating group.



# Distribution of electron density

## Positive inductive effect:

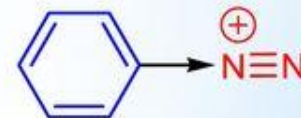
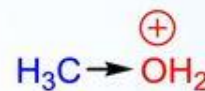
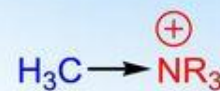
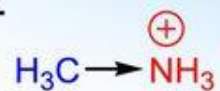
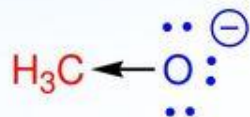
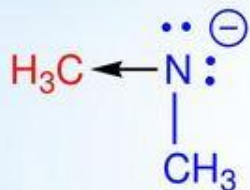
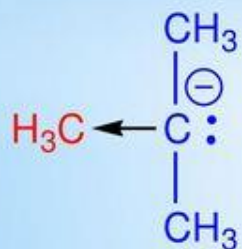


**+|**



**electron-donating groups**

charged groups:

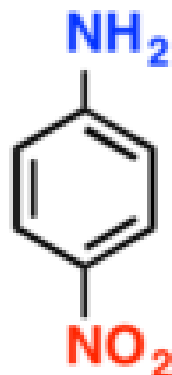


**+|**

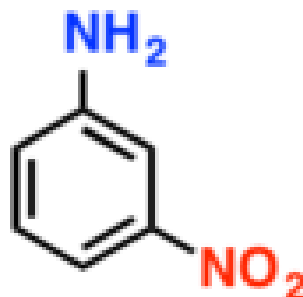
**very strong!**

**-|**

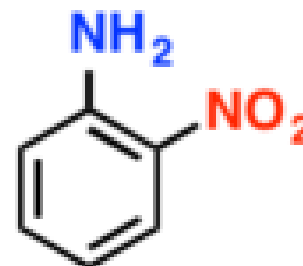
A puzzle: Why is *m*-nitroaniline more basic than *p*-nitroaniline, even though the  $\text{NO}_2$  group is closer to the amine?



*p*-nitroaniline



*m*-nitroaniline



*o*-nitroaniline

$\text{pK}_a\text{H}$

1.0

2.46

-0.26

most basic of the  
three amines pictured

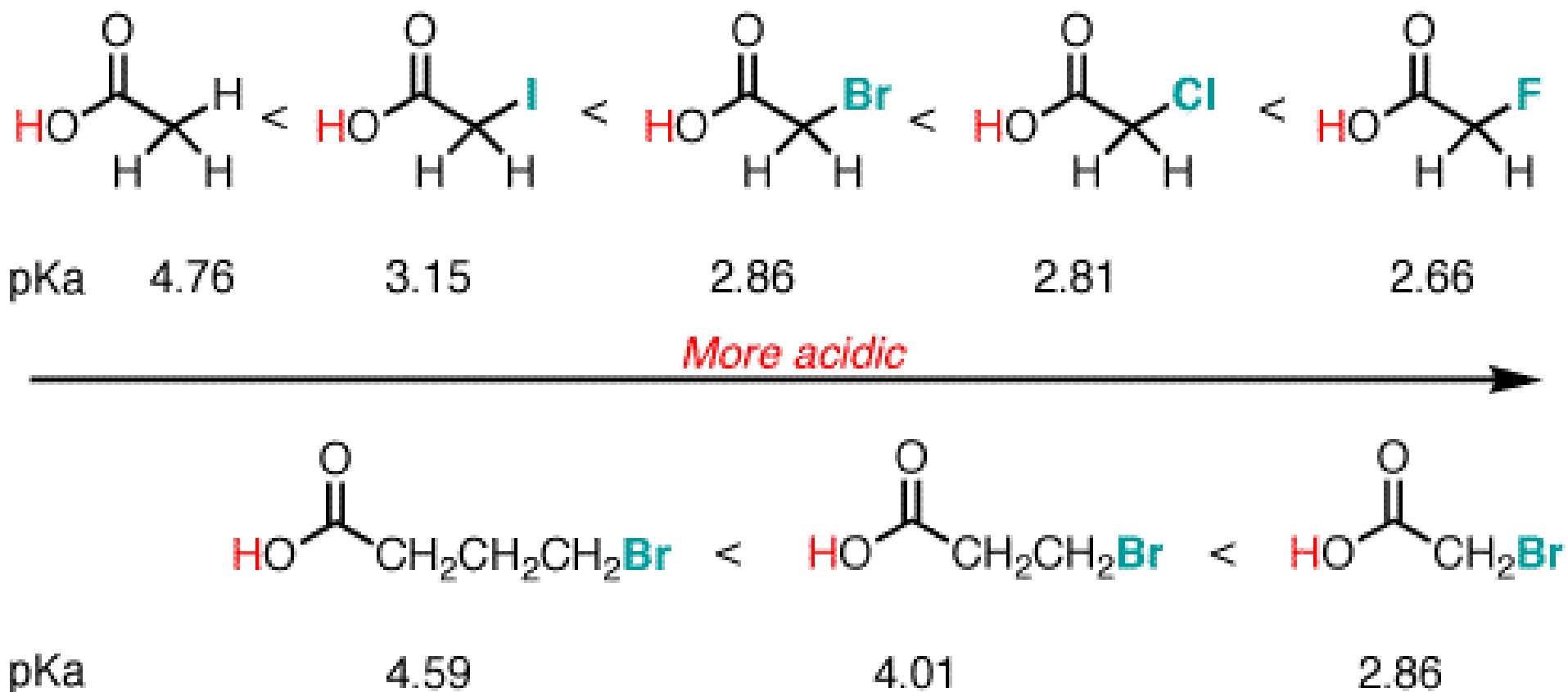
Inductive effects alone can't explain this!



#### 4. Electronegativity and inductive effects:

Two principles - electron-withdrawing substituents can increase acidity of a nearby atom, which **increases with electronegativity** and **decreases with increasing distance to the atom**.

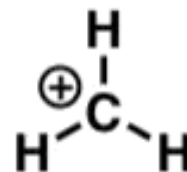
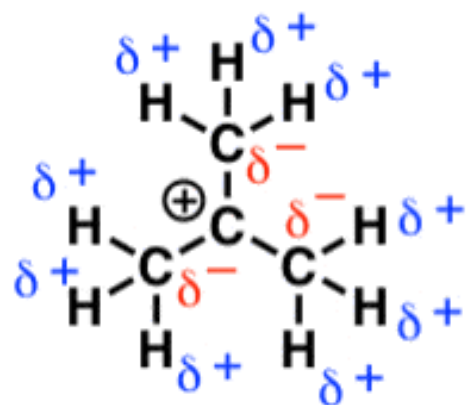
Electronegativity increases in the order  $F > Cl > Br > I$ :



## Factors That Destabilize Carbocations (1): Decreasing Alkyl Substitution

Carbocations are destabilized as alkyl groups are replaced by hydrogen

*The "inductive effect" explanation*



*Carbons are slightly electron rich and can donate these electrons to the carbocation*

*Each alkyl group added to a carbocation will increase stability*

Electronegativity of C = 2.5  
Electronegativity of H = 2.2

Hydrogens do not have excess electron density to donate

*Adjacent hydrogens do not stabilize carbocations*

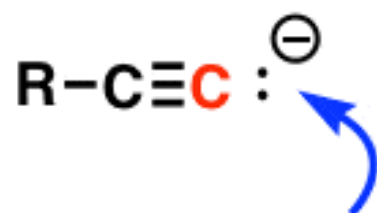
## Review: Alkynes are Unusually Acidic



pKa = 25

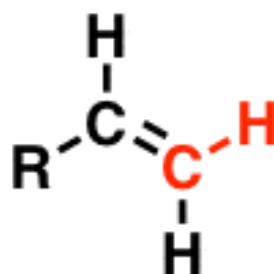
**Most acidic**

*Conjugate base:*

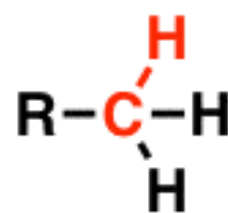


*sp*-hybridized

(50% s-character,  
more closely held to  
nucleus, more stable)



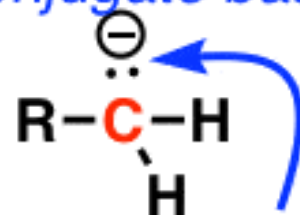
pKa = 42



pKa = 50

**Least acidic**

*Conjugate base:*



*sp*<sup>3</sup> hybridized

(25% s-character,  
less closely held to  
nucleus, less stable)

## Dipole Moment:

A dipole moment arises in any system in which there is a separation of charge. They can, therefore, arise in ionic bonds as well as in covalent bonds. Dipole moments occur due to the difference in electronegativity between two chemically bonded atoms.

A bond dipole moment is a measure of the polarity of a chemical bond between two atoms in a molecule. It involves the concept of electric dipole moment, which is a measure of the separation of negative and positive charges in a system. The bond dipole moment is a vector quantity since it has both magnitude and direction. An illustration describing the dipole moment that arises in an HCl ([hydrochloric acid](#)) molecule is provided below.

## Dipole Moment:



Dipole Moment has a **Magnitude** and a **Direction**

It can be noted that the symbols  $\delta^+$  and  $\delta^-$  represent the two electric charges that arise in a molecule which are equal in magnitude but are of opposite signs. They are separated by a set distance, which is commonly denoted by 'd'.

## Dipole Moment: Important Points

- The dipole moment of a single bond in a polyatomic molecule is known as the bond dipole moment and it is different from the dipole moment of the molecule as a whole.
- It is a vector quantity, i.e. it has magnitude as well as definite directions.
- Being a vector quantity, it can also be zero as the two oppositely acting bond dipoles can cancel each other.
- By convention, it is denoted by a small arrow with its tail on the negative center and its head on the positive center.
- In chemistry, the dipole moment is represented by a slight variation of the arrow symbol. It is denoted by a cross on the positive center and arrowhead on the negative center. This arrow symbolizes the shift of electron density in the molecule.
- In the case of a polyatomic molecule, the dipole moment of the molecule is the vector sum of the all present bond dipoles in the molecule.

## Dipole Moment Formula

A dipole moment is the product of the magnitude of the charge and the distance between the centers of the positive and negative charges. It is denoted by the Greek letter 'μ'.

Mathematically,

$$\text{Dipole Moment } (\mu) = \text{Charge (Q)} * \text{distance of separation (r)}$$

It is measured in Debye units denoted by 'D'.  $1 \text{ D} = 3.33564 \times 10^{-30} \text{ C.m}$ , where C is Coulomb and m denotes a meter.

The bond dipole moment that arises in a chemical bond between two atoms of different electronegativities can be expressed as follows:

$$\mu = \delta \cdot d$$

Where:  $\mu$  is the bond dipole moment,

$\delta$  is the magnitude of the partial charges  $\delta+$  and  $\delta-$ ,

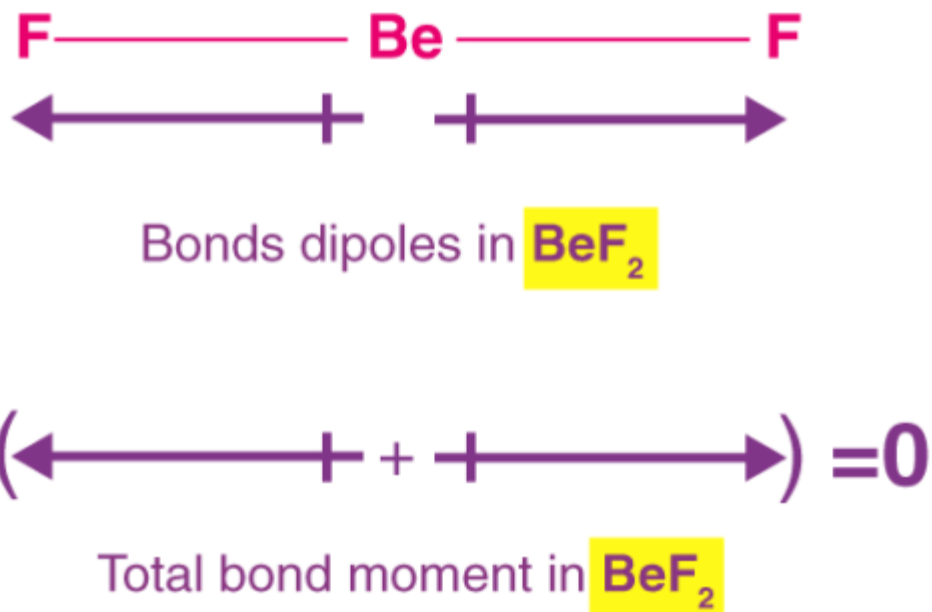
And  $d$  is the distance between  $\delta+$  and  $\delta-$ .

## Examples

### Dipole moment of $\text{BeF}_2$

In a beryllium fluoride molecule, the bond angle between the two beryllium-fluorine bonds is  $180^\circ$ . Fluorine, being the more electronegative atom, shifts the electron density towards itself. The individual bond dipole moments in a  $\text{BeF}_2$  molecule are illustrated below.

It can be understood that the two individual bond dipole moments cancel each other out in a  $\text{BeF}_2$  molecule because they are equal in magnitude but are opposite in direction. Therefore, the net dipole moment of a  $\text{BeF}_2$  molecule is zero.

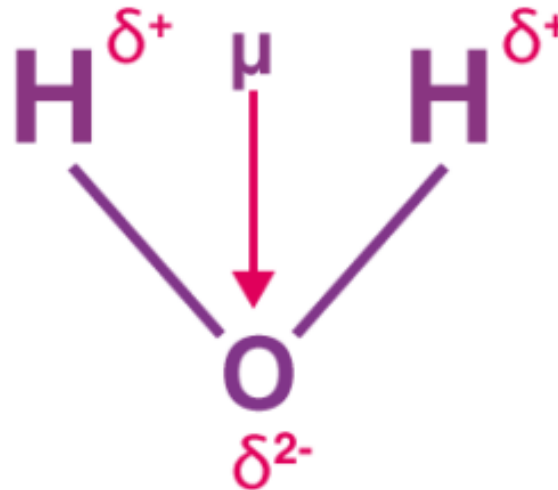




## Dipole moment of H<sub>2</sub>O (Water)

In a water molecule, the electrons are localized around the oxygen atom since it is much more electronegative than the hydrogen atom. However, the presence of a lone pair of electrons in the oxygen atom causes the water molecule to have a bent shape (as per the [VSEPR theory](#)). Therefore, the individual bond dipole moments do not cancel each other out as is the case in the BeF<sub>2</sub> molecule. An illustration describing the dipole moment in a water molecule is provided below.

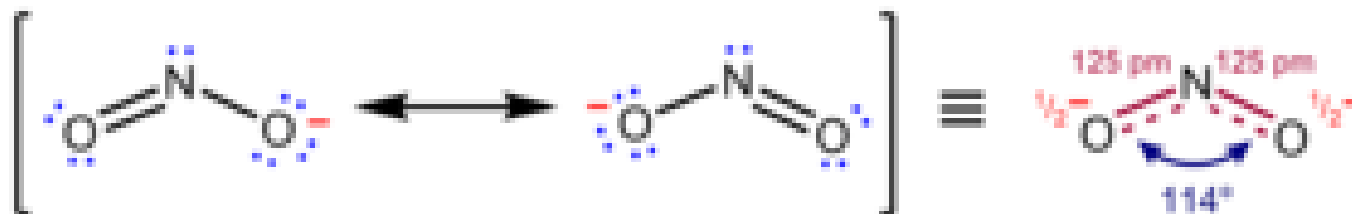
The bond angle in a water molecule is 104.5°. The individual bond moment of an oxygen-hydrogen bond is 1.5 D. The net dipole moment in a water molecule is found to be 1.84D.



## Resonance

**Resonance** is a way of describing bonding in certain molecules or ions by the combination of several **contributing structures** (or *forms*, also known as *resonance structures* or *canonical structures*) into a **resonance hybrid** (or *hybrid structure*) in valence bond theory. It has particular value for describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by one single Lewis structure.

For instance, in  $\text{NO}_2^-$ , [nitrite](#) anion, the two N–O bond lengths are equal, even though no single Lewis structure has two N–O bonds with the same formal [bond order](#).



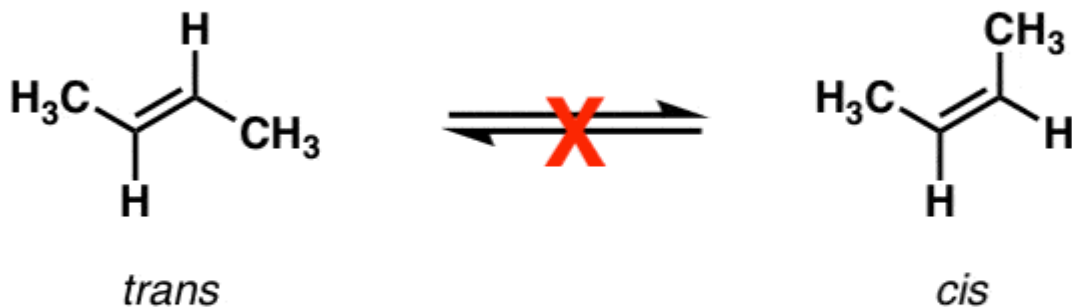
The experimental geometry of the nitrite anion,  $\text{NO}_2^-$ , shown on the right, is best rationalized by describing its structure as a resonance hybrid consisting of two major and equally important contributing forms.

## Revisiting the Pi Bond (and Pi bonding): “Side-On” Orbital Overlap Between Adjacent p-Orbitals

Rotation about the C-C pi ( $\pi$ ) bond does not occur.

For instance, at normal temperatures and pressures., *trans*-2-butene (shown below left) is never observed to spontaneously convert to *cis*-2-butene (right). They're separable compounds, with different melting and boiling points. This wouldn't be possible if there was free rotation about the double bond.

**Free Rotation About Double Bonds (pi bonds) Does Not Happen**

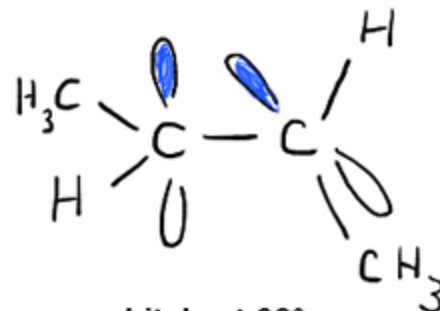


*Why not?* Rotation would disrupt overlap between the two p-orbitals  
(strength of C–C  $\pi$  bond: about 60 kcal/mol)

“pi bonding” – a **side-on overlap of two adjacent p orbitals**, each containing an electron, which results in a preferred orientation where the p-orbitals “line up” next to each other, like soldiers. Due to the dumbbell-like geometry of the p-orbital, overlap isn’t possible when the two p-orbitals are at 90° to each other, which accounts for that “rotational barrier”.



**p-orbitals in same plane  
(overlap possible)**



**p-orbitals at 90°  
(no overlap possible)**

*[The shaded (blue) and unshaded (white) lobes of each p-orbital represents a property called “phase”, which is a property of p-orbitals. As in waves, there is constructive interference between lobes of “like” phase, and destructive interference between lobes of “unlike” phase]*

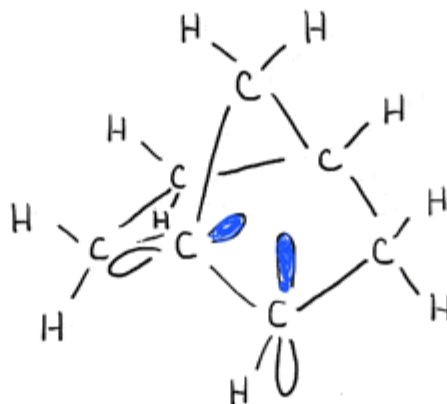
[Bredt](#) observed in 1924 that alkenes tend not to form on “bridgehead” positions, such as in the molecule at bottom left, an observation that came to be called “[Bredt’s rule](#)”.

### "Bridgehead" alkenes - a case where orbital overlap cannot occur



Depiction of a "bridgehead" alkene

(too unstable to be isolated)



Note how p-orbitals are not aligned properly in order for a pi bond to form - they are at 90° to each other

*Resembles a di-radical, not an alkene (very unstable!)*

The geometry of the bicyclic ring forces those p orbitals to be oriented at right angles. **There’s no overlap between the p orbitals.** Therefore, it resembles a carbon with two adjacent [radicals](#) more than it does a real pi bond!

## Beyond Pi Bonds: “Conjugation” Of 3 Or More p Orbitals

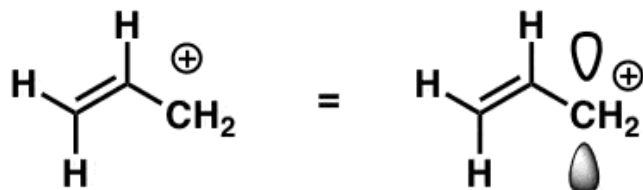
Overlap can extend beyond two p orbitals to include **three, four, five, and even more consecutive p orbitals on consecutive atoms**, building larger “pi-systems” (witness [lycopene](#), for instance).

We also see that definition of “p orbital” is somewhat flexible, and can include examples such as

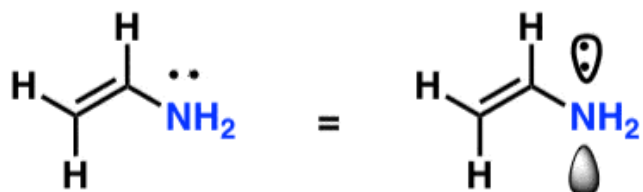
- An empty p orbital (such as that in a carbocation, or the empty p orbital on boron)
- An orbital containing a lone pair (e.g. on nitrogen, oxygen, fluorine, etc.)
- p-orbitals of a pi bond [such as another alkene, C=O (carbonyl), etc.]
- A half-filled orbital (e.g. a radical)

We call this “building up” of p orbitals into larger “pi systems”, “**conjugation**”. In each of the middle molecules below, the alkene (pi bond) is conjugated with an adjacent p orbital.

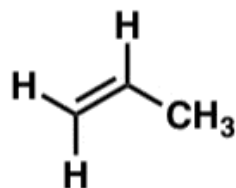
## 4 Examples of Conjugation



1. Conjugation with empty p-orbital (of carbocation)

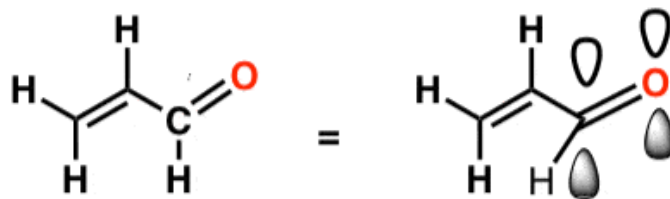


2. Conjugation with lone pair (on nitrogen)

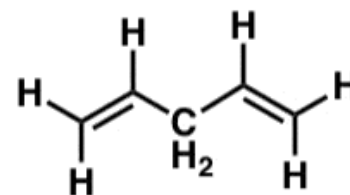


No conjugation

(CH<sub>3</sub> has no available orbitals to overlap with p orbitals of pi bond)

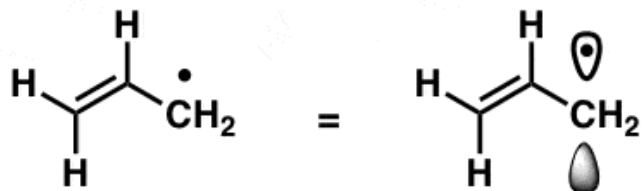


3. Conjugation with another pi bond



Also no conjugation

(CH<sub>2</sub> has no available orbitals to overlap with p orbitals of pi bond)



4. Conjugation with a radical

The “conjugation killer” to watch out for is an atom lacking lone pairs connected to only single bonds, such as CH<sub>2</sub> in the example below-right (1,4-pentadiene). These two pi bonds are **not** conjugated.

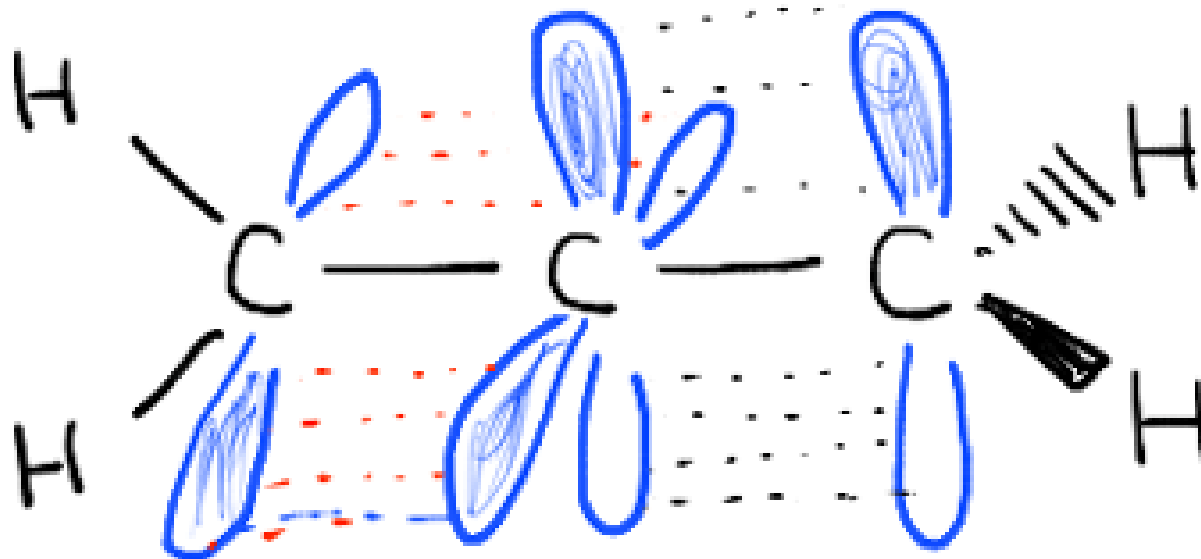
We usually think of the geometry of a nitrogen with three single bonds as [trigonal pyramidal](#) (e.g. as in NH<sub>3</sub>). But in the presence of an adjacent pi bond, there is a slight “re-hybridization” of the nitrogen from sp<sup>3</sup> to sp<sup>2</sup> ([trigonal planar](#)) such that the lone pair is in a p orbital, not an sp<sup>3</sup> orbital. This is a tradeoff: the slightly increased strain of the eclipsed N-H bonds is made up for by a decrease in *overall* energy due to better overlap of a p orbital with the pi bond. We usually think of this as “[resonance energy](#)“.]

Here’s a fun trick question. Are the the double bonds in the molecule below (**allene**) conjugated? Why or why not?





The pi bonds are *not* conjugated. Look at the orbitals comprising the two pi bonds. They are at right angles to each other and cannot overlap.



## The Distinction Between Conjugation And Resonance

- **Conjugation** is what we call it when 3 or more p orbitals **join together** into a larger “pi system”.
- These conjugated pi systems contain electrons, which we often call “pi electrons” to distinguish them from the electrons that comprise single bonds in the molecule.
- The different arrangements of electrons within that “pi system” are called **resonance forms**.

A rough analogy could go like this:

- Think of p orbitals as being a bit like “rooms” for electrons (maximum occupancy:2)
- Joining several rooms together into a larger building is conjugation
- The different allowable *arrangements of people (electrons) within that building* are **resonance forms**.

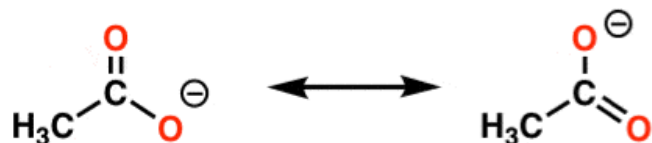
The key requirement for conjugation is *orbital overlap*, which we'll expand on in a bit.

# Consequences of Conjugation (1): Bond Lengths

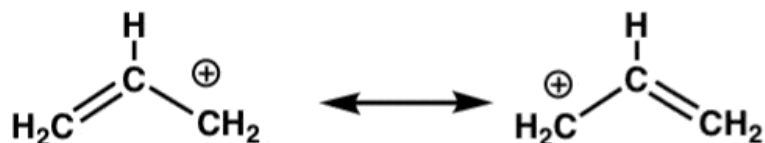
## Consequences of Conjugation (Resonance): Bond Lengths

Equal resonance forms:

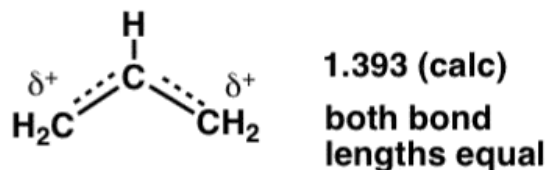
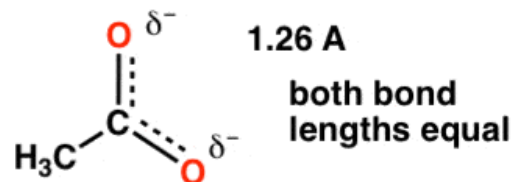
*Acetate ion*



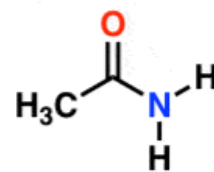
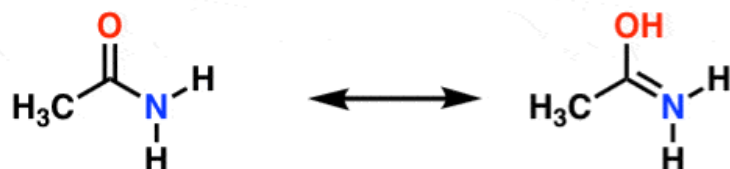
*Allyl cation*



**Actual structure**  
(from X-ray crystallography)

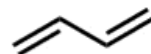
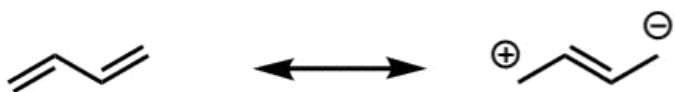


Unequal resonance forms: minor contributor can still have influence on structure



shorter than  
a normal C-N bond

longer than a  
normal C=O bond



shorter than  
a normal C-C bond

The important point to note is that the pi-electrons in these are not constantly switching back-and-forth between atoms; rather, **the “true” structure of the molecule is a hybrid of these resonance forms.**

One important consequence of resonance is **bond lengths that are intermediate between two forms.**

For example, the C-O bond length in the acetate ion (1.26 Å) is **between what we’d expect for a C-O pi bond (1.20 Å) and a C-O single bond (1.4 Å).**

## When Resonance Forms Are Not Identical, The Resonance Hybrid Will Be A “Weighted” Hybrid Of The Most Important Resonance Forms

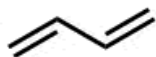
In the acetate ion and the allyl cation the two important resonance forms are **equivalent**, so both end up contributing equally to the hybrid.

A more common situation is found molecules like the ones below there's a blending of unequal resonance forms. Some resonance forms are more important than others.

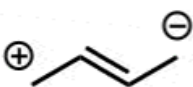
### Unequal resonance forms

The minor resonance contributor can still have influence on structure

Butadiene



Major contributor



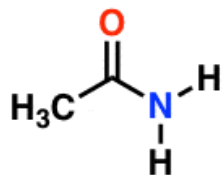
Minor contributor



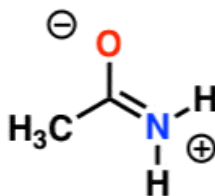
1.48 Å

shorter than  
a normal C-C bond  
(1.51 Å)

Acetamide



Major contributor



Minor contributor



1.26 Å

longer than a  
normal C=O bond  
(1.20 Å)

1.33 Å

shorter than  
a normal C-N bond (1.47 Å)

Our visual language of chemistry with its sharp distinction between single and double bonds does not accurately depict the electron density in the molecules, which are a **weighted hybrid** of resonance forms. Minor resonance contributors influence the bond lengths in the molecule, making them shorter or longer than normal.

In the top molecule (butadiene), that central C-C bond is a little bit **shorter** than a “normal” C-C single bond (i.e. it has a bit of double bond character) due to the influence of the minor resonance contributor to the hybrid. *[Note that the bond length is not halfway between single and double C-C bond, as it was in the allyl cation: that’s because the two resonance forms are not equally important (i.e. do not make equal contributions to the resonance hybrid)]*

In the bottom molecule (“acetamide”) the C-O bond is a little bit **longer** than a “normal” C=O bond (i.e. has more single-bond character) and the C-N bond is a little bit **shorter** than a “normal” C-N bond (i.e. has more double-bond character). This reflects the influence of the “minor contributor” (or “second best” contributor, if you like) in which there is a C-N pi bond and a C-O single bond.

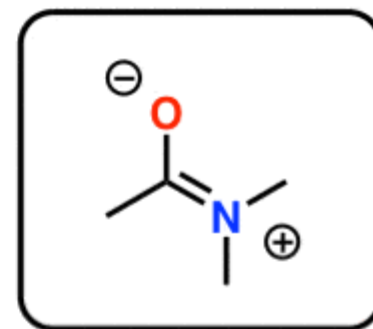
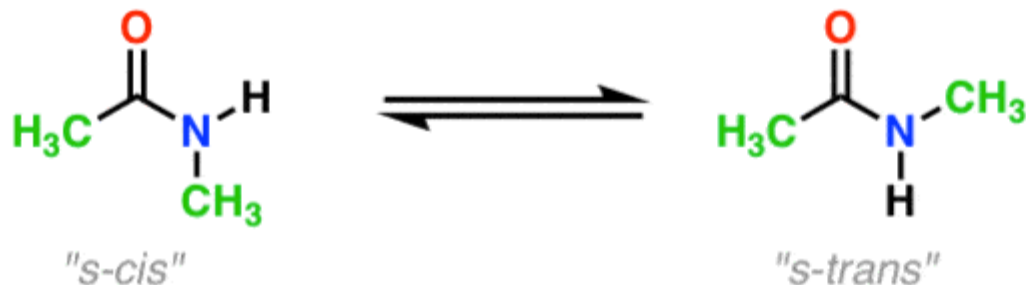
## Consequences Of Conjugation (2): “Partial” Double Bonds

There's an interesting consequence of that “partial double bond character” in the C-N bond. **It has a “barrier to rotation” just like we'd expect from a “double bond”!** The barrier to rotation in the C-N bond of amides is about 15-20 kcal/mol in peptide bonds (compare to about 2-3 kcal/mol for most C-C bonds).

What this means is that the two conformations can still interconvert, but they do so relatively slowly at room temperature. In the molecule below (*N*-methyl acetamide) it's possible to observe the *s*-cis conformer (both green methyl groups on the same side of the C-N bond) and the *s*-trans conformer (green methyl groups on opposite sides of the C-N bond) separately. [\[note\]](#) This usually isn't possible for conformers unless you take the temperature down to 100 Kelvin or so!

A consequence of "partial double bond" character: restricted rotation!

Amides: Interconversion of conformers is slow due to the significant double-bond character of C-N bond



"cis" arrangement of  $\text{CH}_3$  across the the C-N bond (sometimes called "s-cis" since this is a sigma bond)

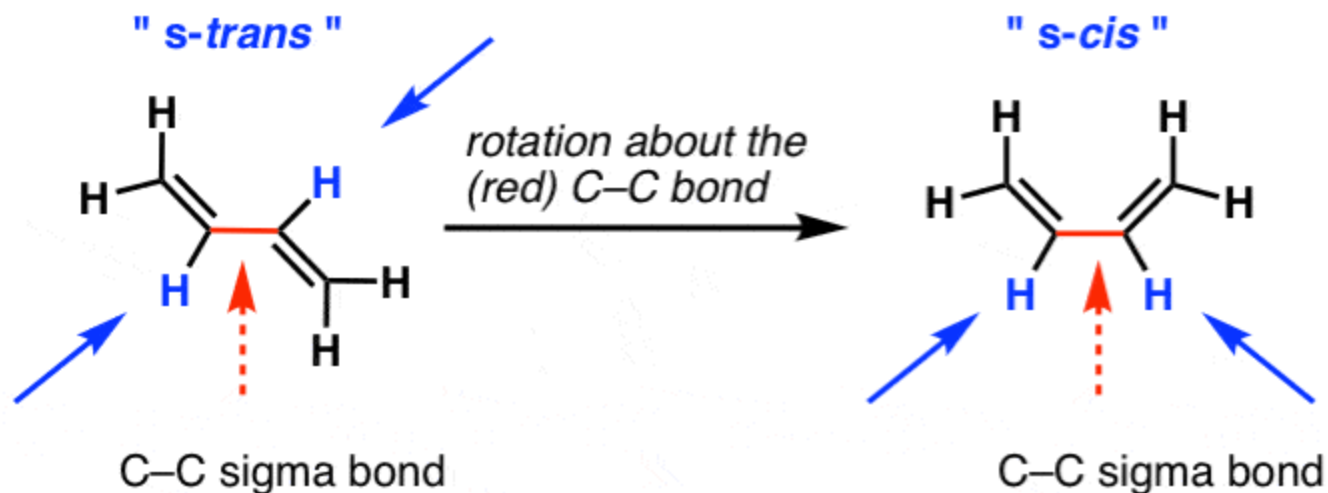
"trans" arrangement of  $\text{CH}_3$  across the C-N bond (sometimes called "s-trans" since this is a sigma bond)

**Consequence: The significant contribution of the resonance form with the C=N bond leads to a barrier to rotation of about 15-20 kcal/mol**

s-cis is when the double bonds are cis in reference to the single bond and s-trans is when the two double bonds are trans in reference to the single bond. The cis conformation is less stable due to the steric interaction of hydrogens on carbon.



## "s-trans" and "s-cis" conformations of a diene

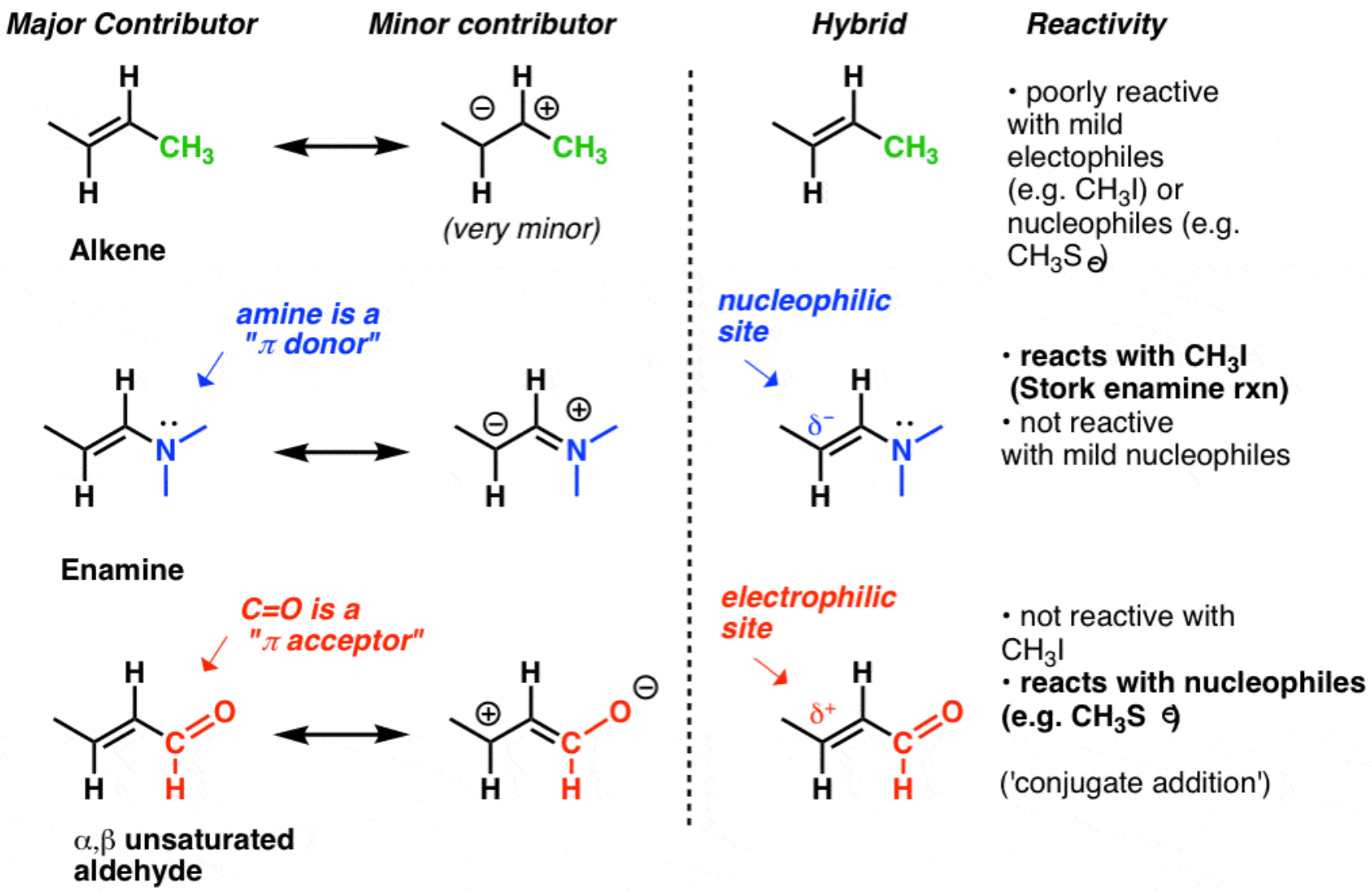


Notice that the two hydrogens are on the **opposite side ("trans")** of the (red) C-C sigma bond

Notice that the two hydrogens are on the **same side ("cis")** of the (red) C-C sigma bond

# Consequences of Conjugation (3): The Reactivity Of A Conjugated System Is Often Revealed By Its "Second-Best" Resonance Form

## Consequences of Conjugation (2) - Effect on Reactivity



*amine is a "π donor"*

*nucleophilic site*

*C=O is a "π acceptor"*

*electrophilic site*

Look at the “second best” resonance form when we attach a [pi-donor](#) such as  $\text{N}(\text{CH}_3)_2$  to an alkene. This results in a build-up of negative charge ( $\delta^-$ ) on terminal carbon of the alkene, with the result that this alkene (which we call an [enamine](#)) is an excellent nucleophile. To take just one prominent example, enamines react with alkyl halides (such as  $\text{CH}_3\text{I}$ ) and other electrophiles in a class of reactions sometimes referred to as [Stork Enamine](#) reactions after their discoverer, [Gilbert Stork](#). Ordinary alkenes such as 2-butene (below) don't work in this reaction.

Attachment of a [pi-acceptor](#) such as  $\text{C}=\text{O}$  results in a build-up of positive charge ( $\delta^+$ ) on the terminal carbon of the alkene, with the result that this species (which we call an  $\alpha, \beta$  unsaturated aldehyde, Michael acceptor, or enone) is an excellent electrophile.  $\alpha, \beta$  unsaturated carbonyls react with nucleophiles (such as  $\text{CH}_3\text{S}^-$ ) and many other classes of nucleophiles in a general type of reaction we call [conjugate additions](#) or sometimes Michael reactions.

## Orbital Overlap (All p-Orbitals In The Same Plane) Is Required For Conjugation (And Resonance)

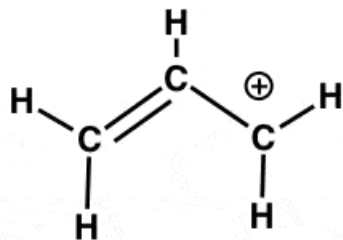
So far we've seen that:

- overlap between p orbitals is necessary to form pi bonds
- some "single bonds" can have "pi bond character" due to contribution from a minor resonance form (such as amides, for example)

Here is the logical consequence of these two statements:

- **In order for conjugation to exist, and therefore in order for resonance to occur, all the p orbitals must overlap. They must therefore all be aligned in the same plane.**
- Remember the "allyl cation" that is "stabilized by resonance"? In order for the carbocation to gain this "resonance stabilization", the empty p orbital on the carbocation **must** be lined up with the adjacent pi bond.
- If the p orbital is at an angle of 90 degrees from the p orbitals in the pi bond, there is no conjugation and thus no resonance stabilization.

Recall that the "allyl cation" is more stable than a normal carbocation.

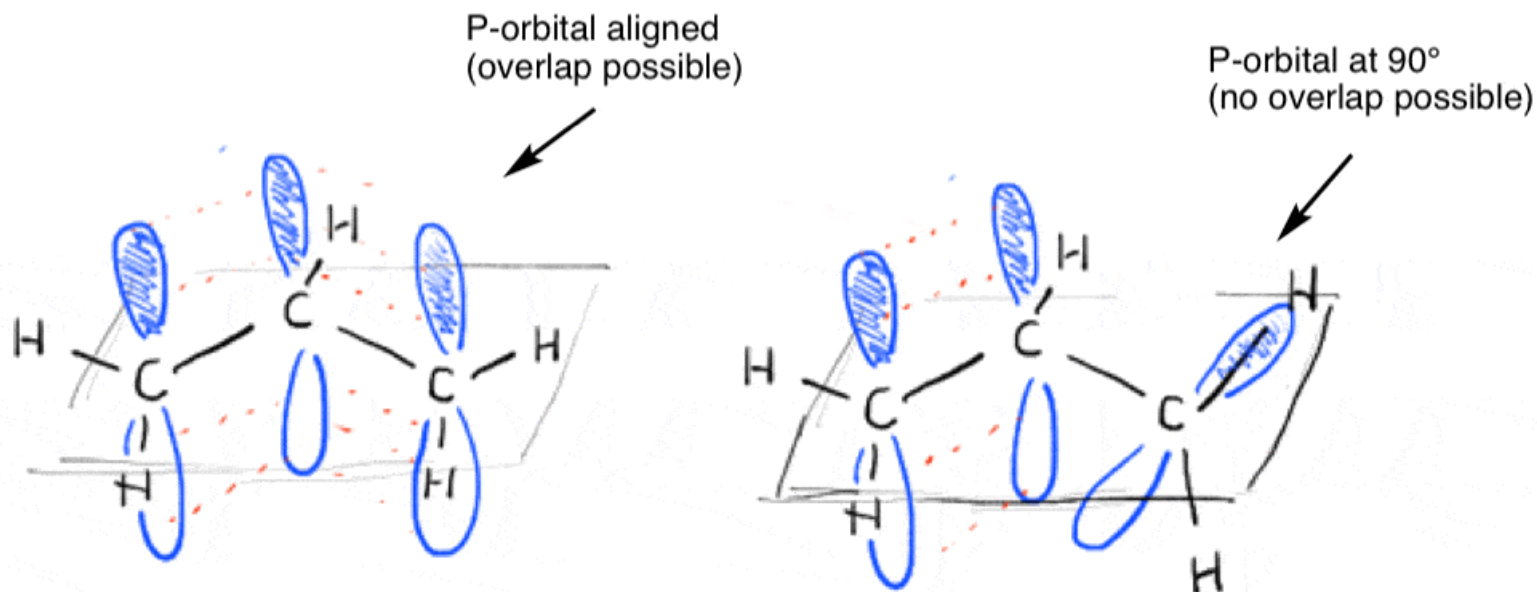


carbocation is "stabilized by resonance"; positive charge can be delocalized over multiple carbons

an equivalent way of looking at it: the empty p-orbital of the carbocation is in conjugation with the pi bond

**But "resonance stabilization" (i.e. conjugation) can only occur if the p orbitals overlap!**

If one of the CH<sub>2</sub> groups is rotated such that the empty p orbital is no longer aligned with the other two p orbitals, orbital overlap can no longer occur

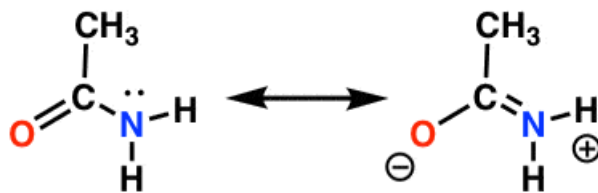


**Consequence: There is a "barrier to rotation" in the allyl cation of about 37 kcal/mol**

We also saw that the C-N bond in amides has partial double bond character, with a barrier to rotation of about 15-20 kcal/mol.

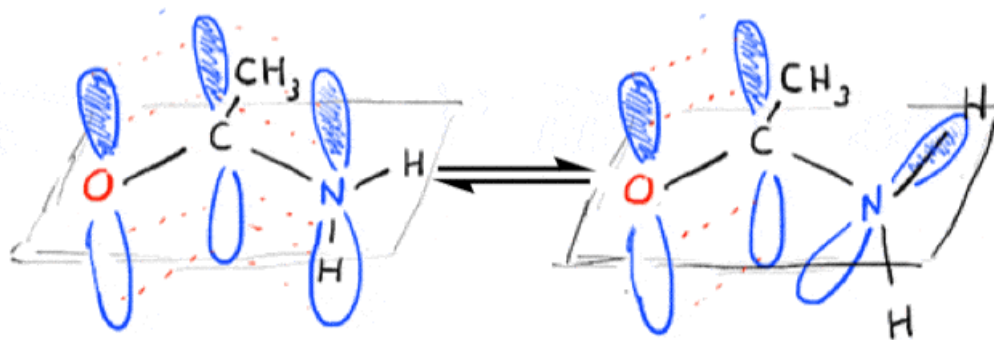
Likewise, this “partial double bond” character is only possible if the p orbital containing the lone pair is able to overlap with the p orbitals comprising the C=O pi bond.

### Amide C-N bonds have "partial double bond" character



This also requires the orbital containing the nitrogen lone pair to be aligned with the C-O  $\pi$  bond

Without this alignment there is no resonance!



More stable  
Orbitals all overlap  
(orbital in conjugation)  
Resonance possible

Less stable  
Orbital on N not overlapping  
(orbital **not** in conjugation)  
Resonance not possible

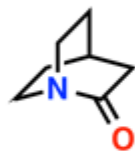
**This explains the barrier to rotation in amides, which is in the range of 15-20 kcal/mol**

# Bridgehead Amides Are Not Conjugated, And Are Much More Easily Broken Than “Ordinary” Amides

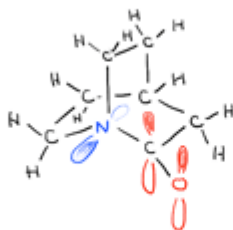
**Bridgehead amides** give an illustration of what happens to amides when overlap is impossible. Just as we saw in bridgehead alkenes, in bridgehead **amides**, orbital overlap between the nitrogen lone pair and carbonyl carbon is impossible due to twisting. The result is that the C-N bond does NOT have partial double bond character and it is much easier to break than a “normal” amide.

The bridgehead amide below is “quinuclidone”, a twisted amide that eluded synthesis for decades. It was only in 2006 that it was finally made (as its conjugate acid) through a clever route by the lab of [Brian Stoltz at Caltech](#).

A “Bridgehead Amide”  
(aka “Twisted Amide”)

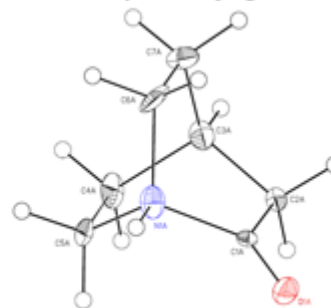


Nitrogen is *not*  
in conjugation  
with C=O



Note how N orbital is  
twisted 90° from C=O  
p orbitals

X-ray structure (of conjugate acid)



C-N bond length: 1.52 Å  
C-O bond length: 1.19 Å

The X-ray crystal structure bears witness to the lack of conjugation in this amide. The C-N bond length is 1.52 Å (typical of a single C-N bond) and the C=O bond length is 1.19 Å, which is typical of a bond length in an aldehyde or ketone (1.20 Å). We would therefore expect that it is quite a bit more unstable towards nucleophilic attack than a normal amide, which was borne out in the Stoltz lab’s study.

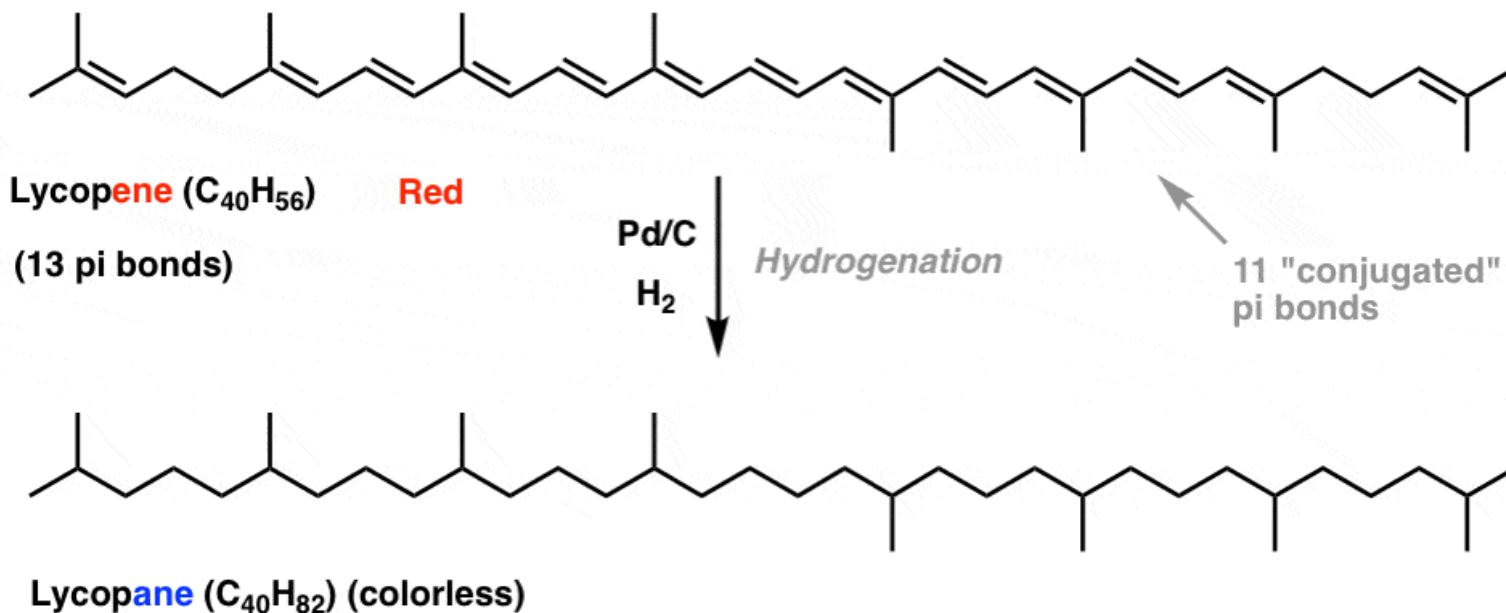
# More Consequences Of Conjugation: Color And Cycloadditions

## First: Conjugation And Color

As have you learned that as we lengthen the conjugation length, we change the wavelength at which molecules absorb light. Some very brightly coloured molecules such as carotene, chlorophyll and lycopene all have very long conjugated double bonds.

For instance, lycopene is responsible for the red colour of tomatoes. If we remove the double bonds, we remove the colour. Why?

The pi bonds of lycopene are responsible for its color:



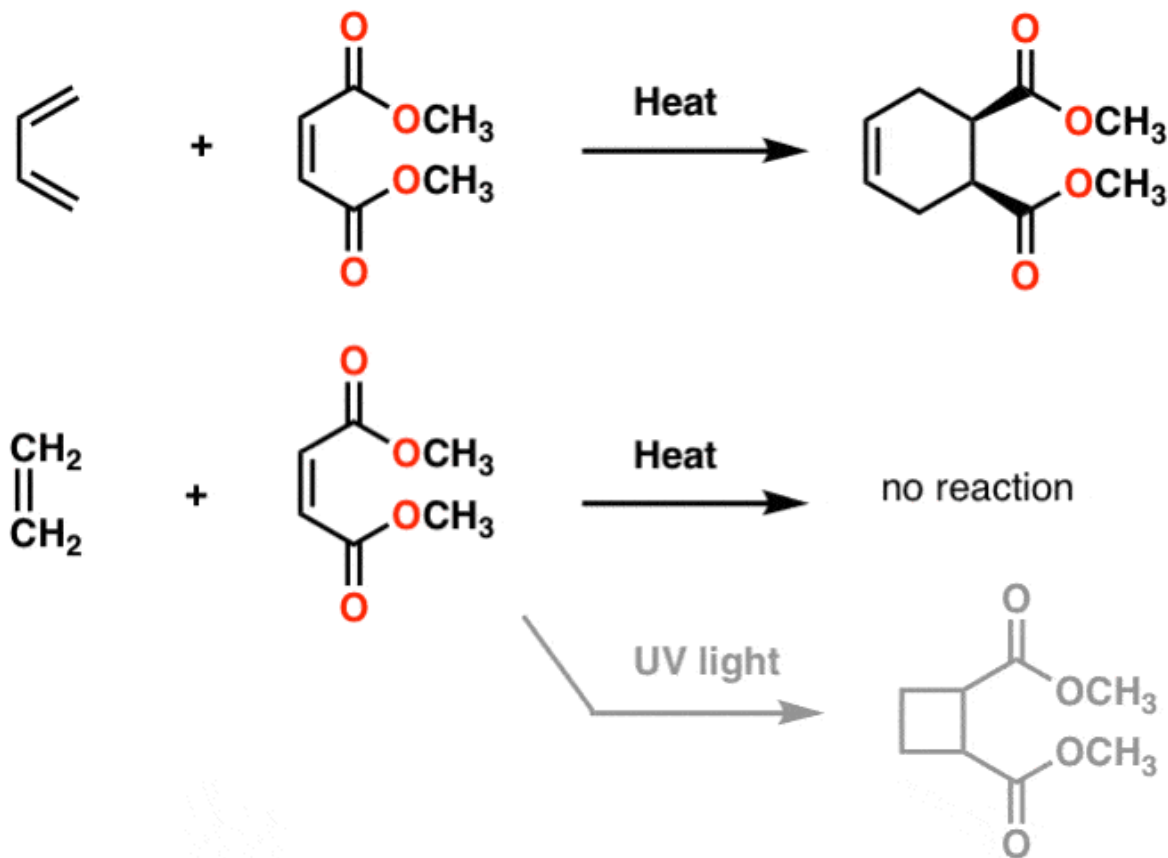


## Second: Reactions of Dienes That Form Rings

If you treat butadiene with the molecule to its right (methyl maleate) you obtain a new product containing a six membered ring. Nothing we've seen so far prepares us for this type of reaction, which is called a "cycloaddition".

Interestingly, if you treat ethene with the same molecule, nothing happens (*except if you treat it with UV light. Then you get a 4-membered ring, but I digress*).

What's going on here?



# INDUCTIVE EFFECT

VERSUS

# RESONANCE EFFECT

Inductive effect is the effect that is caused by the transmission of an electrical charge throughout a chain of atoms

Occurs due to the polarization of bonds

Affected by the electronegativity values of atoms

Resonance effect describes the effect on the stability of a molecule due to the interaction between pi bond electrons

Occurs due to the presence of single bonds and double bonds together

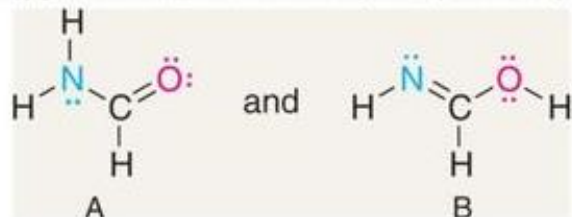
Affected by the number of double bonds and their arrangement

# Rules of Resonance

*When can resonance be considered?*

- **Rule 1.** The connectivity and positions of the atoms must remain the same in all resonance structures

Copyright © McGraw-Hill Education. Permission required for reproduction or display.

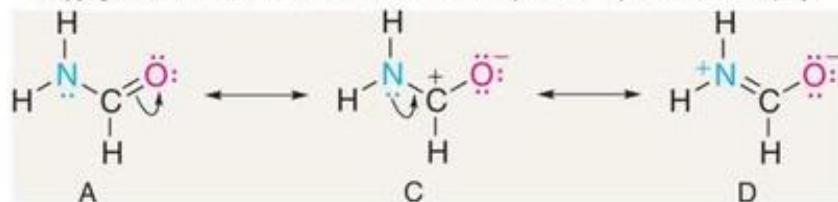


A and B are *not* resonance structures because they differ in connectivity.

They are *constitutional isomers*.

- **Rule 2.** Each contributing structure must have the same number of electrons and the same *net* charge

Copyright © McGraw-Hill Education. Permission required for reproduction or display.



A, C, and D are resonance structures. All have a net charge of zero, although the formal charges of atoms differ between them.

## Rules of Resonance

**Rule 1:** The most significant resonance contributor has the greatest number of full octets (or if applicable, expanded octets).

**Rule 2:** The most significant resonance contributor has the fewest atoms with formal charges.

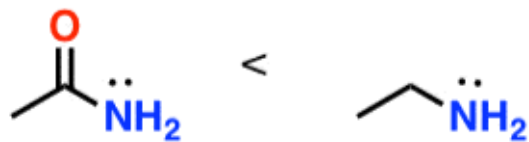
**Rule 3:** If formal charges cannot be avoided, the most significant resonance contributor has the negative formal charges on the most electronegative atoms, and the positive formal charges on the least electronegative atoms.

**Rule 4:** The most significant resonance contributor has the greatest number of covalent bonds.

**Rule 5:** If a pi bond is present, the most significant resonance contributor has this pi bond between atoms of the same row of the periodic table (usually carbon pi bonded to boron, carbon, nitrogen, oxygen, or fluorine).

**Rule 6:** Aromatic resonance contributors are more significant than resonance contributors that are not aromatic.

The basicity of amides is much lower than that of amines. Why?



Less basic

More basic

- Oxygen is more electronegative than nitrogen, so inductive effects play a role
- However, a more important factor is revealed when examining the key resonance forms...

**The Basicity Of Nitrogen Is Decreased When It Is Attached To A Pi-Acceptor**

*oxygen acts as a "pi acceptor"*  $\text{AE}$  (oxygen accepts electron pair from pi bond, forming a new lone pair on oxygen)



*nitrogen acts as a "pi-donor"*

$\text{AD}$

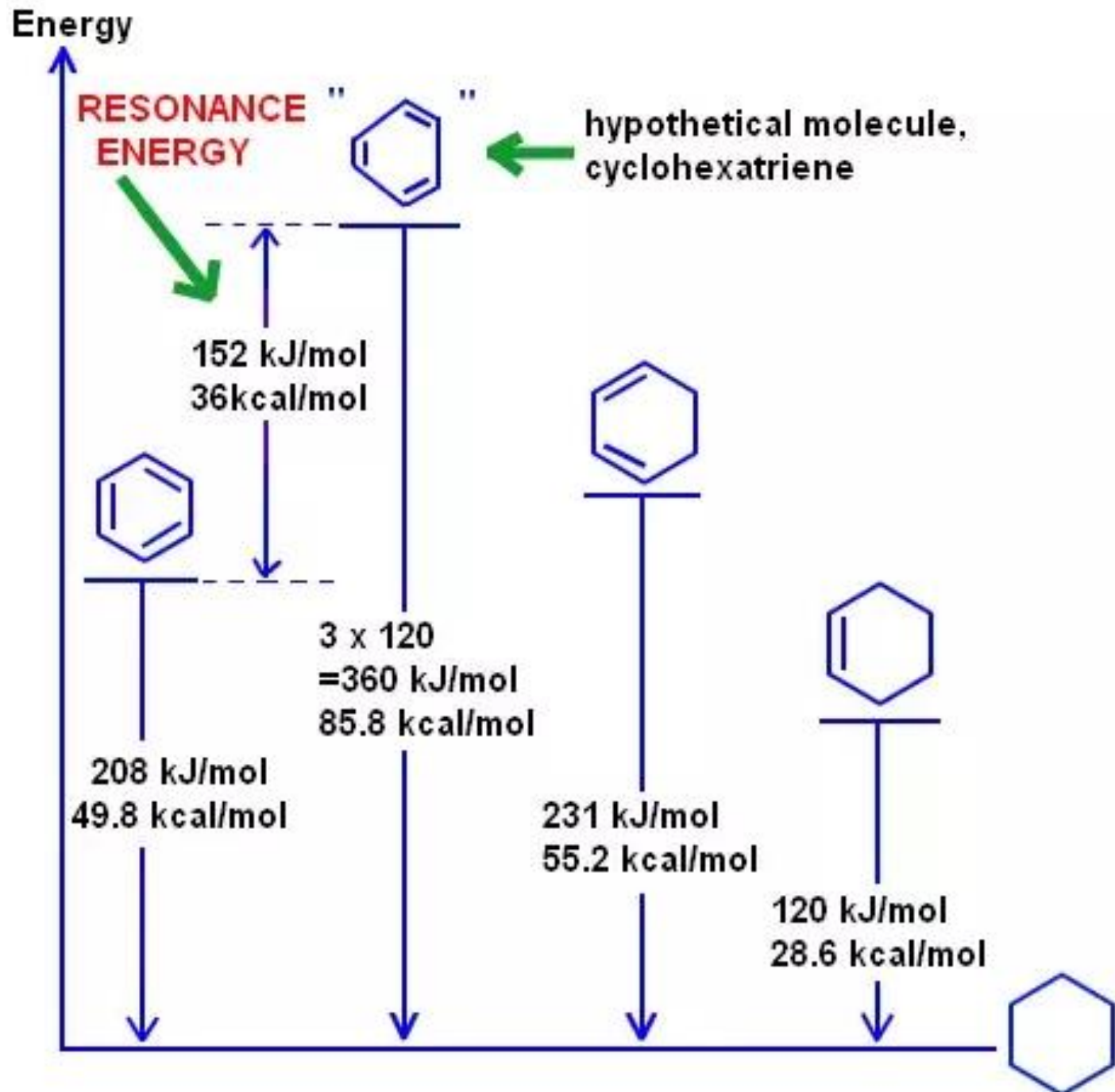
(nitrogen donates a lone pair to form a new pi-bond)

**Major resonance contributor**

Note that nitrogen can't act as a base in this resonance form!

*(Fun fact: the oxygen of amides is more basic than the nitrogen)*

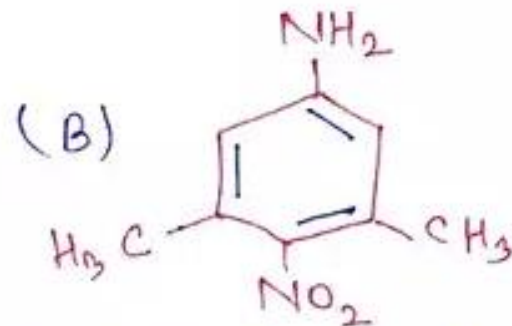
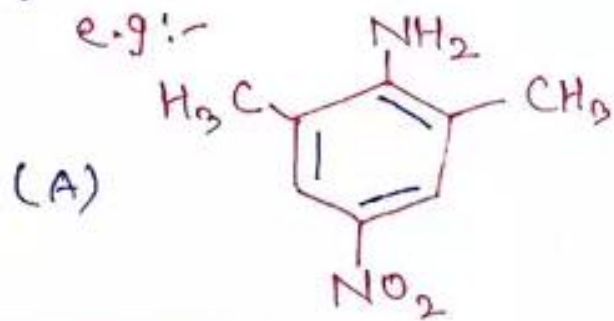
# Resonance Energy



## STERIC INHIBITION OF RESONANCE

- Resonance ability of an atom is lost if it loses planarity with the other part of the system due to steric crowding by bulky group in adjacent positions.

e.g.:-

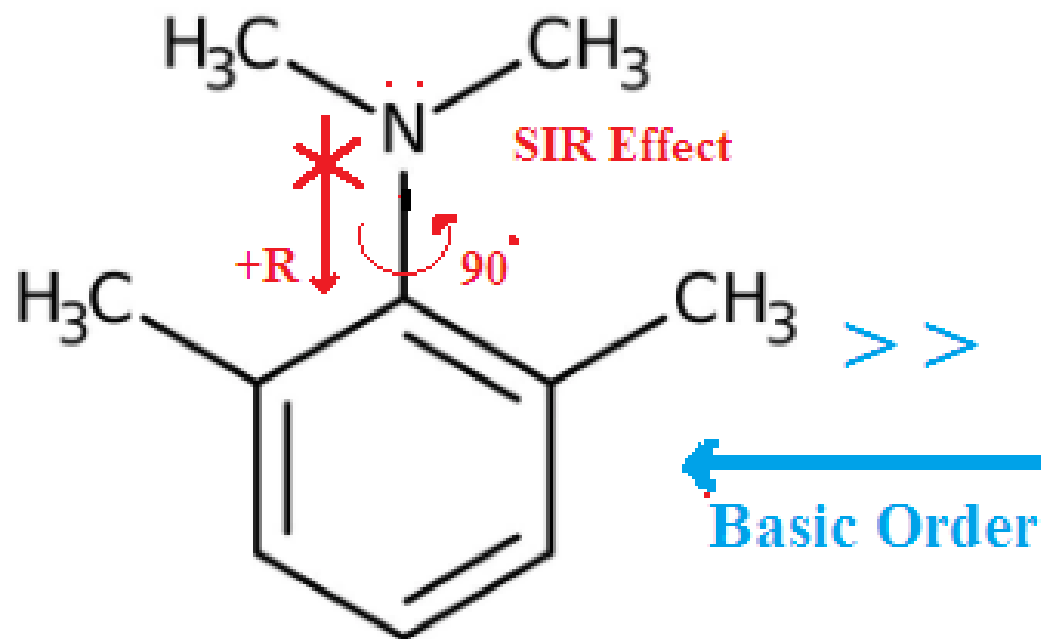
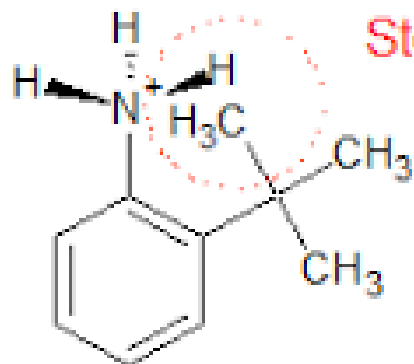


**EXPECTATIONS** :- A should be stronger base than B due to closeness of two methyl group to  $\text{NH}_2$ .

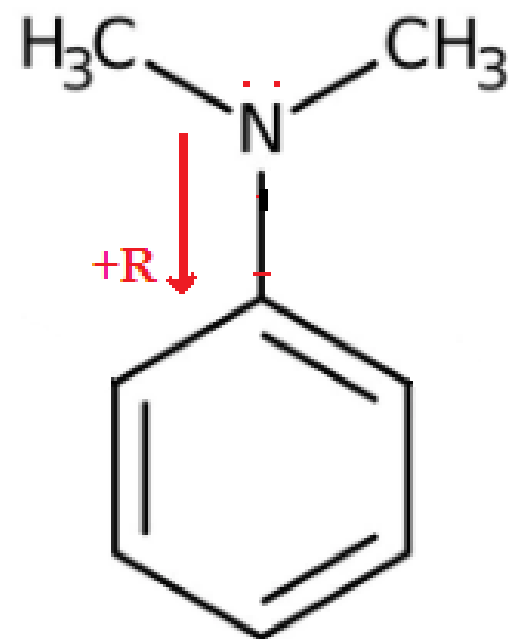
**REALITY** :- In B,  $-\text{NO}_2$  is surrounded by two bulky methyl group & they sterically repel the  $-\text{NO}_2$  group.

In order to minimise the steric repulsion by 2 methyl group, the nitro loses planarity with benzene ring.

Steric Hinderance



N,N,2,6 -Tetramethylaniline

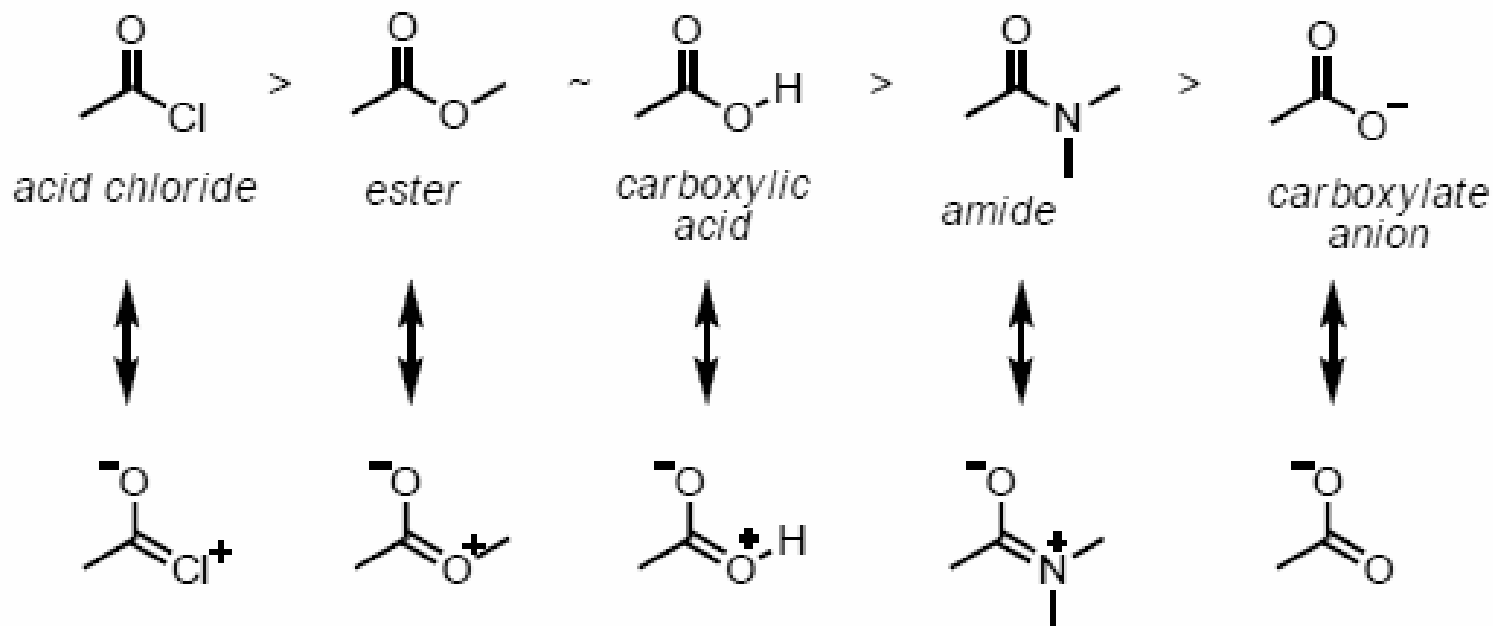


N,N-Dimethylaniline



## Resonance Effect Or Mesomeric Effect In Chemistry

The withdrawal effect or releasing effect of electrons attributed to a particular substituent through the delocalization of  $\pi$  or pi-electrons that can be seen by drawing various canonical structures is called a resonance effect or mesomeric effect. M or R symbols are used to represent the resonance effect.



The concept of resonance effect tells about the polarity induced in a molecule by the reaction between a lone pair of electron and a pi bond. It also occurs by the interaction of 2 pi bonds in the adjacent atoms. Resonance in simple is the molecules with multiple Lewis structures. Resonance in chemistry helps in understanding the stability of a compound along with the energy states.

## Types Of Resonance Effects

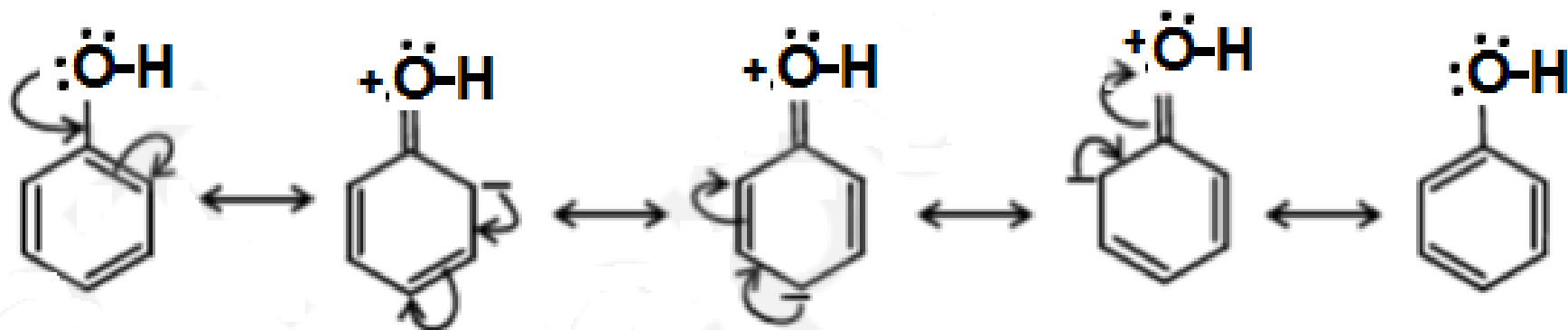
There are two types of Resonance effects namely positive resonance effect and negative resonance effect.

**1. Positive Resonance Effect-** Positive resonance effect occurs when the groups release electrons to the other molecules by the process of delocalization. The groups are usually denoted by +R or +M. In this process, the molecular [electron](#) density increases. For example- -OH, -SH, -OR, -SR.

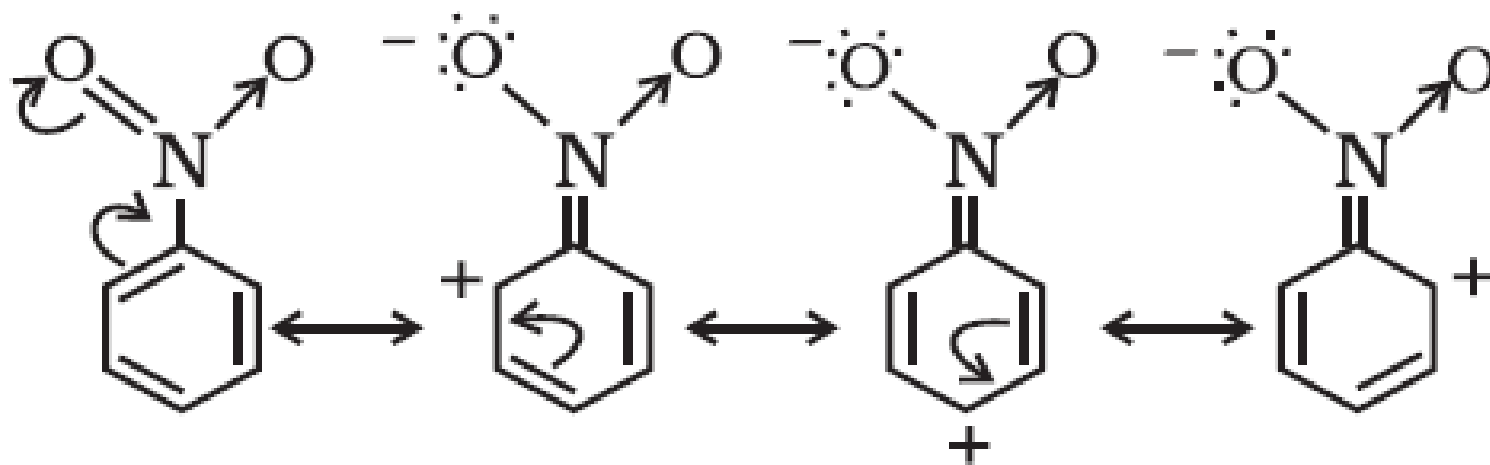
**2. Negative Resonance Effect-** Negative resonance effect occurs when the groups withdraw the electrons from other molecules by the process of delocalization. The groups are usually denoted by -R or -M. In this process, the molecular electron density is said to decrease. For example- -NO<sub>2</sub>, C=O, -COOH, -C≡N.

## Positive resonance effect (+R effect)

### Phenol

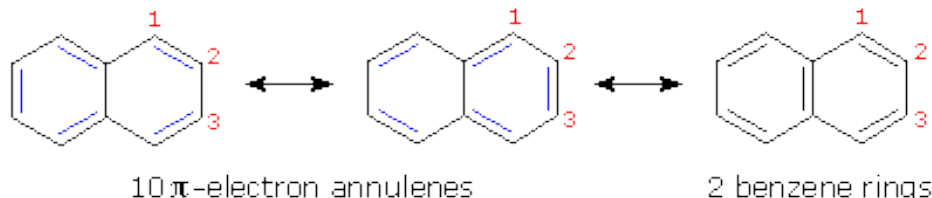


## Negative resonance effect (-R effect) in nitrobenzene



# Resonance Structures of Aromatic Fused Rings

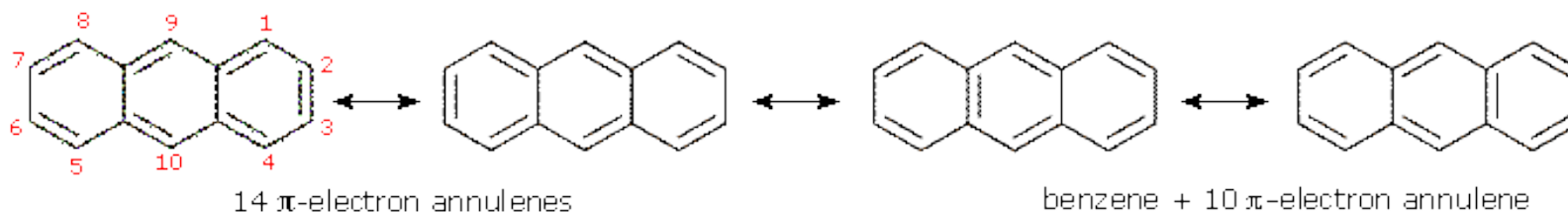
## Napthalene



Resonance Energy = 61 kcal/mole (less than twice benzene)  
(30.5 kcal per ring)

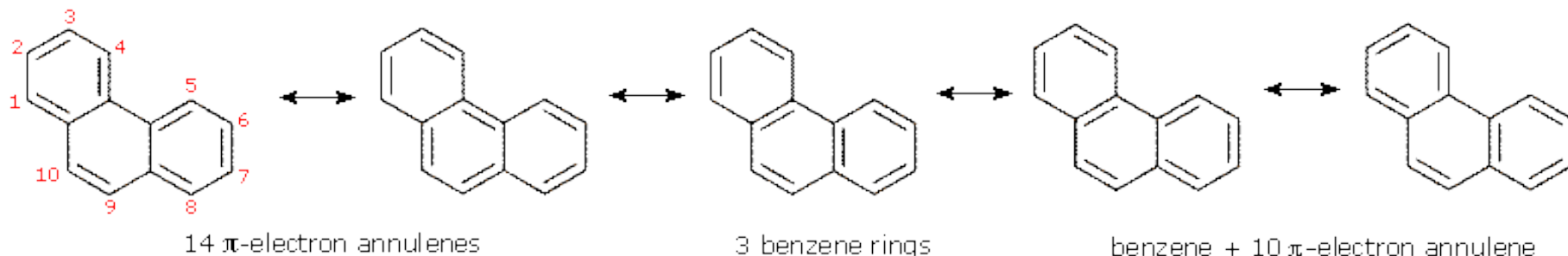
The C-C bond lengths in benzene are all 1.40 Å  
The C<sup>1</sup>-C<sup>2</sup> bond length in naphthalene is 1.36 Å  
The C<sup>2</sup>-C<sup>3</sup> bond length in naphthalene is 1.42 Å

## Anthracene



Resonance Energy = 83 kcal/mole  
(27.7 kcal per ring)

## Phenanthrene



Resonance Energy = 91 kcal/mole  
(30.3 kcal per ring)

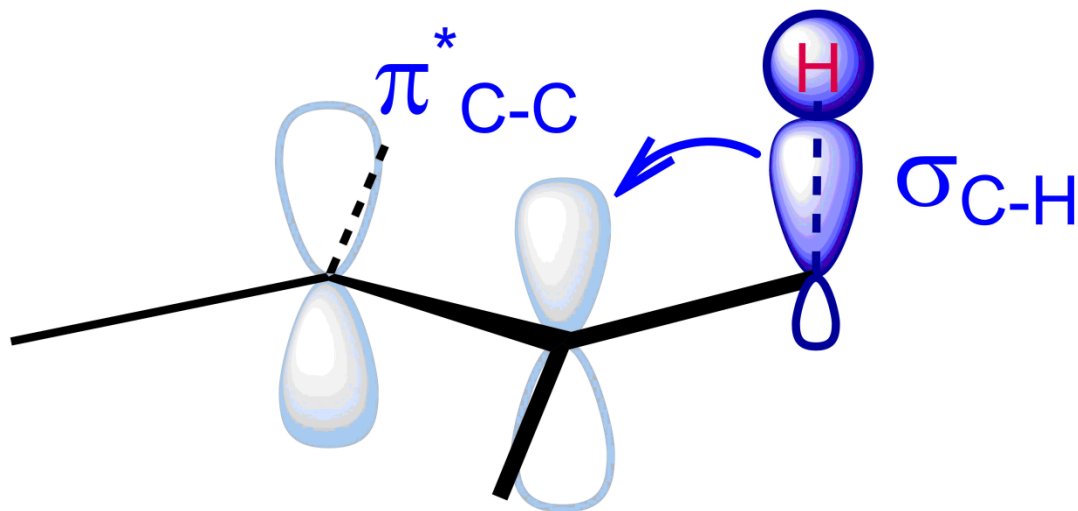
# Hyperconjugation

Hyperconjugation is the stabilising interaction that results from the interaction of the electrons in a  $\sigma$ -bond (usually **C-H** or **C-C**) with an adjacent empty or partially filled p-orbital or a  $\pi$ -orbital to give an extended molecular orbital that increases the stability of the system.

What is the key difference between hyperconjugation and resonance ?

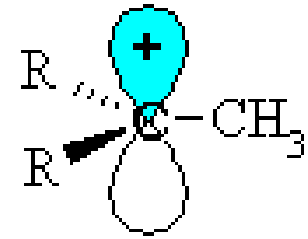
Hyperconjugation involves a sigma orbital component, usually a **C-C** or **C-H** bond.

Resonance involves pi orbitals.

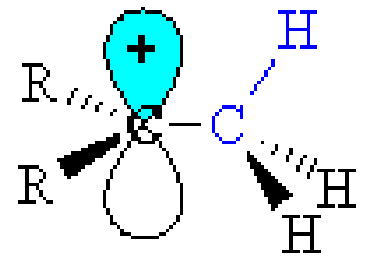


Hyperconjugation is a factor in explaining why increasing the number of alkyl substituents on a carbocation or radical centre leads to an increase in stability.

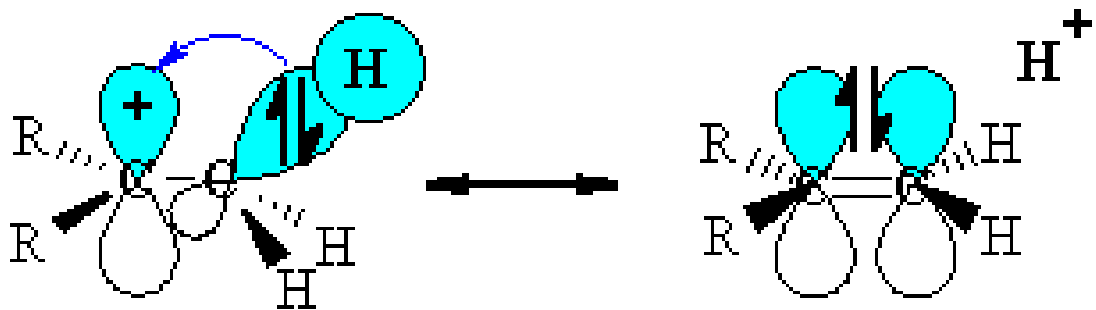
Let's consider how a methyl group is involved in hyperconjugation with a carbocation centre.



First we need to draw it to show the C-H  $\sigma$ -bonds. Note that the empty p orbital associated with the positive charge at the carbocation centre is in the same plane (*i.e.* coplanar) with one of the C-H  $\sigma$ -bonds (shown in blue.)

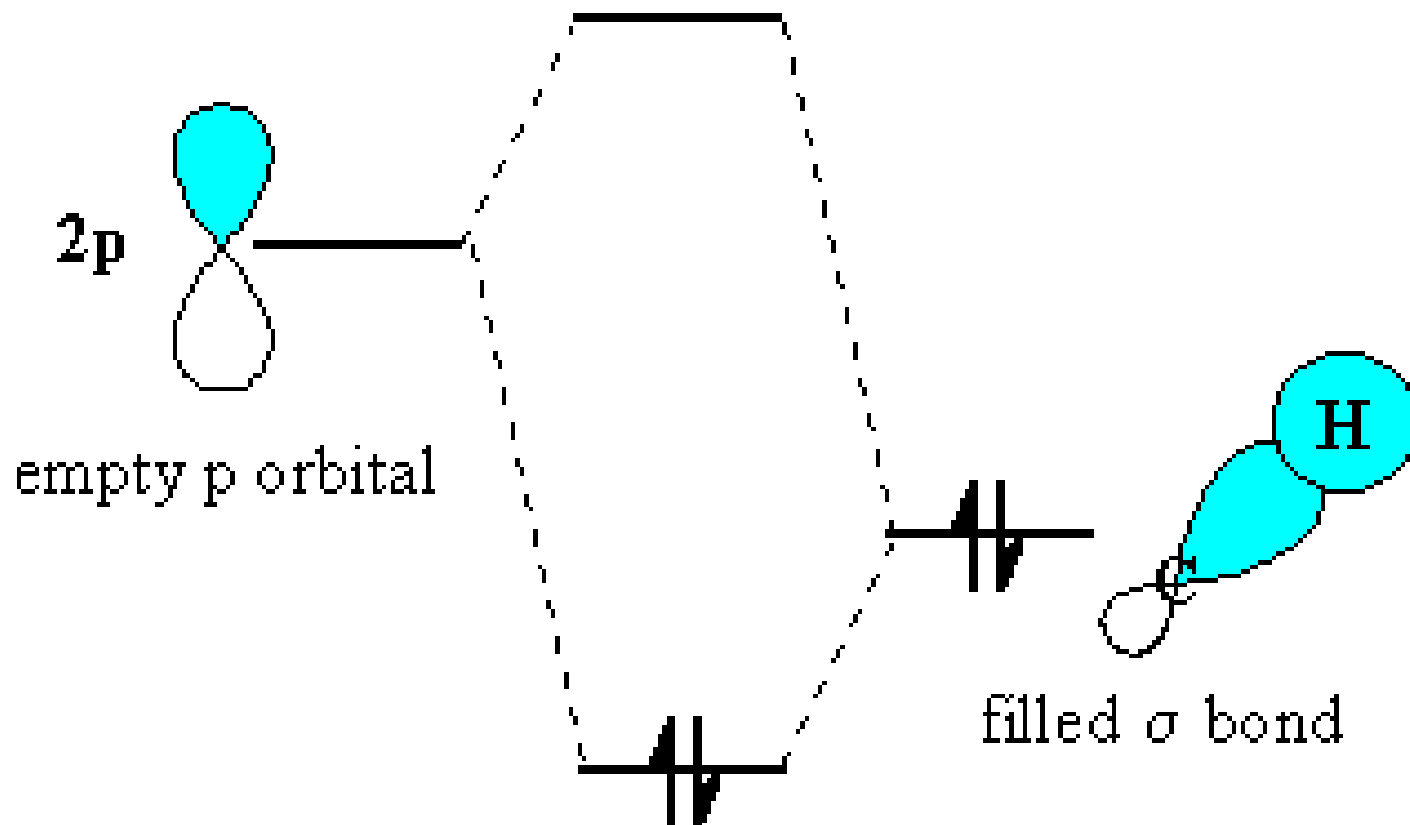


This geometry means the electrons in the  $\sigma$ -bond can be stabilised by an interaction with the empty p-orbital of the carbocation centre.



(this diagram shows the similarity with resonance and the structure on the right has the "double bond - no bond" character)

The stabilisation arises because the orbital interaction leads to the electrons being in a lower energy orbital

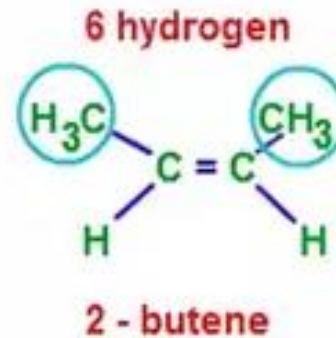
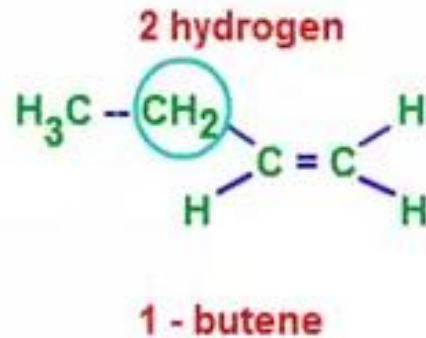


- Of course, the **C-C**  $\sigma$ -bond is free to rotate, and as it does so, each of the **C-H**  $\sigma$ -bonds in turn undergoes the stabilising interaction.
- The ethyl cation has 3 **C-H**  $\sigma$ -bonds that can be involved in hyperconjugation.
- The more hyperconjugation there is, the greater the stabilisation of the system.
- For example, the t-butyl cation has 9 **C-H**  $\sigma$ -bonds that can be involved in hyperconjugation.
- Hence  $(\text{CH}_3)_3\text{C}^+$  is more stable than  $\text{CH}_3\text{CH}_2^+$
- The effect is not limited to **C-H**  $\sigma$ -bonds, appropriate **C-C**  $\sigma$ -bonds can also be involved in hyperconjugation.



# Stability of Unsaturated Hydrocarbons

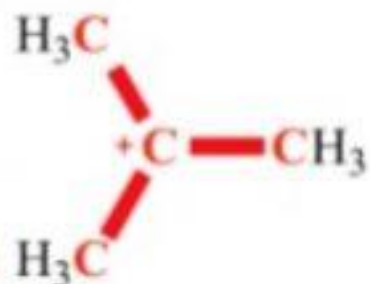
Example:



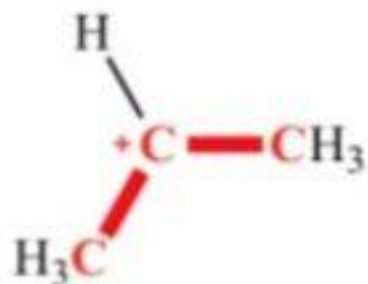
- 2-butene consists of six alpha carbon-hydrogen sigma bonds while there are only 2 carbon-hydrogen bonds next to double bonded carbon atom in 1-butene.
- Hence 2-butene shows six contributing structures while 1-butene shows only two which make 2-butene more stable compare to 1-butene.
- This rule is applicable on other alkenes also. Hence as the number of alkyl group on double bonded carbon atoms increases, hyper conjugation increases which stabilized the molecule.

► The order of stability of the Carbocations is is:

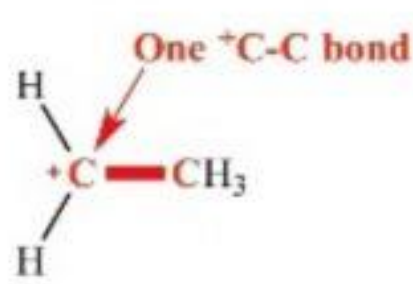
**3<sup>o</sup>alkyl carbocation > 2<sup>o</sup>alkyl carbocation > 1<sup>o</sup>alkyl carbocation > methyl carbocation**



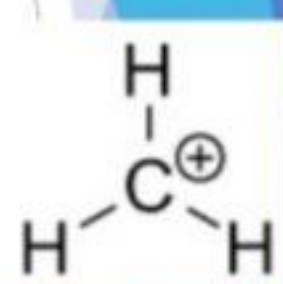
9  
Hyperconjugable  
H



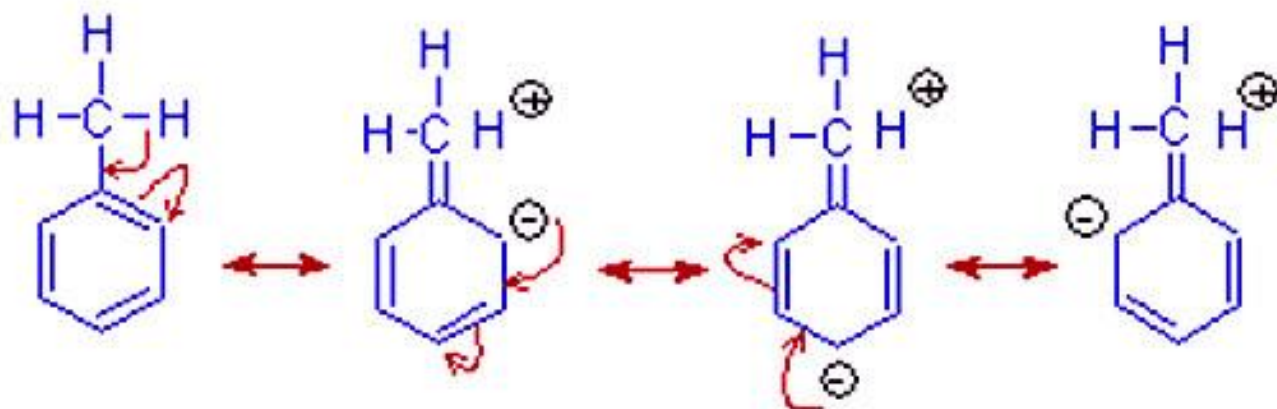
6  
Hyperconjugable  
H



3  
Hyperconjugable  
H



No  
Hyperconjugable  
H



Hyperconjugation in toluene

# Hyperconjugation vs Inductive Effect

More Information Online [WWW.DIFFERENCEBETWEEN.COM](http://WWW.DIFFERENCEBETWEEN.COM)

## DEFINITION

### Hyperconjugation

Hyperconjugation is the interaction of  $\sigma$ -bonds with a pi bond network

### 2D Gel Electrophoresis

Inductive effect is an effect caused by the transmission of an electrical charge throughout a chain of atoms

## THEORY

Stabilizes the molecule through pi electron delocalization

Stabilizes the molecule via transmission of electrical charges through the molecule

## CAUSE

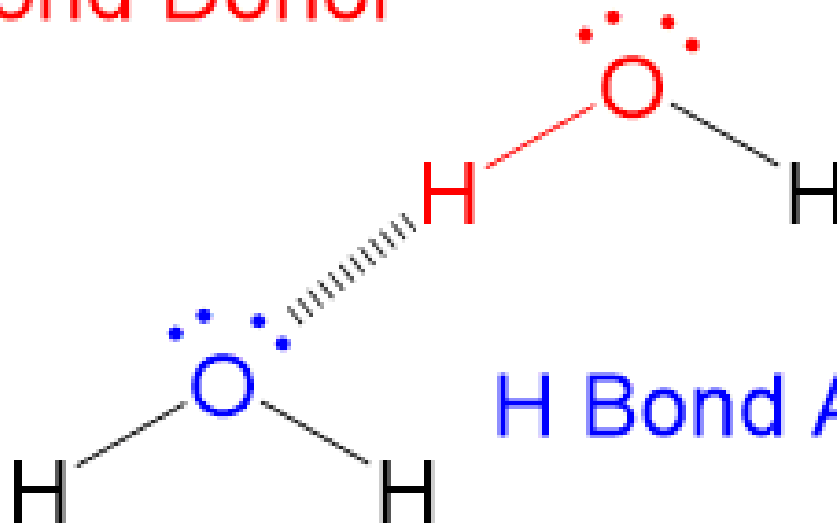
Overlap of bonding electrons in C-H sigma bond with a p orbital or a pi orbital of the adjacent carbon atom due to close proximity

Due to the differences in the electronegative values of atoms of a molecule

# Hydrogen Bonding

A **hydrogen bond** (often informally abbreviated **H-bond**) is a primarily electrostatic force of attraction between a hydrogen (H) atom which is covalently bound to a more electronegative atom or group, particularly the second-row elements nitrogen (N), oxygen (O), or fluorine (F)—the hydrogen bond donor (Dn)—and another electronegative atom bearing a lone pair of electrons—the hydrogen bond acceptor (Ac)

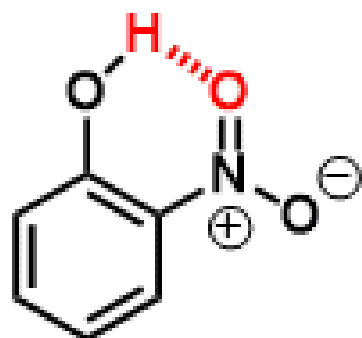
H Bond Donor



H Bond Acceptor

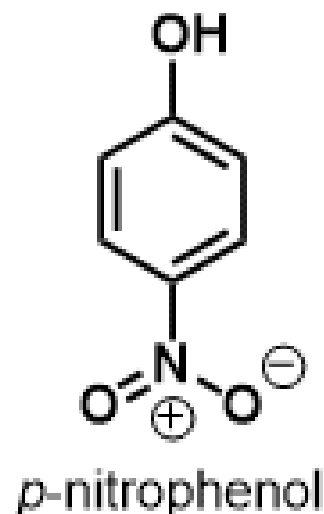
*ortho*-Nitrophenol and *para*-nitrophenol have very different boiling points: one boils at 279 °C, and the other at 215 °C. **Determine** which compound has which boiling point, and **account for the difference**.

bp = 215 °C



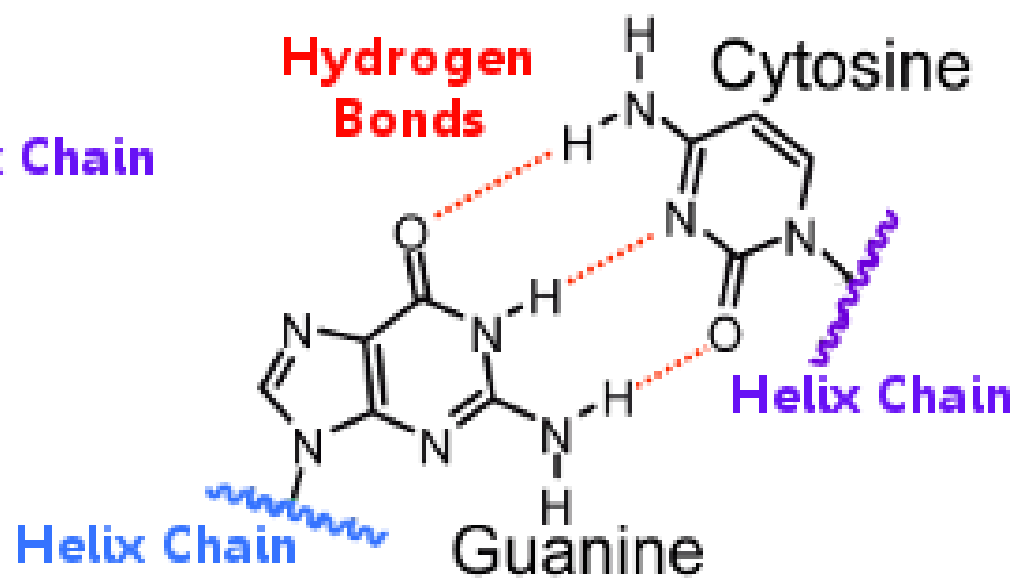
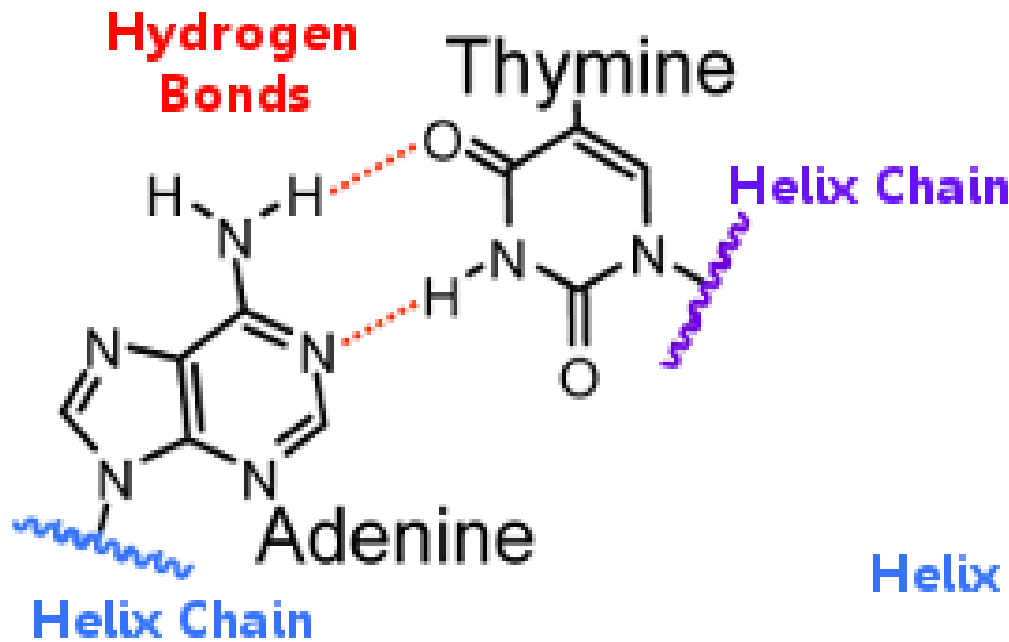
*o*-nitrophenol

bp = 279 °C



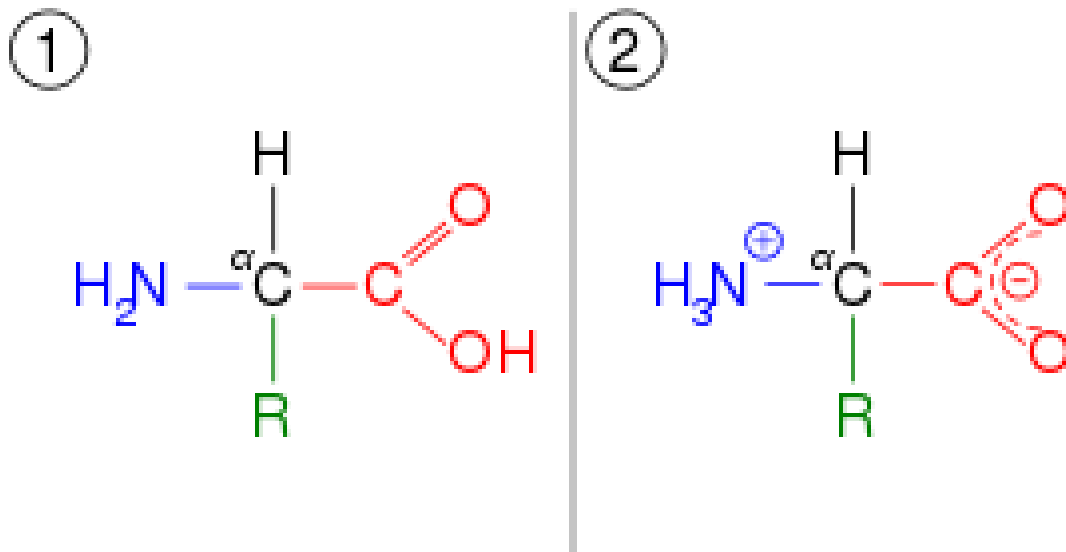
*p*-nitrophenol

The *ortho* isomer can form an **intramolecular hydrogen bond**, leading to a diminished ability to form H-bonds with other molecules. This lowers its boiling point relative to the *para* isomer, which can **only form intermolecular H-bonds**.



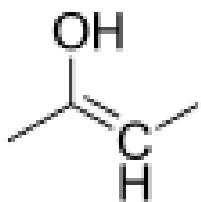
## Tautomerism:

- **Tautomers** are structural isomers (constitutional isomers) of chemical compounds that readily interconvert.
- This reaction commonly results in the relocation of a proton.
- Tautomerism is for example relevant to the behavior of amino acids and nucleic acids, two of the fundamental building blocks of life.
- The concept of tautomerizations is called **tautomerism**.
- Tautomerism is also called desmotropism.
- The chemical reaction interconverting the two is called **tautomerization**.

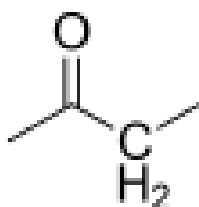


Tautomerization is pervasive in organic chemistry. It is typically associated with polar molecules and ions containing functional groups that are at least weakly acidic. Most common tautomers exist in pairs, which means that the proton is located at one of two positions, and even more specifically the most common form involves a hydrogen changing places with a double bond

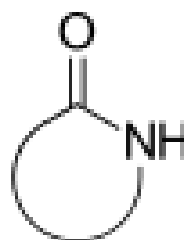
Enol form



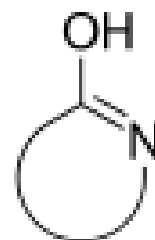
Keto form



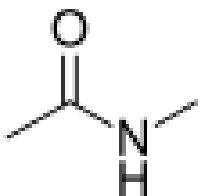
Lactam form



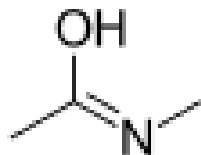
Lactim form



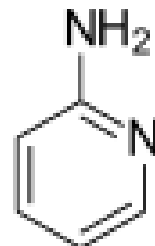
Amide form



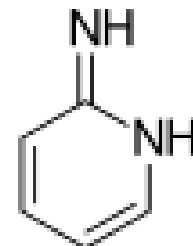
Imidic acid form



Amine form



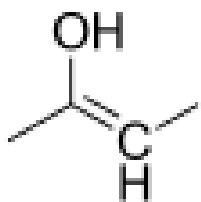
Imine form



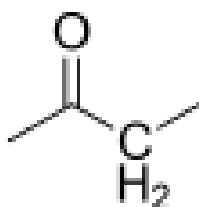


Tautomerization is pervasive in organic chemistry. It is typically associated with polar molecules and ions containing functional groups that are at least weakly acidic. Most common tautomers exist in pairs, which means that the proton is located at one of two positions, and even more specifically the most common form involves a hydrogen changing places with a double bond

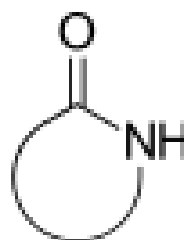
Enol form



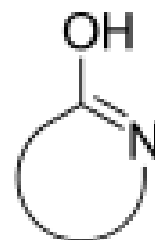
Keto form



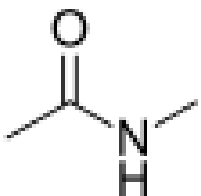
Lactam form



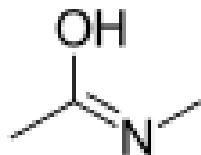
Lactim form



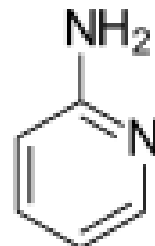
Amide form



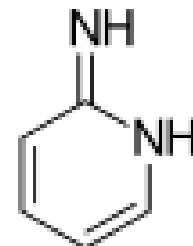
Imidic acid form



Amine form

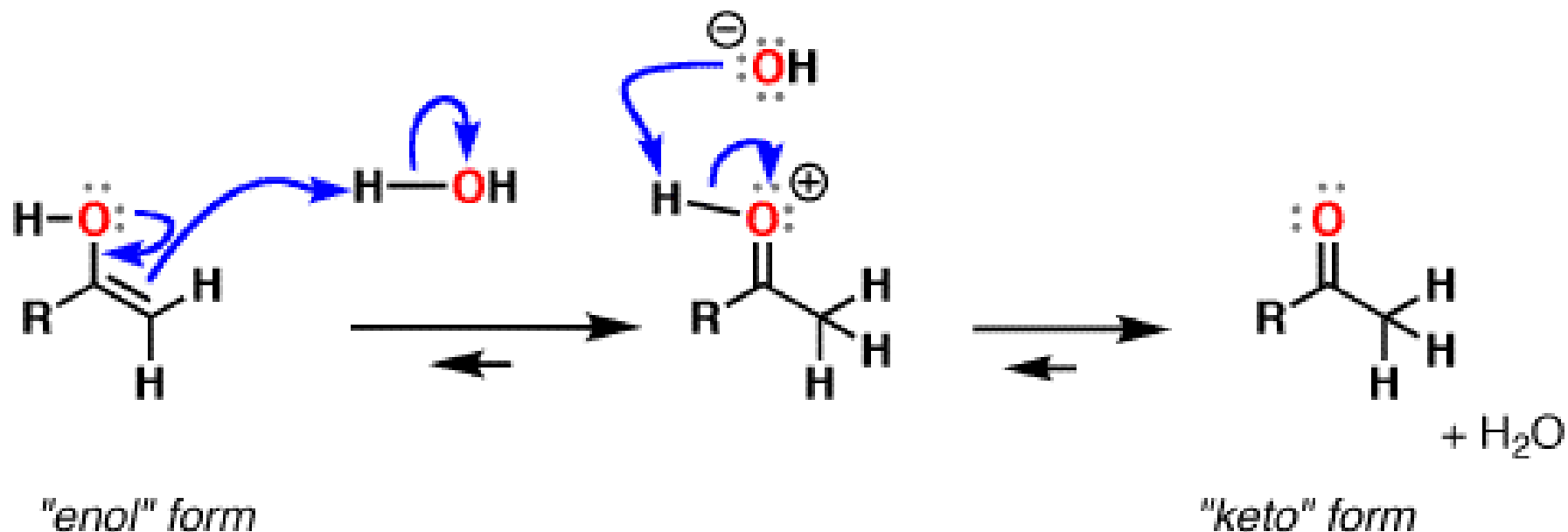


Imine form



The transformation of the enol into the keto form goes by the name “tautomerism”.

## Tautomerism: How it works



*Equilibrium generally favors the keto form*

Tautomerism is a spontaneous process. There's little that can be done to stop it.

What this means is that as soon as the enol is formed, it will be transformed into its more stable keto form.

# Spectroscopy

**Spectroscopy** is the study of the interaction between [matter](#) and electromagnetic [radiation](#) as a function of the wavelength or [frequency](#) of the radiation.

Spectroscopy and spectrography are terms used to refer to the measurement of radiation intensity as a function of wavelength and are often used to describe [experimental](#) spectroscopic methods. Spectral measurement devices are referred to as [spectrometers](#), [spectrophotometers](#), [spectrographs](#) or [spectral analyzers](#).

Spectroscopic studies were central to the development of [quantum mechanics](#) and included Max Planck's explanation of [blackbody radiation](#), [Albert Einstein](#)'s explanation of the photoelectric effect and [Niels Bohr](#)'s explanation of [atomic structure](#) and spectra.

Spectroscopy is used in [physical](#) and [analytical chemistry](#) because [atoms](#) and [molecules](#) have unique spectra. As a result, these spectra can be used to detect, identify and quantify information about the atoms and molecules.

## Nature of the interaction

The types of spectroscopy also can be distinguished by the nature of the interaction between the energy and the material. These interactions include

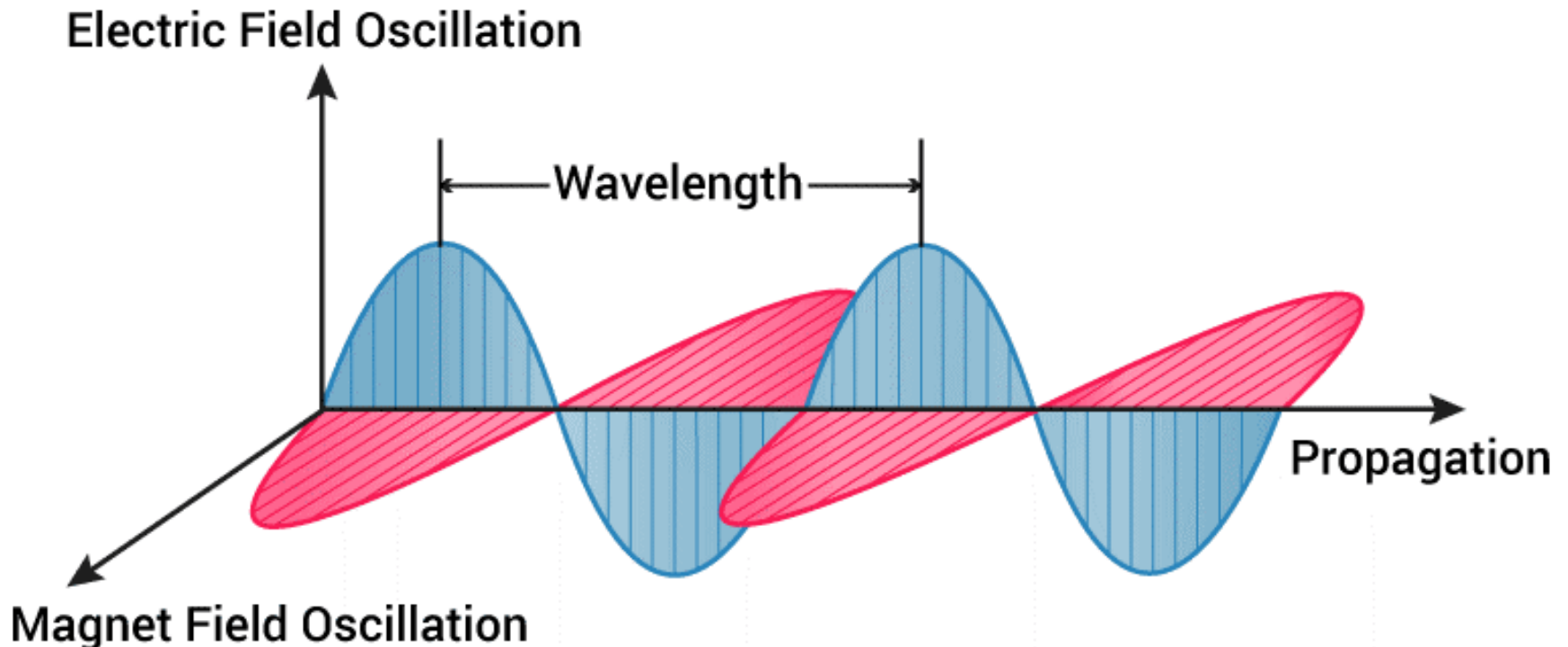
- [Absorption spectroscopy](#): Absorption occurs when energy from the radiative source is absorbed by the material. Absorption is often determined by measuring the fraction of energy transmitted through the material, with absorption decreasing the transmitted portion.
- [Emission spectroscopy](#): Emission indicates that radiative energy is released by the material. A material's [blackbody spectrum](#) is a spontaneous emission spectrum determined by its temperature. This feature can be measured in the infrared by instruments such as the atmospheric emitted radiance interferometer. Emission can also be induced by other sources of energy such as [flames](#), [sparks](#), [electric arcs](#) or electromagnetic radiation in the case of [fluorescence](#).
- [Elastic scattering](#) and [reflection](#) spectroscopy determine how incident radiation is reflected or scattered by a material. [Crystallography](#) employs the scattering of high energy radiation, such as x-rays and electrons, to examine the arrangement of atoms in proteins and solid crystals.

- [Impedance spectroscopy](#): Impedance is the ability of a medium to impede or slow the transmittance of energy. For [optical](#) applications, this is characterized by the [index of refraction](#).
- [Inelastic scattering](#) phenomena involve an exchange of energy between the radiation and the matter that shifts the wavelength of the scattered radiation. These include [Raman](#) and [Compton](#) scattering.
- [Coherent](#) or resonance spectroscopy are techniques where the radiative energy couples two quantum states of the material in a [coherent](#) interaction that is sustained by the radiating field. The coherence can be disrupted by other interactions, such as particle collisions and energy transfer, and so often require high intensity radiation to be sustained. [Nuclear magnetic resonance \(NMR\) spectroscopy](#) is a widely used resonance method, and [ultrafast laser spectroscopy](#) is also possible in the infrared and visible spectral regions.
- [Nuclear spectroscopy](#) are methods that use the properties of specific [nuclei](#) to probe the [local structure](#) in matter, mainly [condensed matter](#), [molecules](#) in liquids or frozen liquids and bio-molecules.

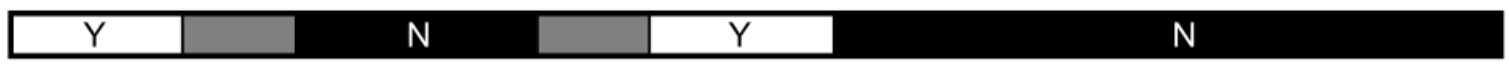
# Electromagnetic radiation

**Electromagnetic radiation** (EM radiation or EMR) refers to the **waves** (or their quanta, photons) of the **electromagnetic** field, propagating (radiating) through space, carrying **electromagnetic** radiant energy. It includes radio **waves**, microwaves, infrared, (visible) light, ultraviolet, X-**rays**, and gamma **rays**.

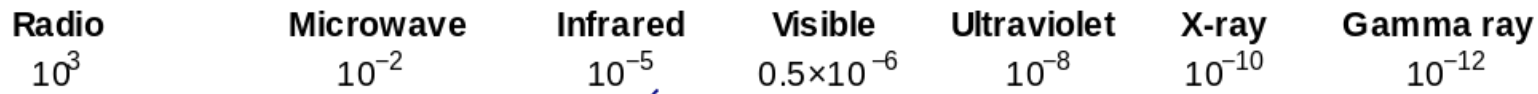
## ELECTROMAGNETIC RADIATION



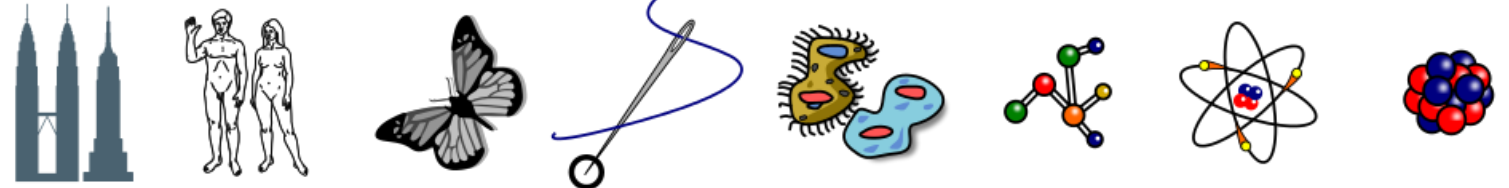
Penetrates Earth's Atmosphere?



Radiation Type  
Wavelength (m)



Approximate Scale  
of Wavelength

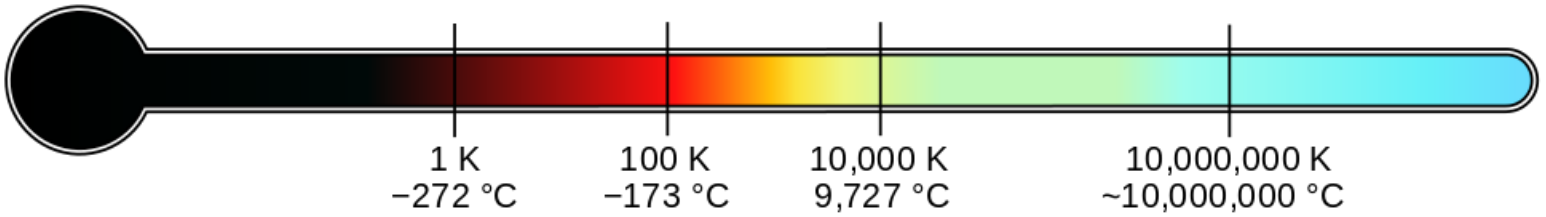


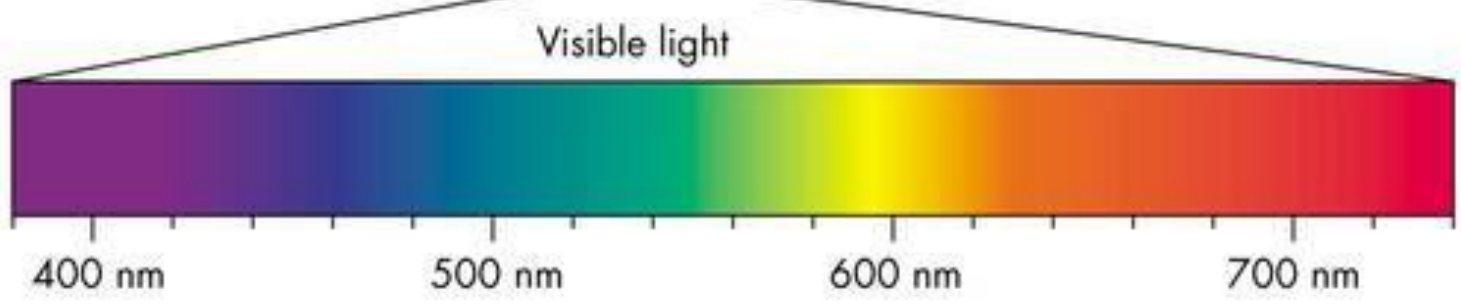
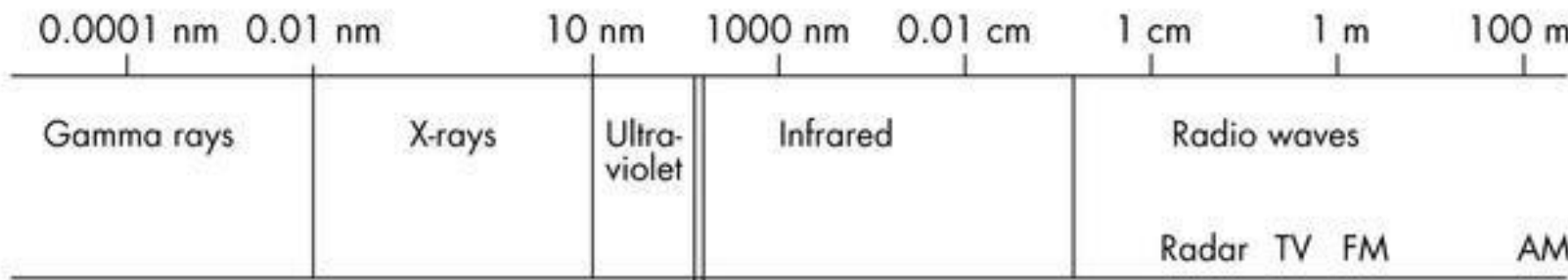
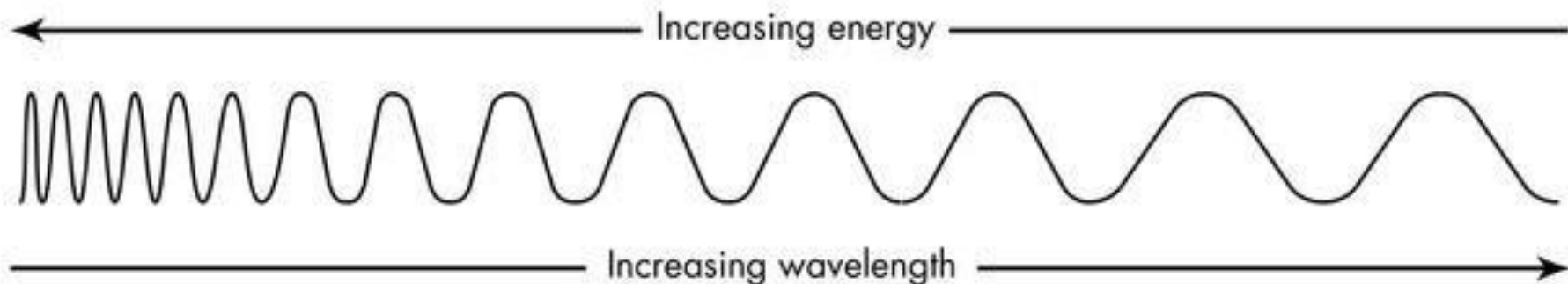
Buildings    Humans    Butterflies    Needle Point    Protozoans    Molecules    Atoms    Atomic Nuclei

Frequency (Hz)



Temperature of  
objects at which  
this radiation is the  
most intense  
wavelength emitted







## Terms describing UV absorptions

1. **Chromophores:** functional groups that give electronic transitions.
2. **Auxochromes:** substituents with unshared pair e's like OH, NH, SH ..., when attached to  $\pi$  chromophore they generally move the absorption max. to longer  $\lambda$ .
3. **Bathochromic shift:** shift to longer  $\lambda$ , also called **red shift**.
4. **Hysochromic shift:** shift to shorter  $\lambda$ , also called **blue shift**.
5. **Hyperchromism:** increase in  $\epsilon$  of a band.
6. **Hypochromism:** decrease in  $\epsilon$  of a band.

### Summary of Qualitative Analysis of Organic Compounds

Test	Reagents	Importance	Positive Result	Notes
Ignition Test		Distinguish aliphatic and aromatic cmpds.	Aliphatic- non-sooty smoke Aromatic- yellow flame, sooty	
Bromine in CCl <sub>4</sub> Test	Br <sub>2</sub> in CCl <sub>4</sub>	Test for Unsaturation (alkenes, alkynes)	Decolorization of Bromine color	*also perform Baeyer Test.
Baeyer Test	dil. KMnO <sub>4</sub>	General Test for Alkenes and Alkynes	Formation of red-brown solid (MnO <sub>2</sub> )	*room temperature
Lucas Test	HCl in ZnCl <sub>2</sub>	Test for alcohols	Appearance of a cloudy second layer or emulsion (alkylhalide)	3° alcohols – 1-3 mins 2° alcohols - 5-10 mins 1° alcohols - no reaction *insoluble cmp'ds in the reagent are not applicable.
Chromic acid Test (or Jones Oxidation)	Chromic acid (Jones Reagent – CrO <sub>3</sub> in H <sub>2</sub> SO <sub>4</sub> )	Test for alcohols and aldehydes	From yellow to blue-green sol'n/suspension (Cr <sup>3+</sup> ) Aldehydes develops in 5 - 15 seconds.	3° alcohols – no reaction Phenols give a dark colored solution which is not blue-green like a positive test.
2,4-Dinitrophenylhydrazine Test	2,4-Dinitrophenylhydrazine in conc. H <sub>2</sub> SO <sub>4</sub>	Test for aldehydes and ketones	Formation of a yellow to orange precipitate, hydrazone or osazone	Some allylic alcohols are oxidized by the reagent to aldehydes and give a positive test.
Iodoform test	Iodine in KI + NaOH	Test for methyl-substituted ketones and alcohols	Formation of yellow precipitate (CHI <sub>3</sub> , iodoform)	
Alcoholic Silver Nitrate	AgNO <sub>3</sub> in 2% ethanol + heat	General test for alkyl halides.	Alkyl halide-Formation of solid AgX salt.	
Hydroxamic acid test	Hydroxylamine HCl in 95% ethanol and 6M NaOH	General test for esters. Also positive for acyl halides and acid anhydrides and amides.	Formation of a magenta-color complex.	*Some carboxylic acids give a positive result.
Ester formation test	Alcohol in sulfuric acid + heat	General test for carboxylic acids	Formation of oily layer on top of the solution, and a sweet, fruity smell (ester)	*large MW carboxylic acids form odorless ester.
Bromine water test	Bromine in water	Test for phenolic compounds	Decolorization of bromine & formation of insoluble white compd	
FeCl <sub>3</sub> test	FeCl <sub>3</sub> sol'n	Test for phenolic compounds	Formation of red colored complex	

