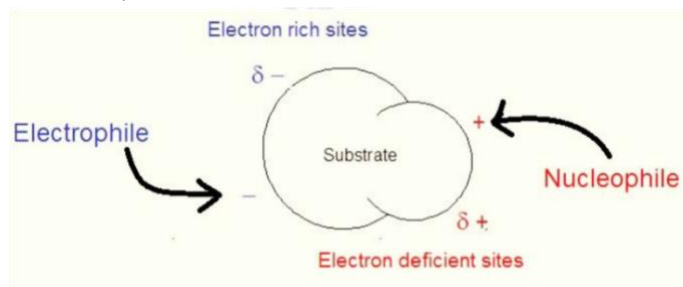


Structure and reactivity of Organic molecule

Molecular Effects: Inductive, resonance, hyperconjugation, steric effects. Oxidation and reduction reactions for organic compounds. Some name reactions: Aldol, Cannizzaro, Michael, Claisen-Schmidt, Wittig reactions.

2L

During most of the organic reactions, reagents either undergo heterolysis to give rise to electrophiles and / or nucleophiles; or they undergo homolysis to give rise to free radicals. Electrophiles being electron deficient search for electron rich site in the organic substrate to attack and form the bond. But, if there are more than one electron rich sites in the organic substrate, the electrophile obviously would prefer to attack on the most electron rich site. On the other hand, nucleophiles being electron rich, search for electron deficient sites in the organic substrate.



Structures of organic compounds and their reactivity originate from the nature of bonding among the atoms in a molecule. Organic compounds are covalent in nature. The electron pair of a covalent bond is displaced by some electronic effects which are responsible for the reactivity of organic molecules.

Electronic effects: The effect involving displacement of electrons in the organic molecule are known as electronic effects. Some of the electronic effects are permanent and others are temporary. The permanent electronic effects are known as polarisation effects and the temporary electronic effects which are brought into play by the attacking groups and disappeared as soon as the attacking groups are removed, are known as polarizability effects. Few electronic effects are inductive effect, electromeric effect, resonance effect, hyperconjugation etc.

Inductive effect

When an electronegative atom or group induces a dipole in a bond of a molecule adjacent to the electronegative atom or in a bond further away is known as inductive effect. This effect implies the atom's ability to cause polarization in a sigma (σ) bond. This effect is represented by an arrow head in the middle of covalent bond pointing in the direction of electron displacement (\rightarrow). The inductive effect is a permanent state of polarization. The electron density in a sigma (σ) bond between two unlike atoms is not uniform. The electron density is more dense toward the more electronegative of the two atoms.

Ideally, a covalent bond between two atoms must share the pair of electrons equally. If the electronegativities of the two atoms are different, this sharing of electrons is not equal and the more electronegative atom gets a fractional negative charge due to the greater attraction of the shared pair of electrons towards itself and the other atom gets a fractional positive charge. Fractional or partial negative charge is represented by δ^- (pronounced as delta minus) and Fractional or partial positive charge is represented by δ^+ (pronounced as delta plus), δ signifying the very less magnitude of charge.

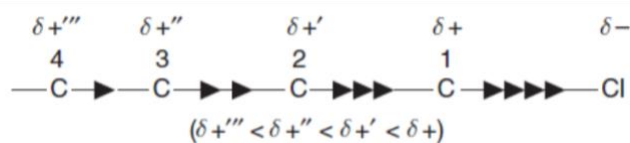
For example, C - X (X = halogen) bond is polar with C having a δ^+ charge and the halogen having a δ^- charge. The magnitude or value of these fractional charges increases with an increase in the electronegativity of the halogen i.e. for halogens, it is in the order $F > Cl > Br > I$.

Let us consider a carbon chain, with the end carbon joined to a more electronegative atom say Cl, then Cl will attract electrons (σ electrons between C and Cl) more towards itself. Hence, the

carbon atom will become slightly electron deficient and get a fractional positive charge (δ^+) due to a difference of electronegativity.

This polarization is not restricted till here, but it induces polarity further and hence the name as inductive effect.

Let us consider the case of chlorobutane to understand this.



Here, C1 acquires slight positive charge (δ^+) due to the electronegativity of Cl which in turn acquires slight negative charge (δ^-). C1 thus becomes electron deficient and it exerts a pull on the electrons forming covalent bond between C1 and C2 but less strongly. As a result, C2 acquires a lesser positive charge ($\delta\delta^+$) as that on C1. C3 similarly acquires even lesser positive charge ($\delta\delta\delta^+$) and so on. Thus, a polarity is slowly induced throughout the carbon chain.

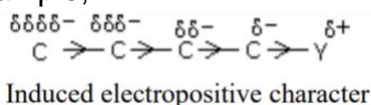
However, the effect is very less beyond carbon 3 or 4. In other words, the effect diminishes as one moves further in the carbon chain relative to the position of the group. The phenomenon of transmission of charge arising due to electronegativity difference in a covalent bond (i.e., dipole) through a chain of carbon atoms linked by sigma bonds is called inductive effect.

Such an effect is therefore propagated in the entire chain of carbon atoms, which were otherwise non-polar (in the absence of group Cl).

So, the atom/group responsible for the induction in polarity is Cl. Remember that group Cl attracting electrons towards itself is normal due to the difference of electronegativity but induction of polarity in an otherwise non-polar bond due to the attachment of a more electronegative atom in the chain is known as inductive effect. The atoms/groups like Cl which are more electronegative than carbon gain a slight negative charge on them and withdraw the electrons of the carbon chain towards themselves are known to exert -I Effect (pronounced as "minus I effect").

An atom or group having more electronegativity than hydrogen pulls away the bonded electron pair from the neighbouring atom and cause a gradual diminishing inductive shift of electron i.e., pairs of other bonds in the same direction is said to be exhibit a negative inductive effect (-I)

Similarly, if a more electropositive group (say Y) is attached to an otherwise non-polar carbon chain, the group Y gets a fractional positive charge and the carbon linked to it gets a fractional negative charge. This slightly electron rich carbon then acquires induced electropositive character and shares its excess electron density with the next carbon, which also acquires a fractional negative charge and so on. For example,



The atoms/groups which are more electropositive than carbon gain a slight positive charge on them and push the electrons of the carbon chain away from themselves are known to exert +I Effect (pronounced as "plus I effect").

An atom or group having less electronegativity than hydrogen repulse the bonded electron pair to the carbon chain is said to have a positive inductive effect (+I)

There are very few atoms or groups forming compounds with carbon which are more electropositive than carbon e.g., H and Mg. However, the most important group exhibiting +I effect is the alkyl group, which due to a difference in electronegativities of hydrogen and carbon, makes the carbon slightly electron rich.

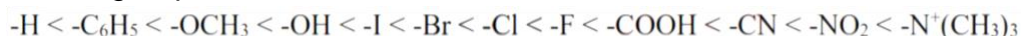
Inductive effect has the following characteristics:

1. It is a permanent effect.

2. It operates through sigma bonds. (Note that all the single, double and triple bonds have a sigma bond in them.)

3. Its magnitude goes on decreasing with increase in distance from the atom/group responsible for the same. Inductive effect is almost negligible after the third or fourth atom.

4. -I effect of some groups is in the order



+I effect of some of the groups is in the following order:



Inductive effect is not a hypothetical phenomenon but is actually operative in the molecules. This has been demonstrated by the fact that it is commonly used to explain the properties like origin of dipole moment, increase or decrease in bond lengths, strength of acids or bases, etc.

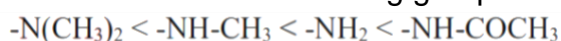
In order to classify most of the neutral groups into +I or -I just look at the following parameters required (given in following table) for the nature of first atom. If it is a charged group, then every positively charged group shall exert -I effect because it shall be electron attracting/withdrawing and similarly every negatively charged group shall exert +I effect because it shall be electron repelling.

Nature of Group	- I Effect	+ I Effect
<ul style="list-style-type: none">Neutral groups	<ul style="list-style-type: none">If the first atom of the group is more electronegative than sp^3 hybridised Ce.g. O, N, S, Hal, =C (sp^2 C), \equivC (sp C), -C of CCl_3	<ul style="list-style-type: none">If the first atom of the group is equal to or lesser electronegative than sp^3 hybridised Ce.g. H, Mg, 3°, 2° and 1° alkyl groups(Except $-CCl_3$)
<ul style="list-style-type: none">Charged groups	<ul style="list-style-type: none">All positively charged groupse.g. $-NH_3^+$, $-CH_2^+$	<ul style="list-style-type: none">All negatively charged groups$-O^-$, $-NH^-$, $-CH_2^-$

How to compare the extent of -I or +I in the comparable groups (having same first atom)?

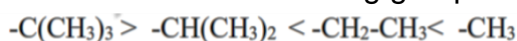
-I Effect: Here, due to the electronegativity of the first atom, the electrons are withdrawn or pulled towards itself. The further attached atoms or groups shall enhance the -I if they also pull by -I effect, but will decrease the -I effect if they are electron donating by +I effect.

For example, the order of -I effect between the following groups is



+I Effect: Here, due to the electropositivity of the first atom, the electrons are pushed away from itself. The further attached atoms or groups shall enhance the +I if they also push by +I effect, but will decrease the +I effect if they are electron withdrawing by -I effect.

For example, the order of +I effect between the following groups is

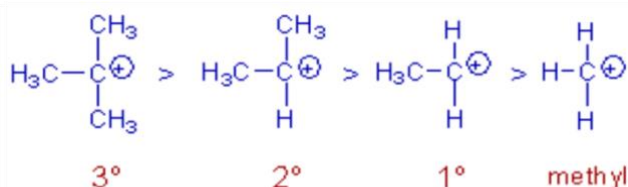


Applications of Inductive effects:

The phenomenon of inductive effect is very important in organic chemistry as it explains several facts, most important of which are given below:

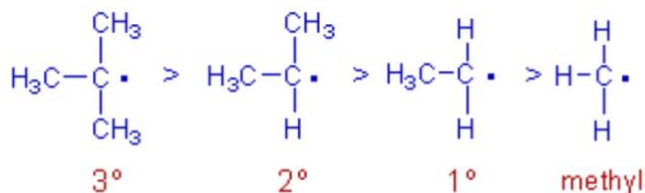
- Dipole moment:** As inductive effect leads to a dipole character in the molecule, it develops some dipole moment in the molecule. Dipole moment increases with increase in inductive effect. e.g., CH_3I [1.64D] < CH_3Br [1.79D] < CH_3Cl [1.83D] this is because -I effect of $Cl > Br > I$. the dipole moment (μ) of cis-2-butene is greater than dipole moment of trans-2-butene. This is because in trans-2-butene ($\mu = 0$), the +I effect of $-CH_3$ groups are cancelled as they act in opposition to each other.
- Bond length:** Since the inductive effect leads to ionic character in the bond, the increase in -I effect usually decreases the bond length. Thus, $CH_3I > CH_3Br > CH_3Cl > CH_3F$.

- (c) **Stability of carbocation:** 1. The stability of carbocation increases with increase in number of alkyl groups due to their +I effect. The alkyl groups release electrons to carbon, bearing positive charge and thus stabilizes the ion.



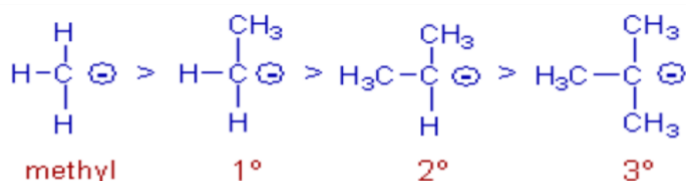
The order of stability of carbocation with decreasing order

2. In the same way the stability of free radicals increases with increase in the number of alkyl groups.



The order of stability of free radical with decreasing order

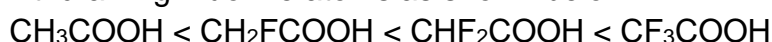
3. However the **stability of carbanions** decreases with increase in the number of alkyl groups since the electron donating alkyl groups destabilize the carbanions by increasing the electron density.



The order of stability of carbanion with decreasing order

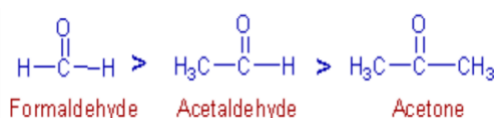
(d) **Acidic strength of carboxylic acids and phenols:**

The electron withdrawing groups (-I) decrease the negative charge on the carboxylate ion and thus by Stabilizes it. Hence the acidic strength increases when - I groups are present. However the +I groups decrease the acidic strength. a) The acidic strength increases with increase in the number of electrons withdrawing Fluorine atoms as shown below.



Basic strength of amines: The electron donating groups like alkyl groups increase the basic strength of amines whereas the electron withdrawing groups like aryl groups decrease the basic nature. Therefore, alkyl amines are stronger Lewis bases than ammonia, whereas aryl amines are weaker than ammonia. Thus, the order of basic strength of alky and aryl amines with respect to ammonia is as, $\text{CH}_3\text{NH}_2 > \text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2$

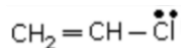
(e) **Reactivity of carbonyl compounds:** The +I group increase the electron density at carbonyl carbon. Hence their reactivity towards nucleophiles decreases. Thus, formaldehyde is more reactive than acetaldehyde and acetone towards nucleophilic addition reactions. Thus, the order of reactivity follows:



Resonance Effect:

In a normal π bond, the π electrons are localised between the constituent atoms. However, if double and single bonds are present alternately in a molecule, it is called conjugation e.g. in 1,3-butadiene, the double bonds are conjugated $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$

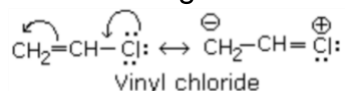
Similarly, if the double, single and a lone pair are present, alternatively, it is also called conjugation e.g., vinyl chloride.



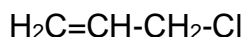
The presence of conjugation alters the properties of the compound and there is a difference in the actual and expected properties.

To explain the anomalous properties of such conjugated compounds, Robinson and Ingold gave the concept of **mesomerism**, which was subsequently modified and developed by Pauling as the theory of **resonance** which you already know.

The **theory of resonance** states that when a molecule can be represented by two or more classical structural (or electronic) formula, all of which can explain some but not all the properties, then the molecule has neither of these structures (called contributing or canonical or limiting structures) but is a hybrid of all these contributing structures.

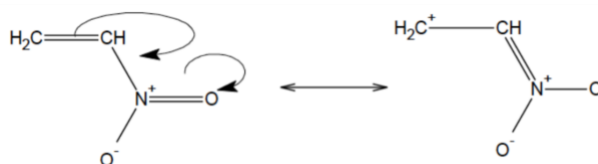


Note that the π electrons are not necessarily present where one would expect them, but are rather delocalised over the entire molecule which gives it extra stability expressed in terms of delocalisation energy or resonance energy. Also, normally, we find chlorine withdrawing electrons towards itself by -I effect but here we find that the same chlorine has got a positive charge and is involved in a double bond. Does this mean that chlorine has lost its -I effect? No, this is not true as -I effect is a permanent effect. In fact, in addition to the -I effect, it now also has an electron donating mesomeric or resonance effect (called +M or +R effect). Since the two effects are operating in opposite directions, one of them will overwhelm the other. Remember there was no such possibility if halogen's lone pair was not conjugated. For example, in the following case, the Cl is not conjugated to the double bond and hence in the following molecule, Cl is exerting its only -I effect.



The atoms/groups like Cl in which lone pair (or electrons of negative charge) is in conjugation with double or triple bond are electron donating and gain a formal positive charge in the resonating structure in the process and are known to exert +M/+R Effect.

Consider the case of $-\text{NO}_2$ joined to a conjugated system, where the nitro withdraws the conjugated electrons and gives rise to polarization as shown below:



The atoms/groups like $-\text{NO}_2$ which are in conjugation with double or triple bond and are electron withdrawing and gain a formal negative charge in the resonating structure in the process and are known to exert -M/-R Effect.

The resonance effect also alters the electron density distribution in the molecule significantly and its direction may be different from the normal inductive effect. In case the two effects are operating in opposite directions, the relative strengths of the two effects will determine which will dominate. Mesomeric/resonance effect introduces total delocalization of charges while inductive effect introduces partial polarization, hence, in general $M > I$. But there are exceptions to it like when halogens are attached to a conjugated system like benzene, $-I > +R$ (negative inductive effect is greater than resonance effect).

In order to classify most of the groups into +M/+R or -M/-R just look at the following parameters required (given in following table) for the nature of first atom.

+ M/+R Effect

- 1. If the first atom of the group either has a lone pair or negative charge.
- e.g. $-\text{NH}_2$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{NHCOCCH}_3$ etc.

- M/+R Effect

- 1. If the first atom of the group has positive charge and after withdrawing a pair of electrons, it is not violating its octet.
- e.g. $-\text{PH}_3^+$ and NOT $-\text{NH}_3^+$ (octet of N will be violated if it withdraws electrons)
- 2. If the first atom of a neutral group has neither a lone pair nor any charge, and is joined to more electronegative atom(s) than itself by double/triple bond.
- e.g. $-\text{CHO}$, $-\text{CN}$, $-\text{SO}_3\text{H}$, etc.

How to compare the extent of $-\text{M}$ or $+\text{M}$ in the comparable groups (having same first atom)?

$-\text{R}$ or $-\text{M}$ Effect: Any groups containing π -bonds when directly attached to the benzene ring (or unsaturated system) and withdraw electrons from ring by participation in delocalization through p-p overlapping is called $-\text{R}$ or $-\text{M}$ groups. The π -bonds of such groups are in conjugation with the π -electrons of unsaturated system. Such groups are said to exhibit minus resonance effects or minus mesomeric effects. $-\text{R}$ groups are $-\text{CN}$, $-\text{N}_2^+$, $-\text{COR}$, $-\text{CHO}$, $-\text{COOH}$, $-\text{COOR}'$, $-\text{NO}_2^-$, $-\text{SO}_3\text{H}$ etc.

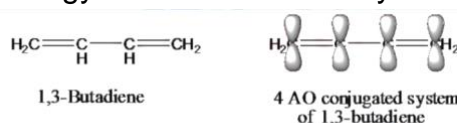
Here, due to the vacant p orbital on the first atom, the conjugated π electrons are withdrawn towards it. The further attached atoms or groups shall enhance the $-\text{M}$ if they also pull by $-\text{I}$ or $-\text{M}$ effect, but will decrease the $-\text{M}$ effect if they are electron donating by $+\text{I}$ or $+\text{M}$ effect. For example, the order of $-\text{M}$ effect between the following groups is $-\text{CHO} > -\text{COC}_2\text{H}_5$

$+\text{R}$ or $+\text{M}$ Effect: The groups or atoms directly attached to the benzene ring (or unsaturated system) through an atom having at least one lone pair of electrons behave as an electron releasing groups are called $+\text{R}$ or $+\text{M}$ groups. The lone pair of electrons in p-orbitals of such groups are in conjugation with the π -electrons of unsaturated system. Such groups are said to exhibit plus resonance effects or plus mesomeric effects. $+\text{R}$ groups are $-\text{OR}$, $-\text{OH}$, $-\text{O}^-$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{NHCOR}$, $-\text{SR}$, $-\text{CH}_2^-$ etc.

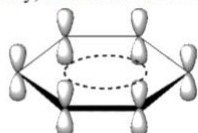
Here, due to the lone pair or $-$ charge in the p orbital of the first atom, the electrons are donated to the conjugated system away from itself. The further attached atoms or groups shall enhance the $+\text{M}$ if they push by $+\text{I}$ or $+\text{M}$ effect, but will decrease the $+\text{M}$ effect if they are electron withdrawing by $-\text{I}$ or $-\text{M}$ effect. For example, the order of $+\text{M}$ effect between the following groups is $-\text{N}(\text{CH}_3)_2 > -\text{NH}-\text{CH}_3 > -\text{NH}_2 > -\text{NH}-\text{COCH}_3$

Delocalization may involve:

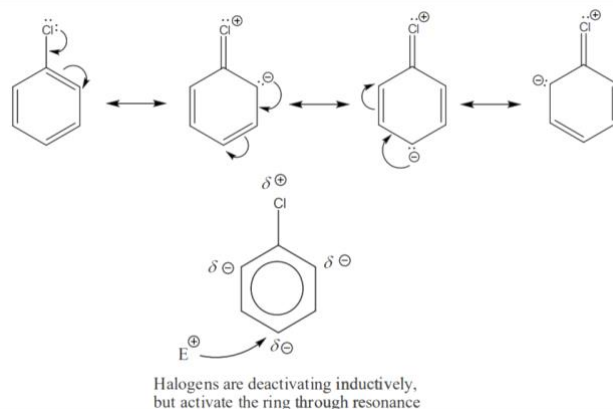
(i) Overlap of p orbitals involved in the formation of π bonds (π - π overlap). Delocalization of π electrons through π - π overlap occurs in conjugated systems (alternate single and double bonds) i.e. systems where π bonds are separated through a sigma bond only, for example, in 1,3-butadiene, each carbon is sp^2 hybridized and thus each carbon has a p orbital. These four p orbitals overlap each other to form π bonds. The π bonds are not localized between two carbons, C-1 and C-2, but are delocalized or distributed equally over all four carbons. It is this delocalization that helps in lowering of energy and stabilizes the system.



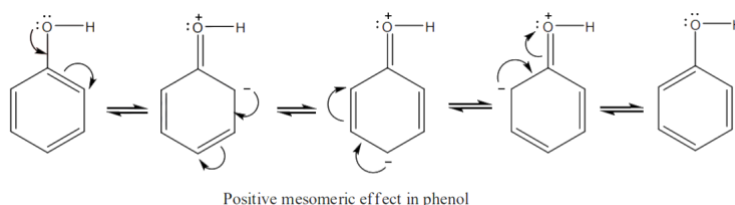
Similarly, in benzene the π electrons are delocalized over all the six carbon atoms.



(ii) Overlap of p orbital of an atom (vacant or filled) with p orbitals involved in π bond formation (p- π overlap) Delocalization of π electrons through p- π overlap occurs in a system where p orbital of an atom (vacant or filled) is separated from a π bond through one σ bond only. In other words, the p orbital may contain a lone pair of electron or a single electron or may be vacant, for example, in case of chlorobenzene or vinyl chloride, the lone pair of electrons is present in p orbital of chlorine. Although chlorine is highly electronegative (-I effect), the lone pair present in p orbital of chlorine is in conjugation with the π bond. As a result, it participates in delocalization by giving its lone pair towards the π bonded systems of vinyl or benzene ring and stabilizes the system. The chlorine behaves as an electron donor when it is in conjugation with the π bond.

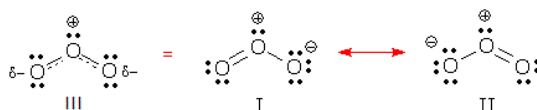


In general, halogens are o, p directing because the electron donating resonance effect is more dominant than the withdrawal through inductive effect of these electronegative elements. The mesomeric effect or resonance effect is a property of substituent or functional group in a chemical compound and is symbolized by the letter M. It is a kind of electron redistribution in unsaturated compounds conjugated with electron releasing or electron withdrawing groups or atoms. When the donation of electrons is by a lone pair, or a π system or by the groups or atoms during delocalization, positive mesomeric effect is shown +M (+R effect). Such +M groups contain lone pair of electrons or π bonds for example, -Cl, -Br, -OH, -OR, -SH, -NR, -N₂, aromatics, alkenes, etc.



Acidity of phenol is due to +M effect of -OH group. Mesomeric transfer of the lone pair on the oxygen atom of phenol to the π system of the benzene ring results in several resonance structures with a positive charge on the oxygen atom. This aids the H atom of OH group to leave as proton.

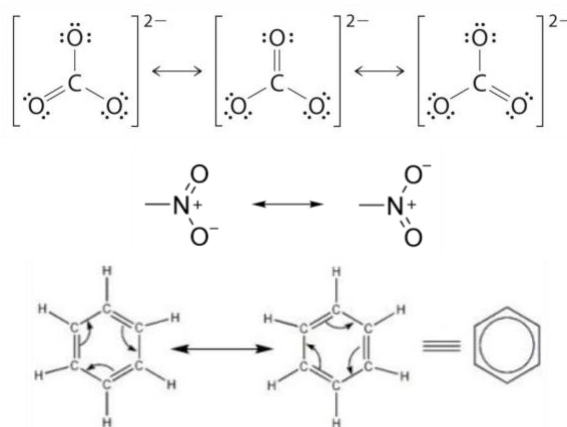
Based on the resonance forms, a beginning chemistry student might wonder if ozone has bonds of two different lengths, since single bonds are generally longer than double bonds. However, the ozone molecule is perfectly symmetrical, with bonds that are the same length. None of the resonance forms represent the true structure of the molecule. Rather, the negative charge of the electrons that would form a double bond are delocalized, or distributed evenly across the three oxygen atoms. The true structure is a composite, with bonds shorter than what would be expected for single bonds, but longer than the expected double bonds.



The resonance hybrid for ozone is found by identifying the multiple resonance structures for the molecule.

Thus, for O₃ the two structures (I and II) shown above constitute the canonical structures or resonance structures and their hybrid (i.e. the III structure) represents the structure of O₃ more accurately. Resonance is represented by a double-headed arrow between the resonance structures, as illustrated above.

More examples:



The resonance hybrid is more stable than its canonical forms, i.e. the actual compound (hybrid) is at a lower energy state than its canonical forms. Resonance stability increases with increased number of resonance structures.

The difference in the experimental and calculated energies is the amount of energy by which the compound is stable. This difference is known as resonance energy or delocalization energy.

All resonance structures are not equivalent. The following rules help determine whether or not a resonance structure will contribute significantly to the hybrid structure.

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.

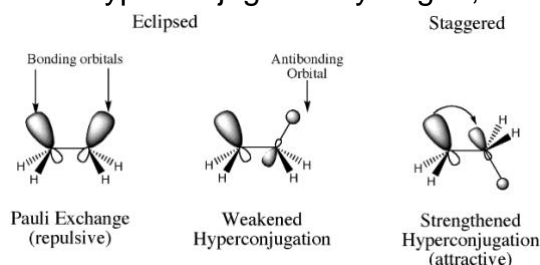
Rule 4: The most significant resonance contributor has the greatest number of covalent bonds.

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).

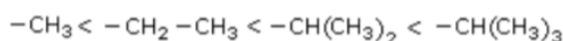
Rule 6: Aromatic resonance contributors are more significant than resonance contributors that are not aromatic.

Hyperconjugation

Hyperconjugation helps explain the stability of alkyl radicals. It involves the delocalization of sigma σ-electrons belonging to the C-H bond of the alkyl group attaching to an atom with an unshared pp orbital. The more the hyperconjugative hydrogen, the more is the stability.

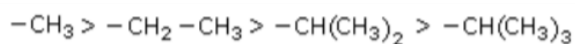


The normal electron releasing inductive effect (+I effect) of alkyl groups is in the following order:



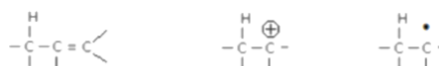
But it was observed by Baker and Nathan that in conjugated system, the attachment of alkyl groups reverses their capability of electron releasing. They suggested that alkyl groups are capable of releasing electrons by some process other than inductive.

When a C - H sigma bond is in conjugation, the sigma electrons of this bond enter into conjugation. This is an extension of normal conjugation and was termed hyperconjugation. Unlike the normal conjugation wherein, the π electrons get delocalized in p orbitals, here σ electrons move to p orbitals. It involves the delocalisation of C - H sigma electrons. It essentially means that hyperconjugation depends on the presence of alpha-hydrogen atoms. With the increase in number of such hydrogens, the electron releasing effect of alkyl group also increases e.g.,

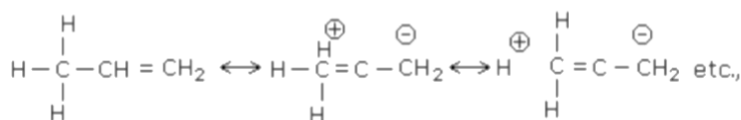


The contributing structures involving sigma electrons of C - H bond do not show any covalent bond between C and H. Hyperconjugation, therefore, is also called no bond resonance. It is important to note that hydrogen does not actually separate from the molecule because if that happens, the necessary condition for resonance to occur will be violated.

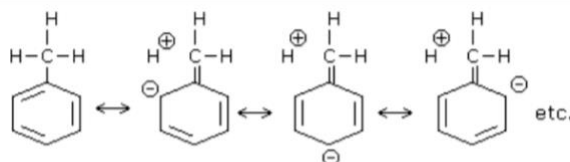
Hyperconjugation exists in the molecules having the following framework, i.e either alkenes or carbocations or free radicals having at least one α -H atom, but not in carbanions.



Examples:



Hyperconjugation in propene

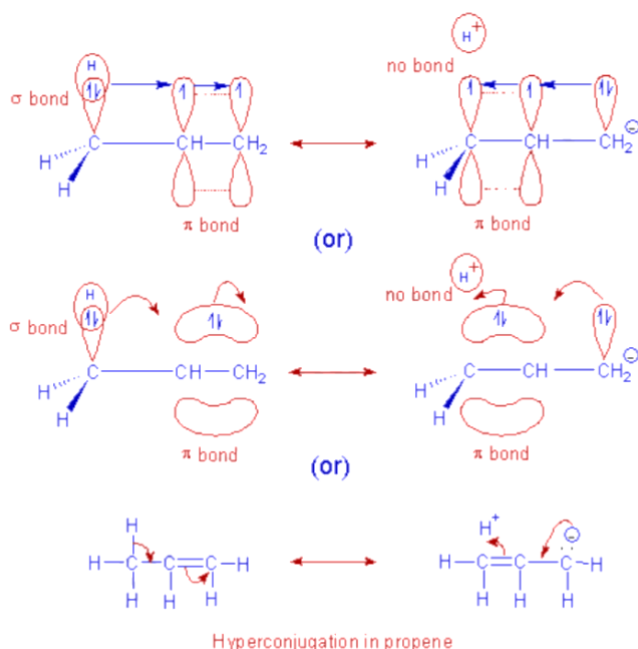


Hyperconjugation in toluene

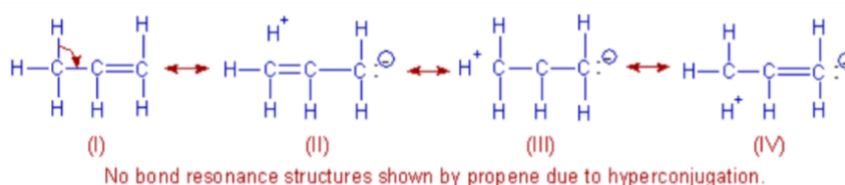
The $-\text{CH}_3$ group can be denoted as having +H effect as it donates or gives electrons to the conjugated system (**Sacrificial hyperconjugation**).

Requirements for Hyperconjugation:

There must be an α -C-H group or a lone pair on atom adjacent to sp^2 hybrid carbon or other atoms like nitrogen, oxygen etc. E.g., Alkenes, alkyl carbocations, alkyl free radicals, nitro compounds with α - hydrogen. Due to the presence of hydrogen on the α - carbon (which is next to the multiple bond) displacement of σ -electrons towards the multiple bond takes place which causes the polarization of the multiple bond. E.g., in propene, the delocalization of σ -electrons of C-H bond of methyl group occurs into the p-orbital of doubly bonded carbon which is shown below.



Likewise, remaining hydrogens on the methyl group also contribute in the hyperconjugation. It is possible because of free rotation of C-C bond so that the other CH bonds can also contribute in the hyperconjugation. Therefore, propene molecule can illustrate the below resonance structures, which suggests its stability.



Notice that in the above hyperconjugative structures: (II), (III) & (IV) of propene, the bond between an α -carbon and one of the hydrogen atom is absent. Thus, the hyperconjugation is also called as "no bond resonance".

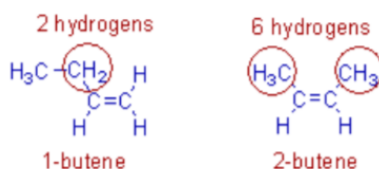
These equivalent contributing structures i.e., (II), (III) & (IV) are also polar in nature and hence are responsible for the dipole moment of propene (0.36 D). The bond length of C-C in propene is equal to 1.48. The range is 1.54 (of C-C) -1.34 (of C=C). Thus, due to hyperconjugation, the approximate bond order of C-C is 1.5. This kind of hyperconjugation is also known as sacrificial hyperconjugation as one bond is missing.

Hyperconjugation is also exhibited by carbocations attached to α -carbon having hydrogen atom and also by free radicals attached to α -carbon having hydrogen atom. Carbanions, however, do not exhibit hyperconjugation.

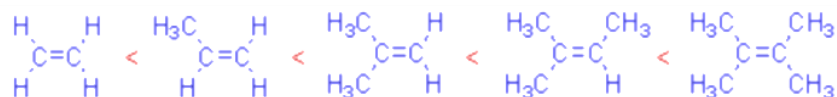
Applications of Hyperconjugation:

1) Stability of alkenes: As a general rule, greater the number of alkyl groups (containing hydrogens) attached on the double bond greater is the stability of alkene. This is because of increase in number of contributing no bond resonance structures. Therefore, 2-butene is more stable than 1-butene. For example, 2-butene is more stable than 1-butene.

This is because in 2-butene, there are six hydrogens involved in hyperconjugation whereas there are only two hydrogens involved in case of 1-butene. Hence the contributing structures in 2-butene are more and is more stable than 1-butene.



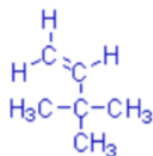
With the increase in the number of methyl groups on the double bonds, the stability of alkenes increases as shown below



The above order has been justified on the basis of heat of hydrogenation data of the given alkenes. With rise in the stability of alkene, the value of heat of hydrogenation decreases. For more substituted alkenes, heat of formation is higher than expected.

It must be kept in mind that the important condition for hyperconjugation to take place in alkenes is that the alkyl group attached to the double bond must have minimum one hydrogen atom.

For example, in case of the following alkene containing a tert-butyl group on doubly bonded carbon, the hyperconjugation is not possible.

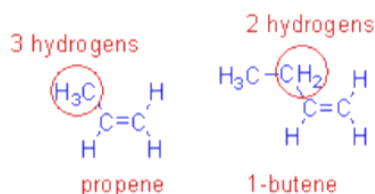


No H atoms on α carbon.
Hence no hyperconjugation.

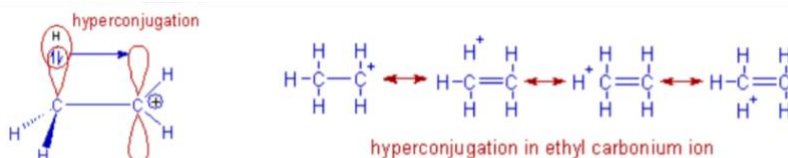
The effect of hyperconjugation is stronger than the inductive effect. It is because, in inductive effect there is partial delocalization of charges, but in hyperconjugation there is total transfer/delocalization of charge.

For example, considering inductive effect one may conclude that 1-butene is more stable than propene as the positive inductive effect of ethyl group is stronger than that of methyl group. But this is not correct; propene is more stable than 1-butene.

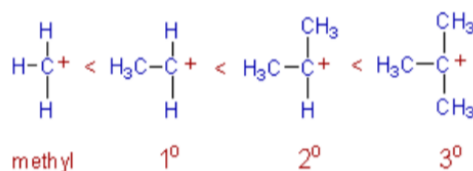
This is due to the fact that there are three hydrogens on α -methyl group involved in hyperconjugation. However, in 1-butene only two hydrogen atoms are there on $-\text{CH}_2$ group that can take part in hyperconjugation.



2) Stability of carbocations (carbonium ions): The ethyl carbocation, $\text{CH}_3\text{-CH}_2^+$ is more stable than the methyl carbocation, CH_3^+ . This is because, the σ -electrons of the α -C-H bond in ethyl group are delocalized into the empty p-orbital of the positive carbon centre and thus by giving rise to 'no bond resonance structures' as shown below. But, hyperconjugation is not possible in methyl carbocation and hence is less stable.



In general, As the number of alkyl groups (containing hydrogen) attached to the positively charged carbon increases, the stability of carbonium ions increases because of increase in the number of contributing structures to hyperconjugation. Note: This kind of hyperconjugation can also be known as **isovalent hyperconjugation**. As there is no decrease in the number bonds in the no bond resonance forms. Note: This type of hyperconjugation can also referred to as isovalent hyperconjugation since there is no decrease in the number bonds in the no bond resonance forms. Thus, the increasing order of stability of carbocations can be given as: methyl < primary < secondary < tertiary as depicted below:

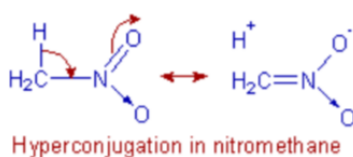


3) Stability of free radicals: The stability of free radicals is influenced by hyperconjugation just as in case of carbonium ions. One of the two σ -electrons of the α -C-H bond can be delocalized into the p-orbital of carbon containing an odd electron.

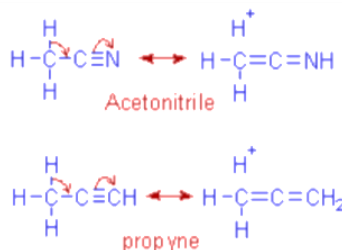
Due to hyperconjugation, the stability of free radicals also follows the same order as that of carbonium ions i.e., methyl < primary < secondary < tertiary.

4) Dipole moment & bond length: The dipole moment of the molecules is greatly affected due to hyperconjugation since the contributing structures show considerable polarity. The bond lengths are also altered due to change in the bond order during hyperconjugation. The single bond might develop partial double bond character and vice versa.

E.g., The experimental dipole moment hyper of nitro methane is higher than the calculated value because of hyperconjugation. The experimental C–N bond length is also less than the expected value because of same reason.



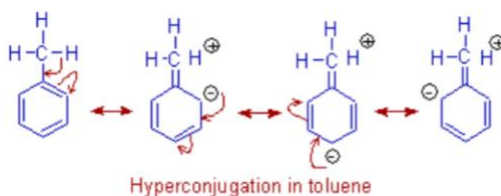
The same explanation can be given to decreasing of C-C bond adjacent to $-\text{C}\equiv\text{N}$ in acetonitrile and also the C-C bond adjacent to the $-\text{C}\equiv\text{C}$ in propyne. Here also, the observed dipole moments are different from their expected values due to hyperconjugation.



5) Reactivity & orientation of electrophilic substitution on benzene ring:

In case of Toluene, the reactivity of the ring towards electrophilic substitution increases and the substitution is directed at ortho and para positions to the methyl group. This can be explained mainly by hyperconjugative effect. The methyl group releases electrons towards the benzene ring partly due to inductive effect and mainly due to hyperconjugation.

The no bond resonance forms of toluene due to hyperconjugation are shown below.



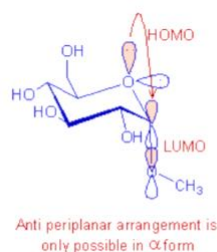
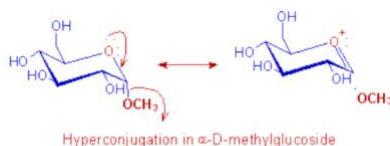
From hyperconjugative structures, it can be seen clearly that the electron density on benzene ring is increased at ortho and para positions. These positions thus attract the electrophiles more than meta position. The inductive effect is comparatively weaker effect and hyperconjugation overpowers it.

As a proof, consider the substitution (e.g. nitration) on the following disubstituted benzene occurs ortho to the methyl group and not ortho to the tert-butyl group. This is because, although tert-butyl group has greater inductive effect than methyl, the tert-butyl group cannot exhibit hyperconjugation.



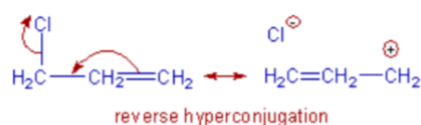
Also note that the tert-butyl group is bulky and hinders the approach of electrophile.

6) Anomeric effect: The overall tendency of anomeric substituents to favour an axial position is called Anomeric effect. For example, the α -methyl glucoside is more stable than the β -methyl glucoside due to hyperconjugation. The non-bonding HOMO with a pair of electrons on the ring oxygen is antiperiplanar to the antibonding LUMO of C-O bond in methoxy group. This arrangement of orbitals allows hyperconjugation between them and thus stabilizing the α form.



Whereas, in β -methyl glucoside the methoxy group is at equatorial position and cannot be involved in hyperconjugation since it is not antiperiplanar to the lone pair on ring oxygen. Therefore, β -methyl glucoside is less stable than the α -methyl glucoside.

Reverse Hyperconjugation: For α -halo alkenes, the delocalization of electrons takes place towards the halogen group through hyperconjugative mechanism because of electron withdrawing nature of halogen. It is known as reverse hyperconjugation. The dipole moments of α -halo alkenes are remarkably increased because of this phenomenon.

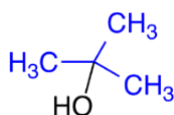


4. Steric Effects:

In general, the steric effect refers from the fact that the atoms composing molecules occupy some degree of space, and when atoms come too close together there's a rise in the energy of the molecule due to the atoms being forced to occupy the same physical space.

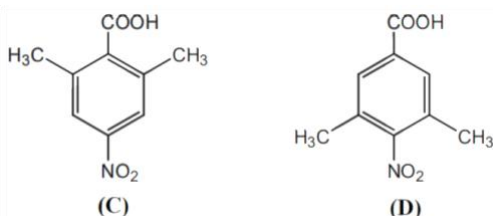
It turns out that steric effects can have a dramatic effect on the observed or preferred shape of a molecule and in some cases even its chemical reactivity. In its very simplest form, steric effects can be thought of as a 'crowding' effect kind of like that crowded room of people we mentioned earlier.

Consider as an example the molecule known as tert-butanol. The three bulky methyl groups labelled in blue are what makes this molecule so sterically crowded. Both the central carbon atom and the alcohol group are what we would call 'sterically shielded' due to the presence of the large methyl groups.



Tert-butanol is an example of a very sterically crowded molecule

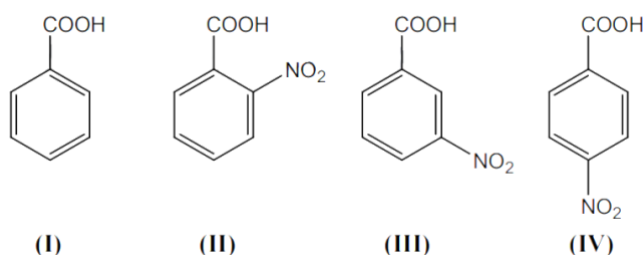
NO_2 lies in the plane of the ring, it is in resonance with the ring, decreases basic strength of $-\text{NH}_2$ by resonance, hence weaker base. Similarly, we can explain the acidic strength of C and D



C is stronger acid in spite of closeness of two electron donating methyl group to $-\text{COOH}$.

(b) Ortho effect: If any electron withdrawing group present on ortho position of the benzoic acid. It always increases acidic nature of acid because this group increases outer resonance of the ring toward acidic nature. Similarly, if any group present on ortho position of aniline, it decreases basic nature. This effect is known as ortho effect.

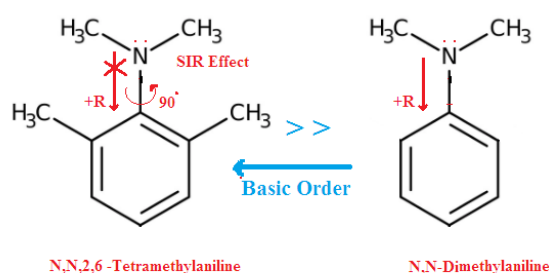
Problem: The correct order of acidity among the following compound I-IV is



(a) II > III > IV > I (b) IV > II > III > I (c) II > IV > III > I (d) IV > III > II > I

Solution. Because of ortho effect o-nitro benzoic acid is most acidic followed by para and meta. Thus order will be II > IV > III > I. Hence, option (c) is correct.

N,N,2,6-Tetramethyl aniline is more basic than N,N-Dimethyl aniline. In case of N,N-Dimethyl aniline its di alkyl derivatives the NMe_2 group is coplanar with benzene ring. So, p-electron (lone pair) on N atom and pi orbitals are remain in the same plane. For this the p-electron on N-atom can delocalized via pi orbital in the benzene ring and its result the electron availability in para position is high and less available at nitrogen atom and hence less basic.



On the other hand, in case of N,N,2,6 tetramethyl aniline having two bulky methyl group in ortho position of the benzene ring, the NMe_2 group cannot remain in the same plane. That is why the p-electron on N-atom cannot delocalized through pi orbital in para position. (due to steric inhibition of resonance). It is localized at nitrogen atom Thus 2,6-Dimethyl aniline derivative is more basic.

Basicity: $\text{Me}_3\text{N} > \text{Me}_2\text{NH} > \text{MeNH}_2$ (In aprotic solvent)

$\text{CF}_3\text{NH}_2 \ll \text{CH}_3\text{NH}_2$

$\text{MeO}^- > \text{OH}^-$

Stability: $\text{Ph}_3\text{C}^+ > \text{Ph}_2\text{CH}^+ > \text{PhCH}_2^+$; $(\text{CH}_3)_3\text{C}^+ > (\text{CH}_3)_2\text{CH}^+ > (\text{CH}_3)\text{CH}_2^+$

$\text{Ph}_3\text{C}^- > \text{Ph}_2\text{CH}^- > \text{PhCH}_2^-$; $(\text{CH}_3)_3\text{C}^- < (\text{CH}_3)_2\text{CH}^- < (\text{CH}_3)\text{CH}_2^-$

Acidity: $\text{CH}_3\text{COOH} > \text{C}_6\text{H}_5\text{OH}$

3,5-dimethyl 4-nitro aniline is a stronger base than **2,6-dimethyl 4-nitro aniline** because, in **3,5-dimethyl 4-nitro aniline**, the nitro group cannot enter into resonance due to steric inhibition of resonance.

