Electron displacement in molecules

Dr. Kanika Ghosh
Assistant Professor
Department of Chemistry
Bidhan Chandra College, Asansol
Email: kanika@bccollegeasansol.ac.in

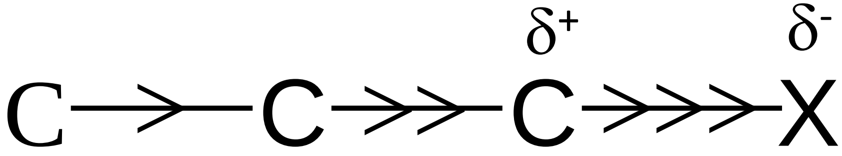
Electron displacement in molecules

- Concepts of Inductive Effect,
- Electromeric Effect,
- Hyperconjugation,
- Resonance,
- Steric inhibition of resonance,
- Tautomerism &
- Aromaticity

Concepts of Inductive Effect

The permanent dipole induced in a bond by another directly along a chain of atoms within a molecules is called inductive effect

Example:



$$\mathrm{C} \rightarrow \mathrm{C} \rightarrow\rightarrow \overset{\delta^{+}}{\mathrm{C}} \rightarrow\rightarrow\rightarrow \overset{\delta^{-}}{\mathrm{X}}$$

Here X is electronegative atom or group

The inductive effect is a permanent effect in the ground state of a molecule and supposed to operate through single bonds. So inductive effect is called permanent polarisation of single bonds. But the effect **decreases** with **increase in distance from electronegative** atom or group.

The effect is called **-I** if a group or atom pulls the electrons from the carbon chain. Such group are called **Electron withdrawing group or -I effect.**

Increasing order of **-I effect:**

$H < R_2C{=}CH < Ar < RC{\equiv}C < OH < SR < SH < OR < COOR < OAr < I < Br < Cl < F < COOH < CN < NO_2 < \overset{+}{N}H_3 < \overset{+}{N}R_3$

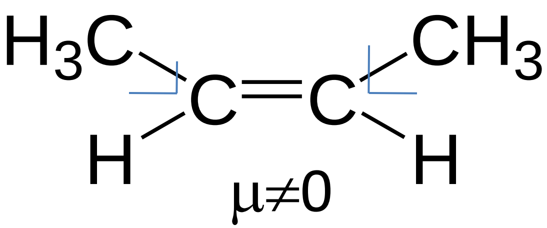
The effect is called **+I** if a group or atom pushes the electrons towards the carbon chain. Such group are called **Electron Releasing group or +I effect.**

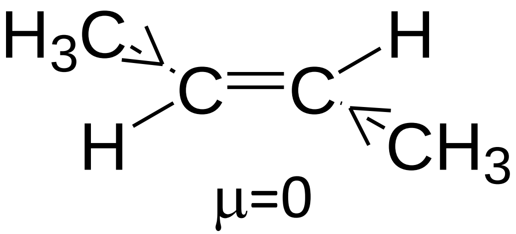
Decreasing order of **+I effect**

$COO^- > R_3C > R_2CH > RCH_2 > D > H$

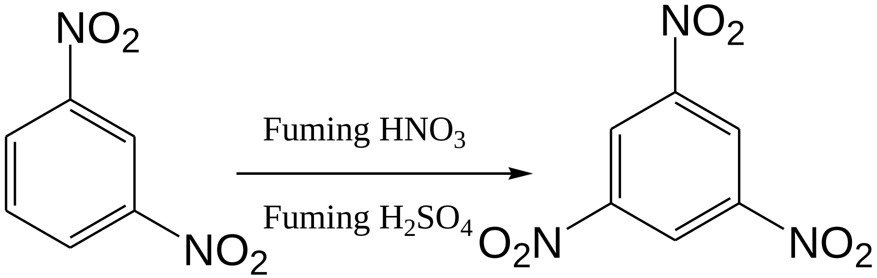
Concepts of Inductive Effect: Application

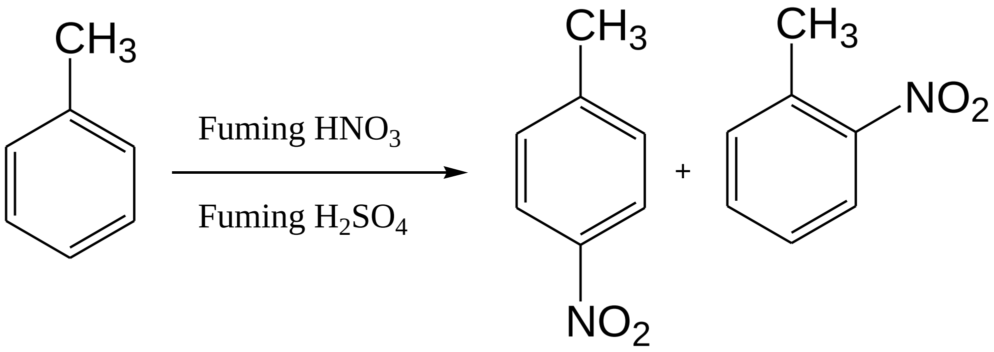
- **Dipole moment**: Dipole moment increases with increase in inductive effect of alkyl group Incase of *cis*-isomer but for *trans*-isomer effects are cancelled.



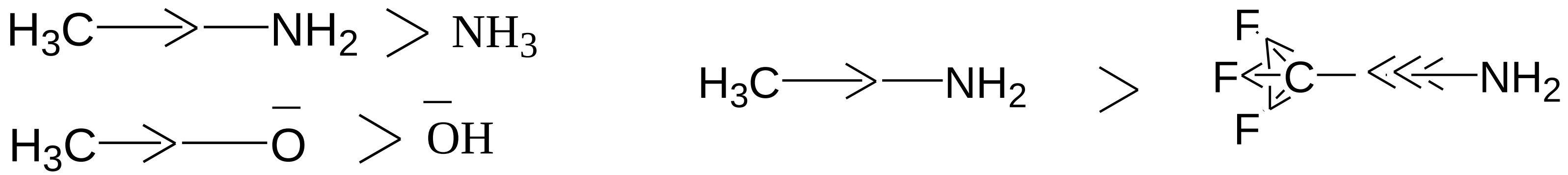


- **Chemical Reactivity**: The **-I effect** of –NO$_2$ group in *meta*-dinitrobenzene makes the molecule much less reactive and *meta* directing. But in toluene due to presence of activating group-CH$_3$(**+I effect**), nitration occurs at *ortho*- and *para* position.



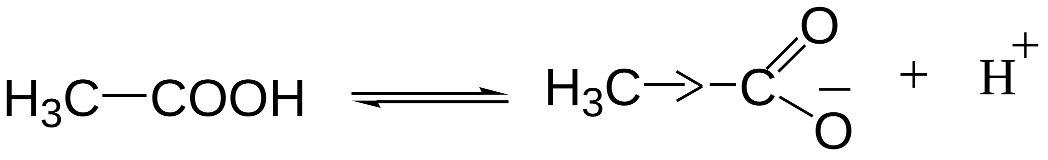


➢**In comparing of basicity of bases**: Due to presence of activating group-CH_3(**+I effect**) basicity of methoxide and methyl ammine increases.

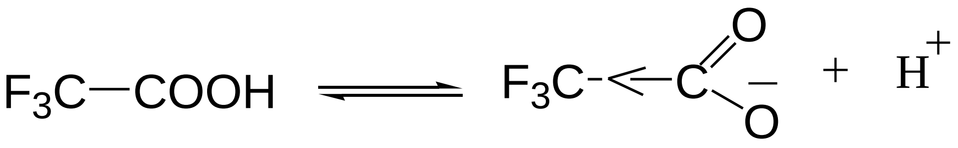


➢**In comparing of acidity of acids**: Due to presence of electron density releasing group-CH_3(**+I effect**), acidity of acetic acid decreases.

$$F_3C{-}COOH \quad > \quad H_3C{-}COOH$$



The + I effect of –CH_3 group, destabilises the conjugate base of acetic acid



The - I effect of –CF_3 group, stabilises the conjugate base of trifluroacetic acid .

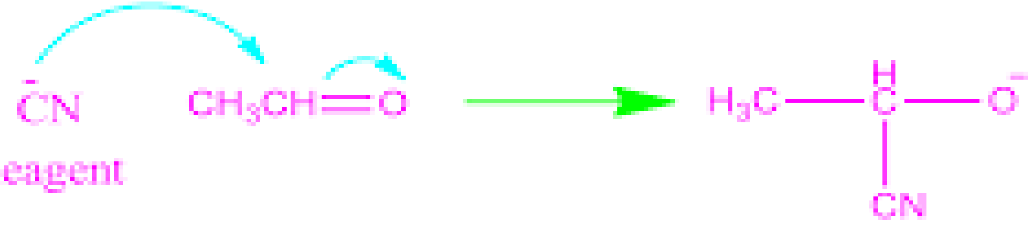
Concepts of Electromeric Effect

The temporary or time-variable effect involving the complete transfer of a shared pair of π electrons to one of the atoms joined by a multiple bond, double or triple at the requirement of an attacking reagent is known as **electromeric effect**.

- Temporary Effect
- Only presence of an attacking agent
- Occur in compound having multiple bond
- Two types of effect (+E effect and –E effect)

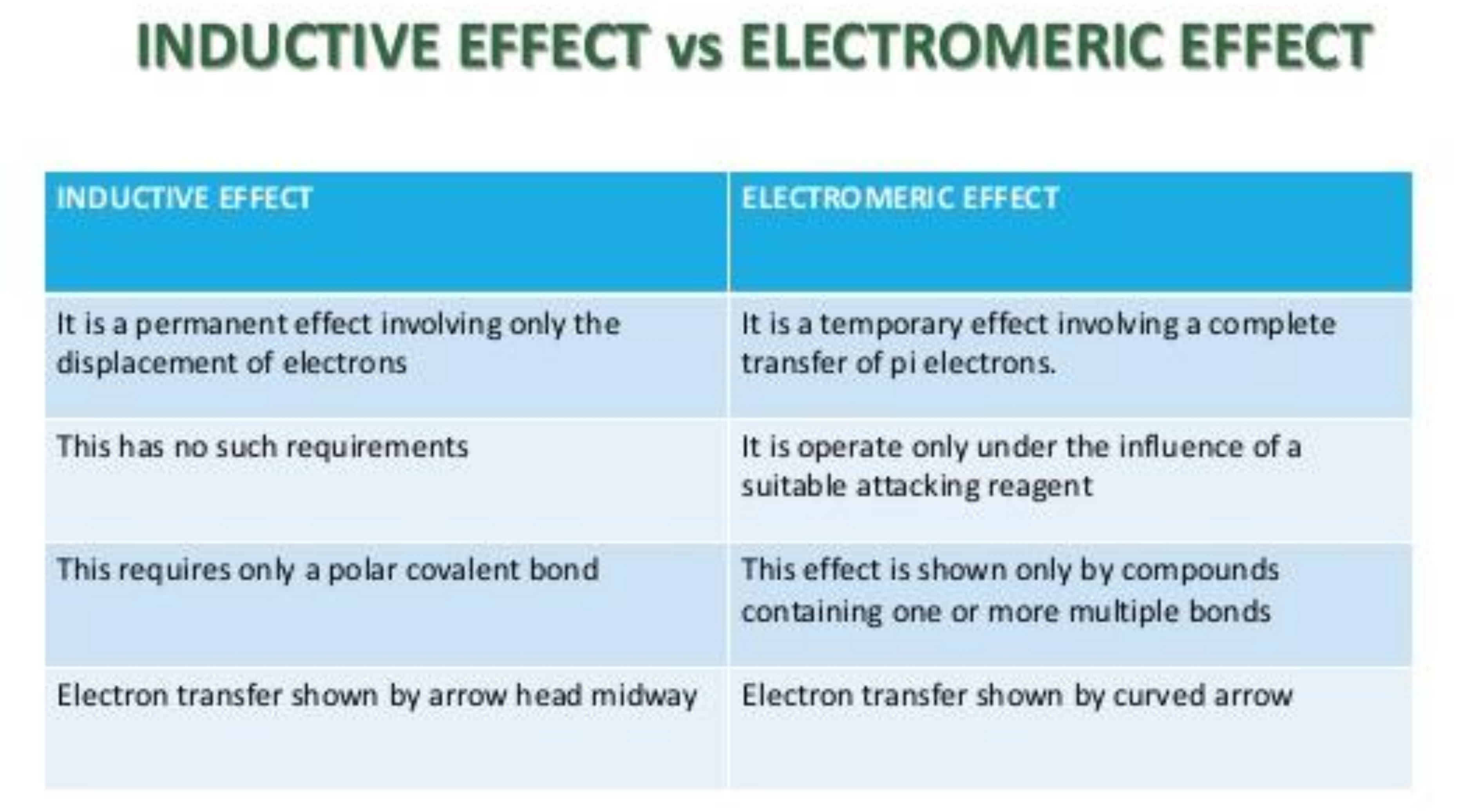
+E effect :

- E effect :



❖Application:

Electromeric effect, the close approach of the reagent to a multiple bond, enhances the reactivity of the reactant molecules and explain its addition reactions product.



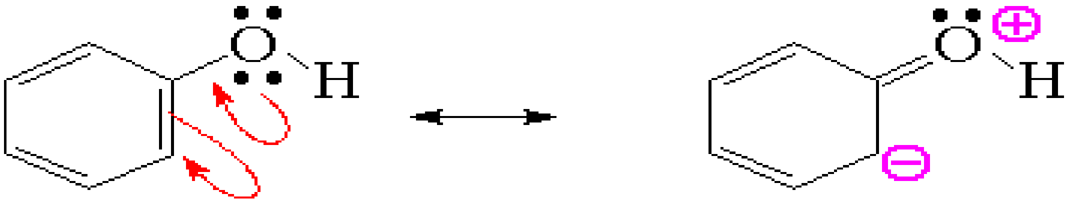
INDUCTIVE EFFECT vs ELECTROMERIC EFFECT

INDUCTIVE EFFECT	ELECTROMERIC EFFECT
It is a permanent effect involving only the displacement of electrons	It is a temporary effect involving a complete transfer of pi electrons.
This has no such requirements	It is operate only under the influence of a suitable attacking reagent
This requires only a polar covalent bond	This effect is shown only by compounds containing one or more multiple bonds
Electron transfer shown by arrow head midway	Electron transfer shown by curved arrow

Concepts of Resonance and Mesomeric Effect

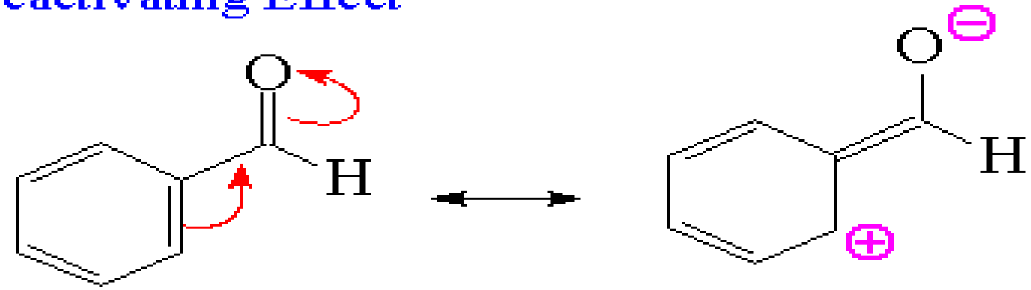
We may recall that the resonance is a hypothetical state of chemical entity in which its electronic structure can be hypothetically represented by two or more Lewis' dash-dot structures, each differing in the distribution of electrons; the properties of entity will not be expected from any of the structures but it will expected from combination called a **resonance hybrid** of them, each of structures of the hybrid being known as **resonating or canonical structure.**

Activating Effect



A negative ring is more likely to react with an electrophile (positive).

Deactivating Effect



A positive ring is less likely to react with an electrophile (positive).

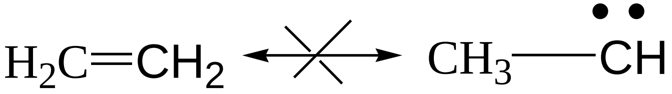
Methods of writing Resonance hybrid

Lewis's Structure

All the canonical structures must be written according to the Lewis's method showing bonds, lone pair of electrons and formal charges were required.

Position of atom

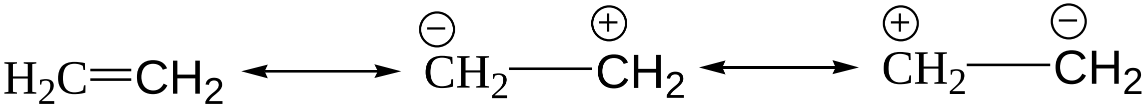
The positions of atomic nuclei of the chemical entity must remain unchanged in all the resonating structures.



$$H_2C{=}CH_2 \nleftrightarrow CH_3{-}\ddot{C}H$$

π Bonds

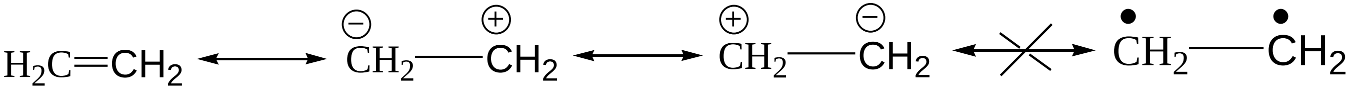
To write the resonating structures, only π bonds can be converted to lone-pairs of electrons and vice versa.



$$H_2C{=}CH_2 \longleftrightarrow \overset{\ominus}{C}H_2{-}\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2{-}\overset{\ominus}{C}H_2$$

Unpaired electrons

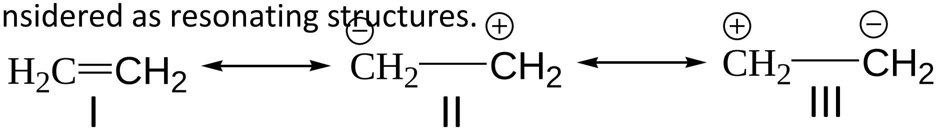
The number of unpaired electrons in each resonating structure must be same.



$$H_2C{=}CH_2 \longleftrightarrow \overset{\ominus}{C}H_2{-}\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2{-}\overset{\ominus}{C}H_2 \nleftrightarrow \dot{C}H_2{-}\dot{C}H_2$$

Energy of Resonating Structure

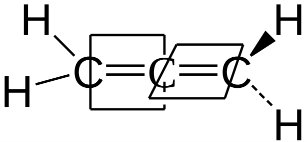
The several resonating structures must be comparable energies. Structures II and III are very high, should not be considered as resonating structures.



$$\underset{\text{I}}{H_2C{=}CH_2} \longleftrightarrow \underset{\text{II}}{\overset{\ominus}{C}H_2{-}\overset{\oplus}{C}H_2} \longleftrightarrow \underset{\text{III}}{\overset{\oplus}{C}H_2{-}\overset{\ominus}{C}H_2}$$

Planarity

All atoms involved in the resonance must lie on the same plane or nearly on the same plane.

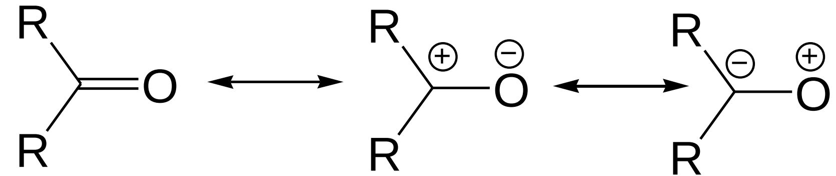


don't form resonating structures

Contributing Resonance Structures

Covalent Bonds

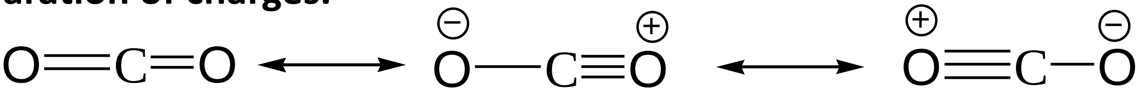
The larger the number of the covalent bonds in the structure, greater is the stability



Most important

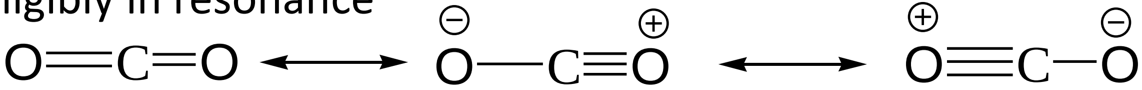
Electronegativity Of bonded atoms

The structures having same number of covalent bonds involving separation of positive and negative charges are less stable than those which do not involve any separation of charges.


$O=C=O \longleftrightarrow \overset{\ominus}{O}-C\equiv\overset{\oplus}{O} \longleftrightarrow \overset{\oplus}{O}\equiv C-\overset{\ominus}{O}$

Octet Rule

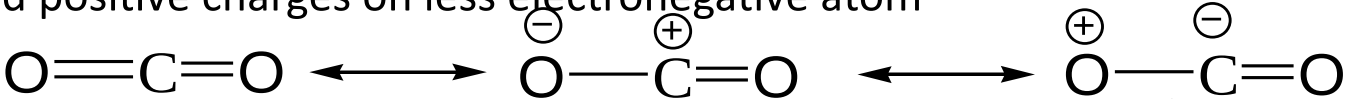
Structure having second row element don't follow octet rule, contributes negligibly in resonance


$O=C=O \longleftrightarrow \overset{\ominus}{O}-C\equiv\overset{\oplus}{O} \longleftrightarrow \overset{\oplus}{O}\equiv C-\overset{\ominus}{O}$

Almost not contributing structure

Formal Charges

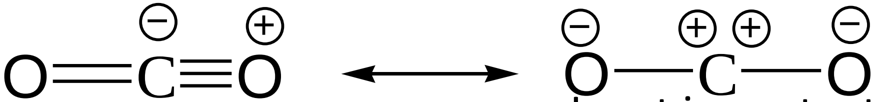
Structure having positive charges on most electronegative atom and positive charges on less electronegative atom


$O=C=O \longleftrightarrow \overset{\ominus}{O}-\overset{\oplus}{C}=O \longleftrightarrow \overset{\oplus}{O}-\overset{\ominus}{C}=O$

Most important

Least important

Structure having like charges crowded together are highly unstable


$O=\overset{\ominus}{C}\equiv\overset{\oplus}{O} \longleftrightarrow \overset{\ominus}{O}-\overset{\oplus\,\oplus}{C}-\overset{\ominus}{O}$

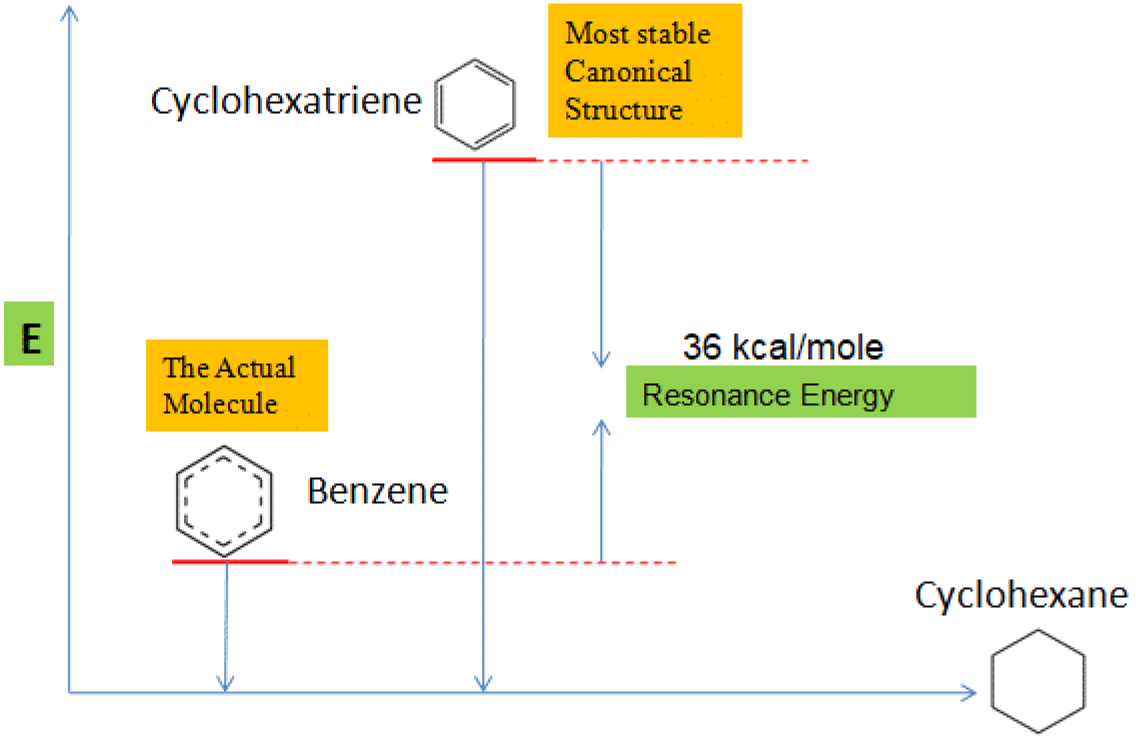
Least important

Resonance Energy

Resonance Energy = Observed heat of formation - Calculated heat of formation of the most stable resonating structure of hybrid

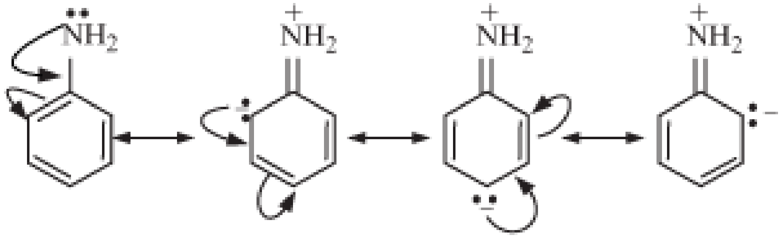
Resonance Energy = Observed heat of combustion - Calculated heat of combustion of the most stable resonating structure of hybrid

Resonance Energy = Observed heat of combustion - Calculated heat of combustion of the most stable resonating structure of hybrid



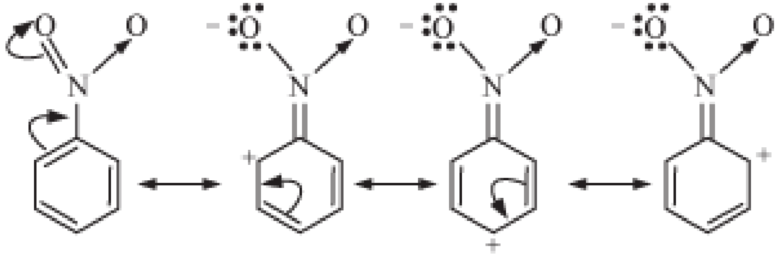
Resonance Effect

Positive Resonance Effect (+R Effect): Transfer of electrons is away from an atom or substituent group attached to the conjugated system.



+R effect showing groups: − halogen, − OH, − OR, − OCOR, − NH_2, − NHR, − NR_2, − NHCOR

Negative Resonance Effect (− R Effect): Transfer of electrons is towards the atom or substituent group attached to the conjugated system.



− R effect showing groups: − COOH, − CHO, $>C=O$, − CN, − NO_2

Inductive Effect VS Resonance Effect

	Inductive Effect	Resonance Effect
Definition	Inductive effect is an effect that occurs due to the transmission of an electrical charge throughout a chain of atoms	Resonance effect is an effect on stability of molecules with both single and double bonds
Cause	Occurs due to polarisation of bonds	Occurs due to presence of both single and double bonds in alternating pattern
Factors	Electronegativity values of atoms in a molecule affect the inductive effect	Number of double bonds and the pattern of their positions affect the resonance effect

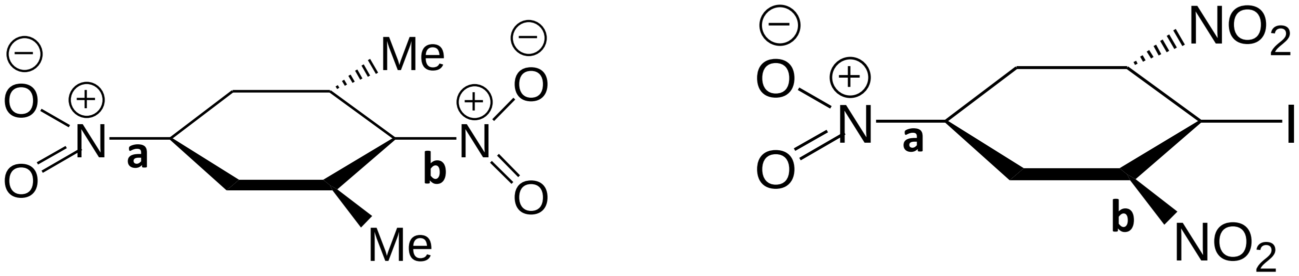
Steric Inhibition of Resonance

The most important condition for resonance is that the involved atoms in resonating structures must be coplanar or nearly coplaner for maximum resonance energy. If this condition does not fulfil, the involved orbitals cannot be parallel to each other and as a consequence delocalisation of e's or positive charges can not occur. There are many examples in which the resonance is inhibited or reduced because the involved atoms or orbitals are sterically forced out of planarity and the phenomenon is called steric inhibition of resonance.

Steric inhibition has profound effects on

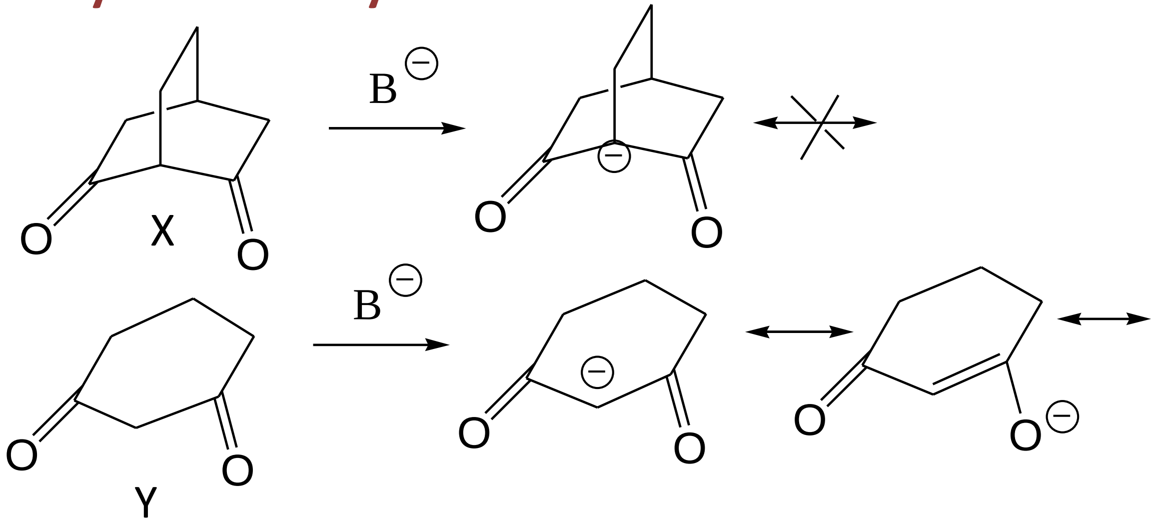
(a) Physical Properties
(b) Acidity and basicity
(c) The reactivity of organic compound

❑ Physical Properties & Steric inhibition of Resonance



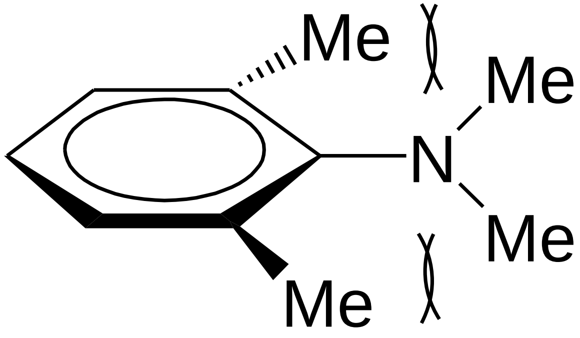
C-N bond "a" is shorter and stronger than C-N bond "b"

Acidity and basicity & Steric inhibition of Resonance



Y is much more acidic than X

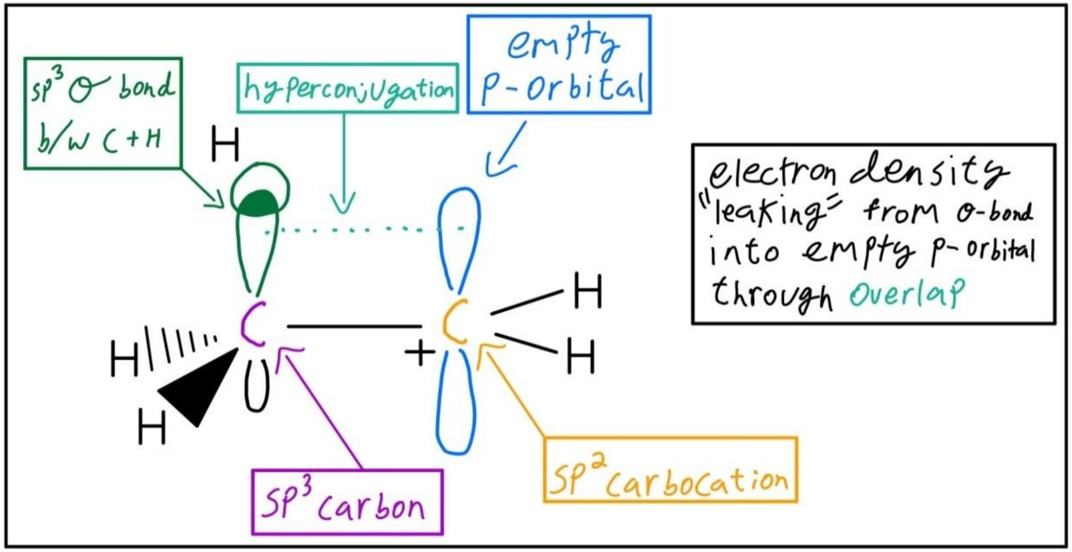
The reactivity of organic compound & Steric inhibition of Resonance



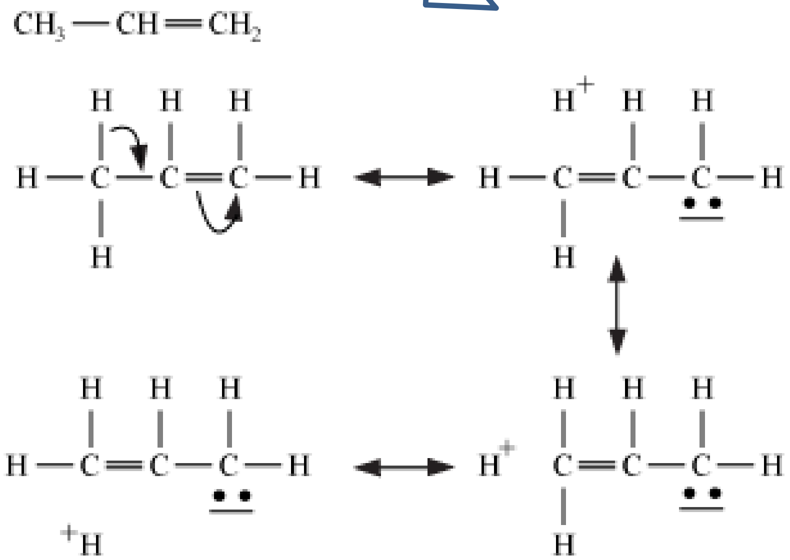
This compound does not couple with benzene diazonium ion as lone pair of N atom does not maintain planarity and hence does not takes part in resonance with the –Ph ring.

Hyperconjugation: No bond resonance

- The electrons of the sigma bond between C and H are involved in delocalization.
- In structure to the right: No bond between C and H due to migration of the sigma bond. Hence Hyperconjugation is also called as 'NO BOND RESONANCE'.
- This does not indicate that hydrogen is completely detached from the structure, but some degree of ionic character in the C – H bond and some single bond character between carbon – carbon double bond.



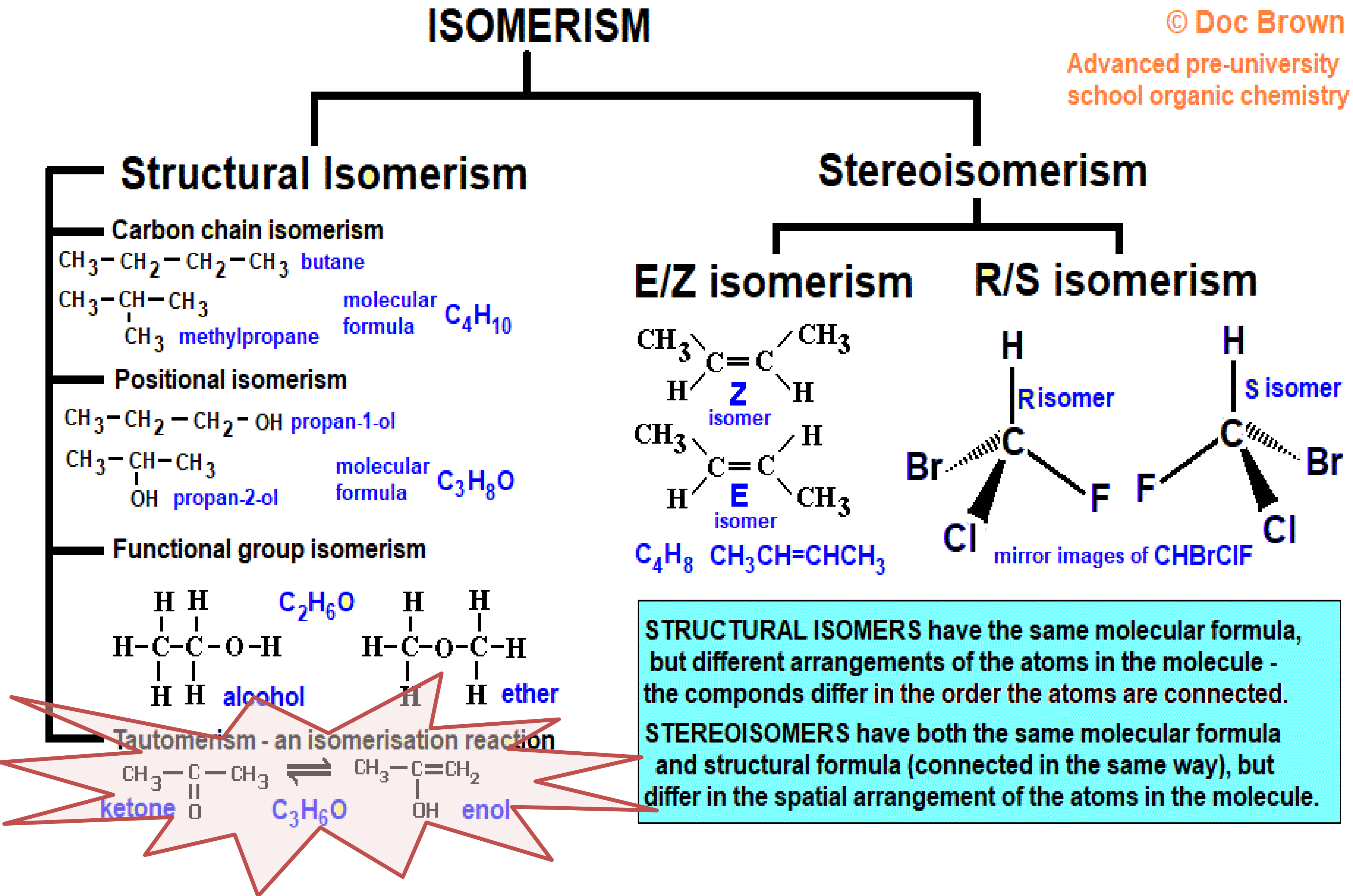
electron density "leaking" from σ-bond into empty p-orbital through overlap



HYPERCONJUGATION
VERSUS
RESONANCE

Hyperconjugation is the stabilization effect on a molecule due to the interaction between a sigma bond and a pi bond	Resonance is the stabilizing of a molecule through delocalization of bonding electrons in the pi orbital
Involves sigma bond orbitals and p orbitals or pi bond orbitals	Involves only pi bond orbitals
Causes the sigma bond length to be shortened	Has no effect on sigma bonds

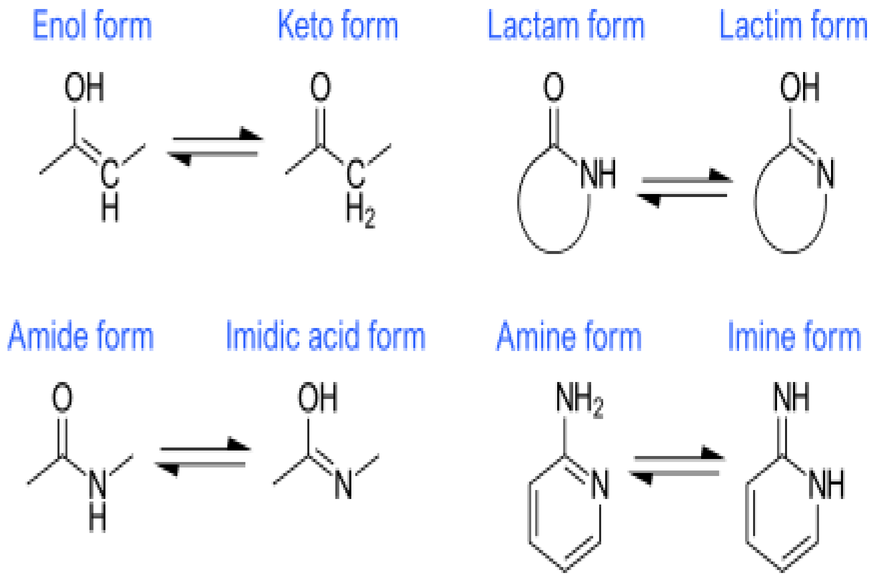
Tautomerism

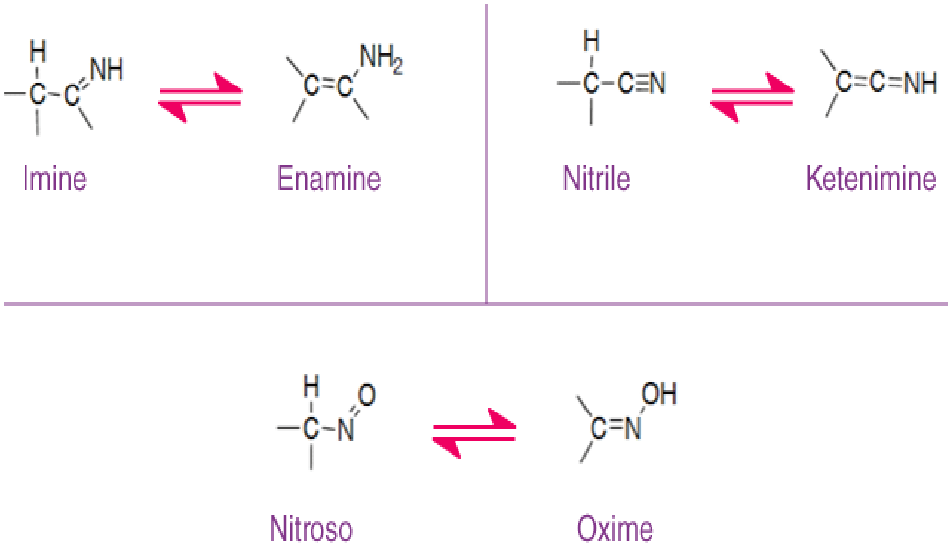


STRUCTURAL ISOMERS have the same molecular formula, but different arrangements of the atoms in the molecule - the componds differ in the order the atoms are connected.

STEREOISOMERS have both the same molecular formula and structural formula (connected in the same way), but differ in the spatial arrangement of the atoms in the molecule.

Types of Tautomerism





Tautomerism	Resonance
	
Change in the position of atoms	Change in the position of the unshared or π electrons
Definite compounds	Imaginary compounds
Can be separated	Can't be separated
It is real.	**It is hypothetical.**

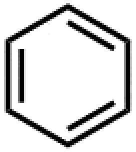
Aromaticity

Aromatic compounds are unusually **STABLE** and have important chemical and synthetic uses.

According to Huckel's Rules:

Four Rules For Aromaticity

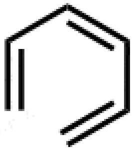
Condition #1: The molecule must be cyclic No exceptions!



cyclic

Benzene

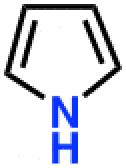
Aromatic



acyclic

(Z)-1,3,5 hexatriene

Not aromatic



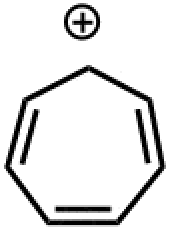
cyclic

Pyrrole

Aromatic

acyclic

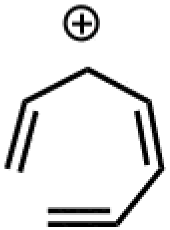
Not aromatic



cyclic

"Tropylium" ion

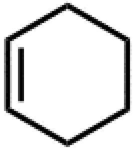
Aromatic



acyclic

Not aromatic

Just to be clear: not all cyclic molecules are aromatic...



cyclohexene
(not aromatic)

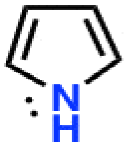
tetrahydrofuran
(not aromatic)

Four Rules For Aromaticity

Condition #2: Every Atom In The Ring Must Be Conjugated

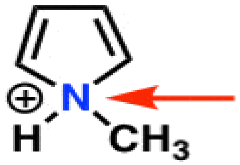
(alternative): every atom in the ring must have an available p orbital **(Vacant or filled)**

(alternative): every atom in the ring must be able to participate in resonance



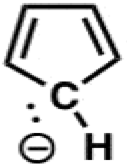
Aromatic

All ring atoms conjugated



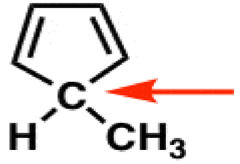
Not aromatic

Nitrogen atom is not conjugated



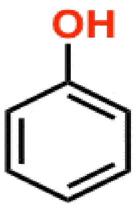
Aromatic

All ring atoms conjugated



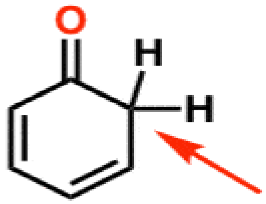
Not aromatic

Carbon is not conjugated (sp^3)



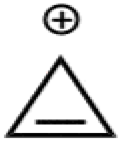
Aromatic

All ring atoms conjugated



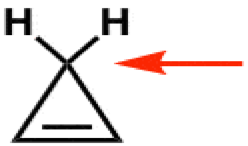
Not aromatic

Carbon is not conjugated



Aromatic

All ring atoms conjugated



Not aromatic

Carbon is not conjugated

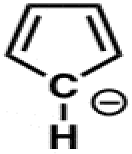
Note: Any atom in the ring is SP^3 hybridised, will ne non-Aromatic

4 Rules For Aromaticity

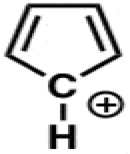
Condition #3: The Molecule Must Contain [4n + 2] Pi electrons *

- where [4n+2] is a formula describing the number series: 2, 6, 10, 14, 18, 22, 26....
- These are "magic numbers" for aromaticity: the number of pi electrons in the molecule **must be in this series** in order for the molecule to be aromatic (We often call numbers in this series, "Huckel numbers")

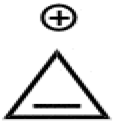
6 pi electrons



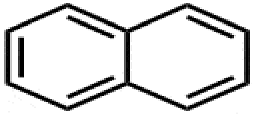
6 pi electrons



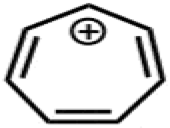
4 pi electrons



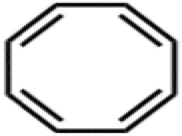
2 pi electrons



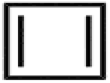
10 pi electrons



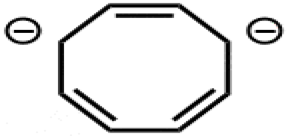
6 pi electrons



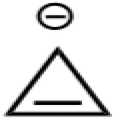
8 pi electrons



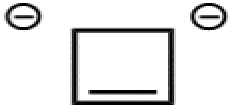
4 pi electrons



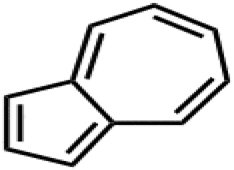
10 pi electrons



4 pi electrons



6 pi electrons



10 pi electrons

*** Another way of saying the same thing:**

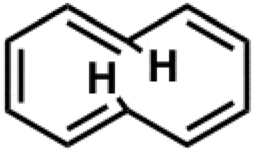
- the number of pi electrons is equal to an odd-numbered pair: 1 pair, 3 pairs, 5 pairs, 7 pairs.... (This also produces the series 2, 6, 10, 14 ...)

Four Rules For Aromaticity

Condition #4: The molecule must be Planar

Generally, if the first three conditions are met then it's usually safe to assume that the molecule is Planar.

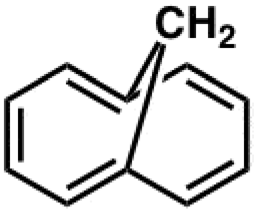
A prominent exception is the isomer of [10]-annulene below left.



not aromatic

Although it is cyclic, conjugated, and has 10 pi electrons, it is not flat
due to repulsions between hydrogens that arise when it is in the flat conformation.

Since it is not flat, it is not aromatic.

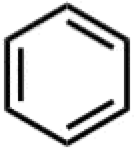
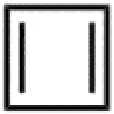
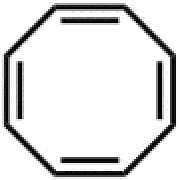


aromatic !

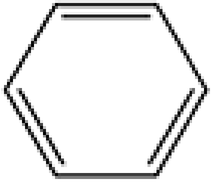
However, replacing the hydrogens with bonds to a bridging carbon allows all C-C pi bonds to be in the same plane - aromatic!

According to Huckel’s Rule:

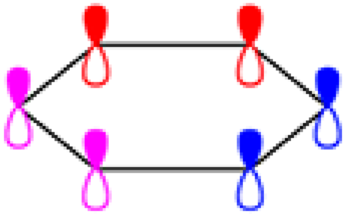
Summary

Aromatic	**Anti-Aromatic**	**Non-Aromatic**
unusually stable	***unusually unstable***	***everything else***
·Cyclic **·Conjugated** **·(4n+2) Pi electrons** **· Planar**	**·Cyclic** **·Conjugated** **·(4n) Pi electrons** **· Planar**	*Fails any one of the 4 criteria on the left*
e.g. 	e.g. 	e.g. 
benzene	**cyclobutadiene**	**cyclooctatetraene**
(resonance energy of 36 kcal/mol)	(only stable below –100 °C)	(adopts a tub-like shape to "escape" anti-aromaticity)

Examples

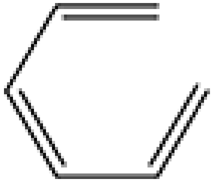


benzene

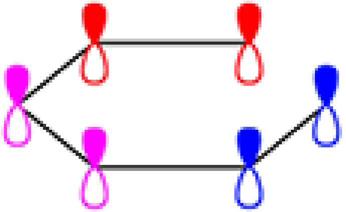


1. Cyclic
2. *p*-orbital for each member of the ring
3. Planar ring (sp^2 hybridized)
4. **4n+2 π–bond electron count.**

Aromatic

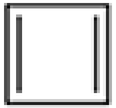


hexatriene

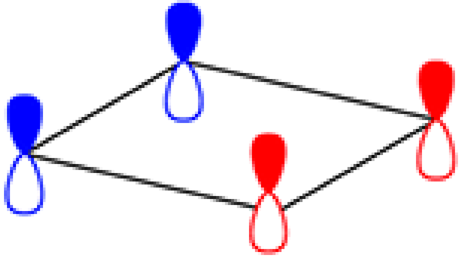


1. NOT Cyclic
2. *p*-orbital for each member of the ring
3. Planar ring (sp^2 hybridized)
4. **4n+2 π–bond electron count.**

Non-Aromatic

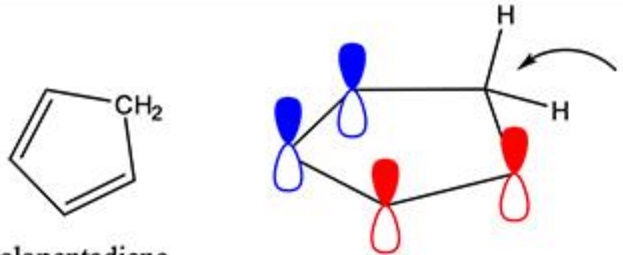


cyclobutadiene



1. Cyclic
2. *p*-orbital for each member of the ring
3. Planar ring (sp^2 hybridized)
4. **Closed 4n π–bond electron count.**

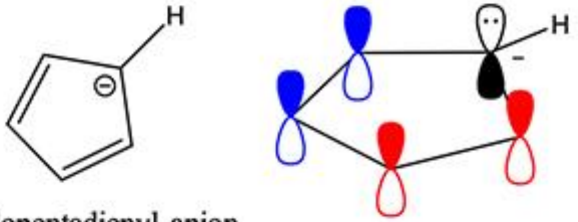
Anti-Aromatic



cyclopentadiene

1. Cyclic
2. NOT *p*-orbital for each member of the ring
3. NOT Planar ring (sp^2 hybridized)
4. **NOT Closed 4n+2 π–bond ring.**

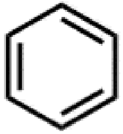
Not Aromatic



cyclopentadienyl anion

1. Cyclic
2. *p*-orbital for each member of the ring
3. Planar ring (sp^2 hybridized)
4. **Closed 4n+2 π–bond ring.**

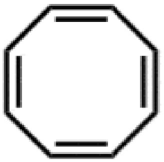
Aromatic



Benzene

- cyclic
- conjugated
- 6 π electrons

Aromatic



Cyclooctatetraene

- cyclic
- conjugated
- 8 π electrons

Not Aromatic

References

- Organic Chemistry by R T Morrison, R N Boyd & S K Bhattacharjee
- Organic Chemistry by F A Carey
- Organic Chemistry by Solomons, Fryhle & Snyder
- www.google.com