CHAPTER 1

Nature of Bonding in Organic Molecules

❖ Delocalized Chemical Bonding

The bonding in most of the organic compounds can be described by using a single Lewis structure (localized bond), and the orbital picture of such chemical bonds is treated either by the valence bond approach or by the molecular orbital theory. However, in some organic compounds, the electron density is not confined between two nuclei only, and therefore, cannot be depicted by a single Lewis structure. These types of molecules are said to possess "delocalized bonds"; and like localized bonds, the wave mechanical picture of such molecules can also be obtained by valence bond theory, as well as from the molecular orbital approach.

The valence bond approach is to consider many possible Lewis structures and then averaging out them all. These possible Lewis structures are generally called as canonical or resonating structures, and the phenomenon is labeled as "resonance". For instance, let us consider the case of the benzene molecule. If we treat it by the first extension of valence bond theory, three carbon-carbon bonds should be shorter and three carbon-carbon bonds should be longer due to their double and single bond order character.

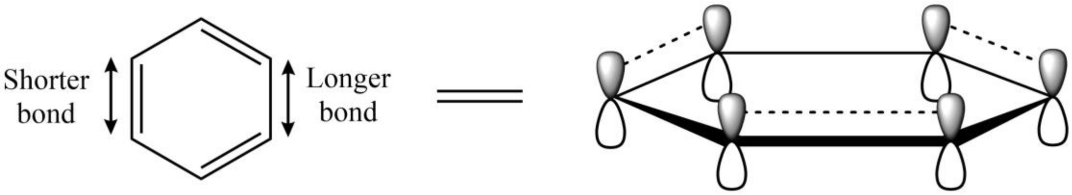


Figure 1. The expected structure of benzene molecule without resonance.

However, in the actual molecule, all the bond lengths and bond angles were found equal. All this can be explained only after considering the phenomenon of resonance in which all the possible resonating structures are given below.

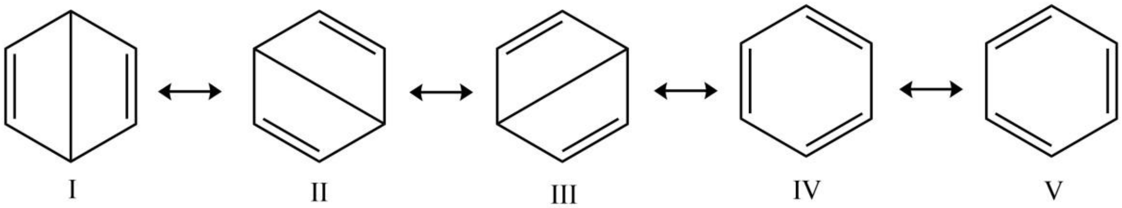


Figure 2. Different canonical structures of benzene molecule from resonance.

It has been found that after quantum mechanical calculations that Dewar structures (I–III) contribute only 7.33% each whereas Kekule structures (IV and V) contribute around 39% each to the resultant structure of benzene in which all the bond lengths and bond angles are equal. The bond-order of carbon-carbon bonds is greater than one but less than two showing an averaged strength for the resonance hybrid. It is also worthy to note that the energy of resonance hybrid is always less than the most stable resonating structure, and the energy difference between the two is simply called as resonance energy.

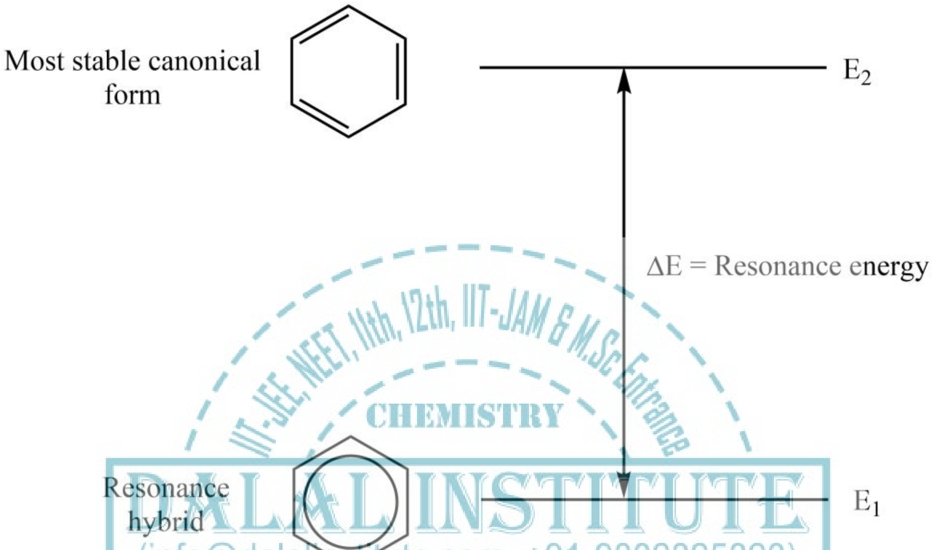


Figure 3. The depiction of resonance hybrid, most stable canonical form, and resonance energy in benzene molecule.

Now although the introduction of the concept of resonance in valence bond theory is quite useful in explaining the nature of “delocalized bond” in a lot of organic compounds, serious complications arise during the similar treatment of some other molecules like pyridine or the naphthalene. So, the molecular orbital theory, which is a more sophisticated approach, must be used to rationalize the nature of delocalization in such cases. However, for a comparative purpose, we will the discuss superficial molecular orbital treatment of benzene here. In this case, σ-bonding is treated in a valence bond framework and only π-bonding is examined in molecular orbital theory. In this method, the mixing of six atomic p_z-orbitals from six sp^2-hybridized carbons gives rise to six molecular orbitals, in which three are bonding and three are non-bonding. The number of nodes in the most bonding molecular orbital is zero whereas two other degenerate bonding molecular orbitals are with one node. The degenerate set of antibonding atomic orbitals, ψ_4 and ψ_5, are having two mutually perpendicular nodes; whereas three nodes are present in the most antibonding molecular orbital in benzene. All the six π-electrons are filled in bonding molecular orbitals leaving antibonding orbitals empty. The pictorial representation of various molecular orbitals in the benzene molecule is given below.

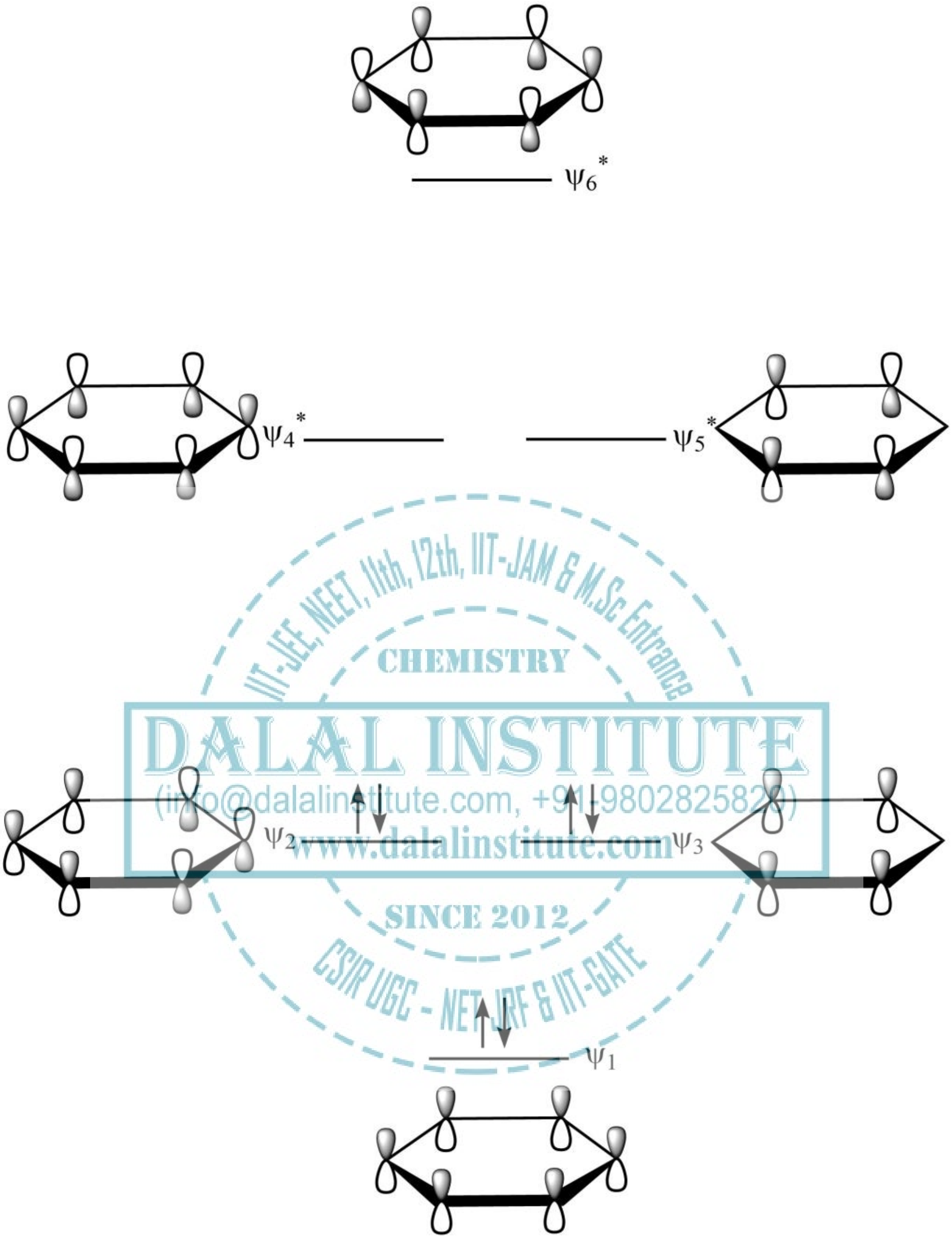


Figure 4. The depiction of molecular orbitals in benzene molecule.

Now, after having the general discussion on delocalized chemical bonds, it's time to discuss some phenomena and effects that arise due to delocalized bonds like conjugation, cross conjugation, resonance, hyperconjugation, and tautomerism.

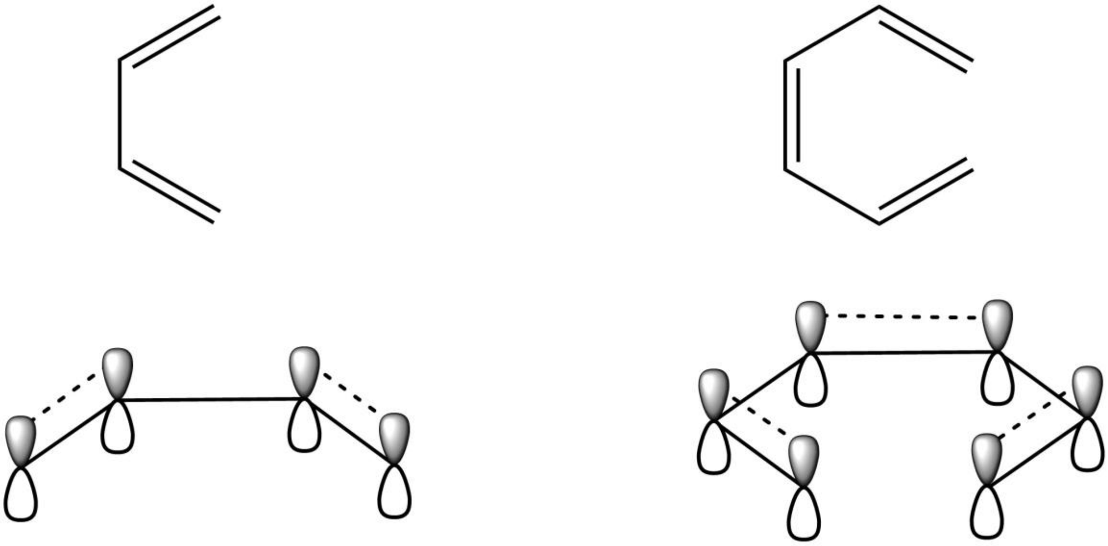
❖ Conjugation

The phenomenon of conjugation in organic compounds is typically characterized by the presence of alternate single and double bonds which are perpendicular to the molecular plane.

Typically, the orbitals required for the perpendicular π-bonding are supplied by the *sp*^{2}-hybridized carbon atom; nevertheless, it is not the hard-and-fast condition for the conjugation to take place because as long as the adjacent atoms are in a chain and have *p*-orbitals, the system can be treated as conjugated in nature. For instance, the furan molecule is a 5-membered cyclic system with two alternating double bonds neighboring oxygen in a five-membered ring. The oxygen atom has two lone pairs of electrons, one pair fills a *p* orbital perpendicular to the molecular plane, and therefore, sustaining the conjugation of that 5-membered cyclic system by overlap with the perpendicular *p* orbital on every adjacent C atoms. The 2nd lone pair remains in the molecular plane and does not contribute to the phenomenon of conjugation. The two main types of conjugations are given below.

➢ *Double Bond in Conjugation with a Double Bond*

In these compounds, a double or triple bond is in conjugation with another double or triple bond. Some of the common examples of these types of molecules are given below.



1, 3 butadiene

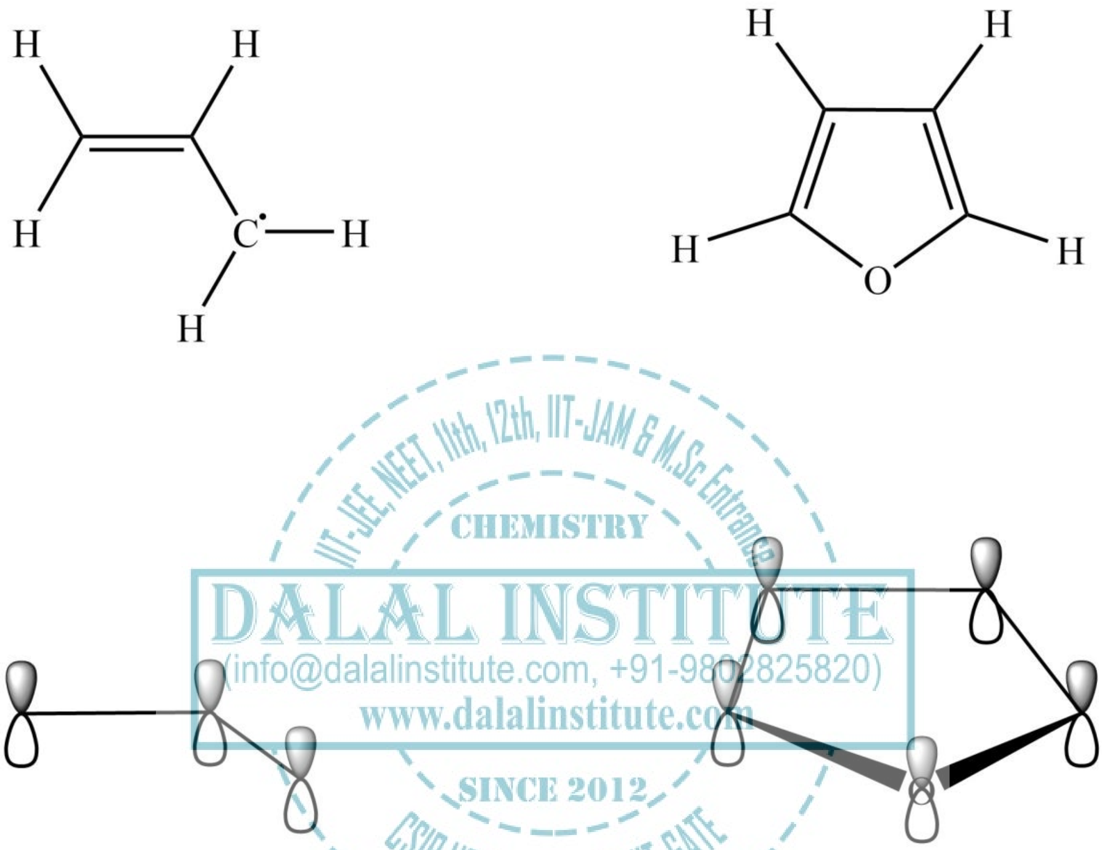
1, 3, 5 hexatriene

Figure 5. Some of the most common examples of acyclic molecular geometries bond-conjugated systems in them.

It should also be noted that the carbon that possesses the conjugated orbital is almost always got *sp*^{2} hybridization even if contains a lone pair of electron.

- ***Double Bond in Conjugation with p-Orbital on the Neighboring Atom***

In these compounds, a double or triple bond is in conjugation with the atomic p-orbital of an adjacent carbon or heteroatom. Some of the common examples of these types of molecules are given below.



Allyl radical

Furan

Figure 6. Common examples of some bond-orbital conjugated molecules.

It should also be noted that the carbon that possesses the conjugated orbital is almost always got *sp*^{2} hybridization even if contains a lone pair of electrons.

❖ Cross Conjugation

The phenomenon of cross-conjugation is a special type of conjugation in a molecule when in a set of three π-bonds only two pi-bonds interact with each other by conjugation, the third one is excluded from the interaction.

Alternatively, we can also say that a system with cross-conjugation has an alkene fragment bonded to one of the central atoms of a 2nd conjugated chain via a single bond. It is different from normal conjugation in which a polyene typically has alternating single and double bonds along with consecutive atoms. Some of the common examples of these types of molecules are given below.

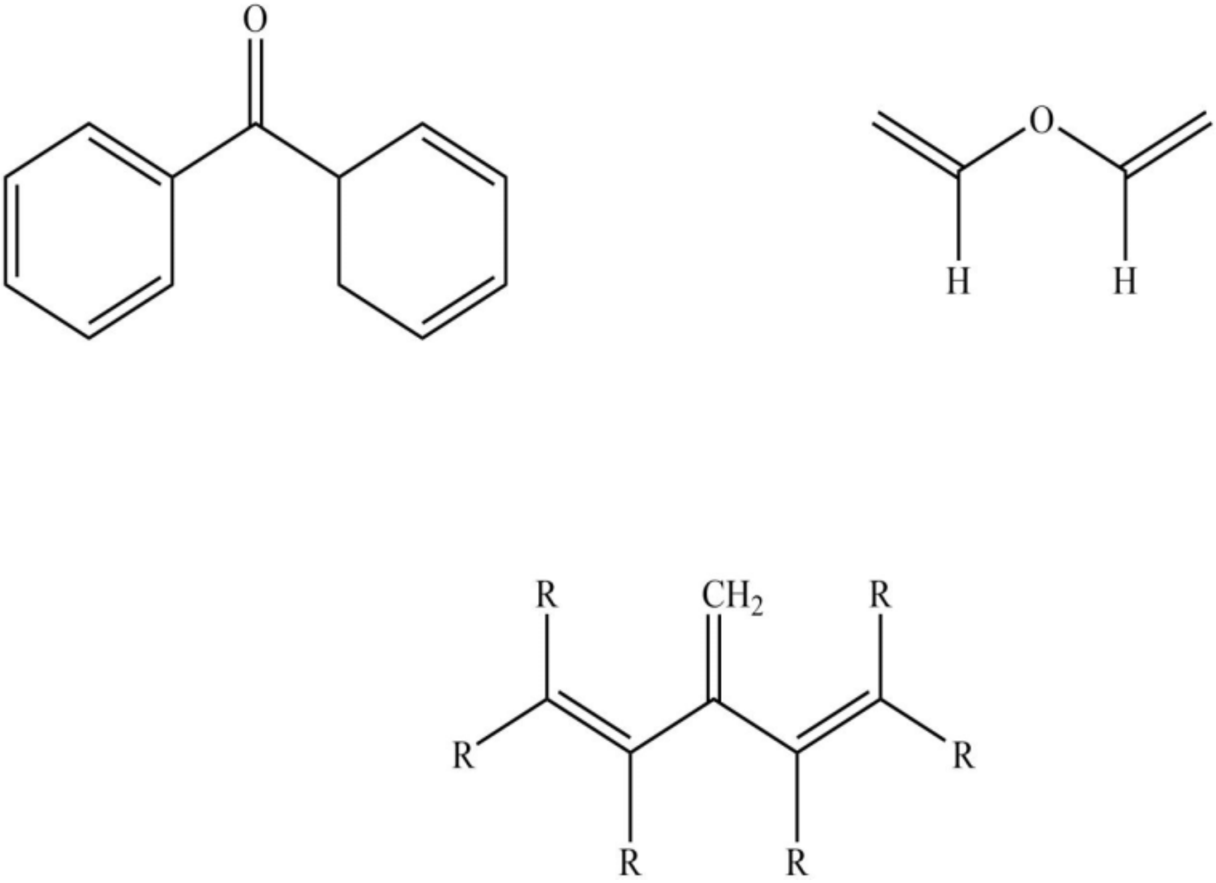


Figure 7. Common examples of molecules with cross-conjugation.

Classically speaking, the branching of double-bonds happens instead of continuous conjugation, and the fragment of that same primary chain is in conjugation with the side group, but all portions are not conjugated with each other very firmly. Common examples of the cross-conjugation effect can be found in molecules such as divinylketones, benzophenone, dendralenes, p-quinones, radialenes, Indigo dye, and fullerene.

Furthermore, it should also be mentioned that the phenomenon of cross conjugation affects the reactivity and molecular electronic transitions in a significant manner. For instance, the lone pair on nitrogen activates the ring at *o*- and *p*-position in aniline (I), supporting the formation of tribromo aniline for bromination reaction. On the other hand, the bromination leads to only monosubstituted acetanilide due to cross conjugation in acetanilide.

Figure 8. The effect of cross-conjugation upon reactivity.

It is also worthy to note that the phenomenon of cross conjugation is different than homoconjugation-which arises when two π-systems are separated by one non-conjugating group.

❖ Resonance

The concept of resonance is an extension of valence bond theory to explain the nature of the "delocalized bond" in a lot of organic compounds which cannot be described by a single Lewis structure.

The valence bond approach to delocalized bonds is to consider many possible Lewis structures and then averaging out them all. These possible Lewis structures are generally called as canonical or resonating structures, and this phenomenon is labeled as "resonance". For instance, let us consider the case of the benzene molecule. If we treat it by the first extension of valence bond theory, three carbon-carbon bonds should be shorter and three carbon-carbon bonds should be longer due to their double and single bond order character.

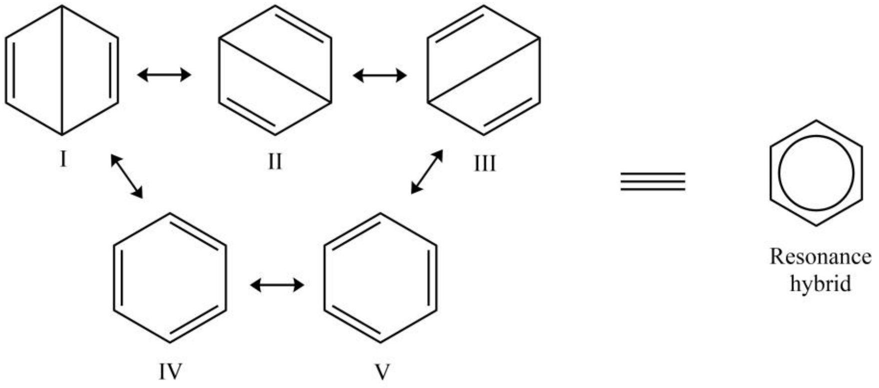


Figure 9. Different resonating structures of the benzene molecule.

However, in the actual molecule, all the bond lengths and bond angles were found equal. All this can be explained only after considering the phenomenon of resonance in which all the possible resonating structures are given in 'Figure 8'. It has been found that after quantum mechanical calculations that Dewar structures (I–III) contribute only 7.33% each whereas Kekule structures (IV and V) contribute approx. 39% each to the resultant structure of benzene in which all the bond lengths and bond angles are equal. The bond order of carbon-carbon bonds is greater than one but less than two showing an averaged strength for the resonance hybrid. The resonance phenomena in some other molecules is given below.

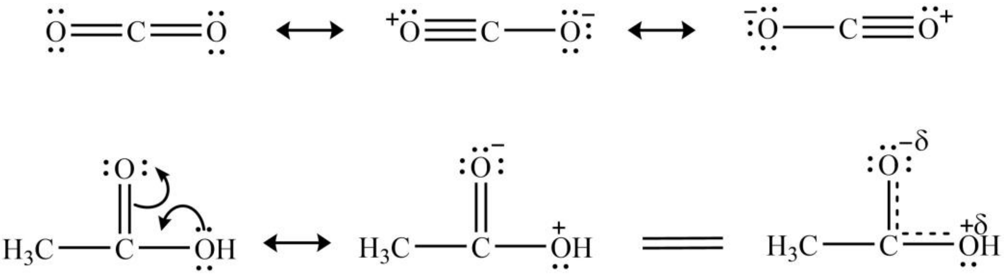


Figure 10. Resonance phenomena in carbon dioxide and acetic acid.

Calculation of resonance energy: It is also worthy to note that the energy of resonance hybrid is always less than the most stable resonating structure, and the energy difference between the two is simply called as resonance energy.

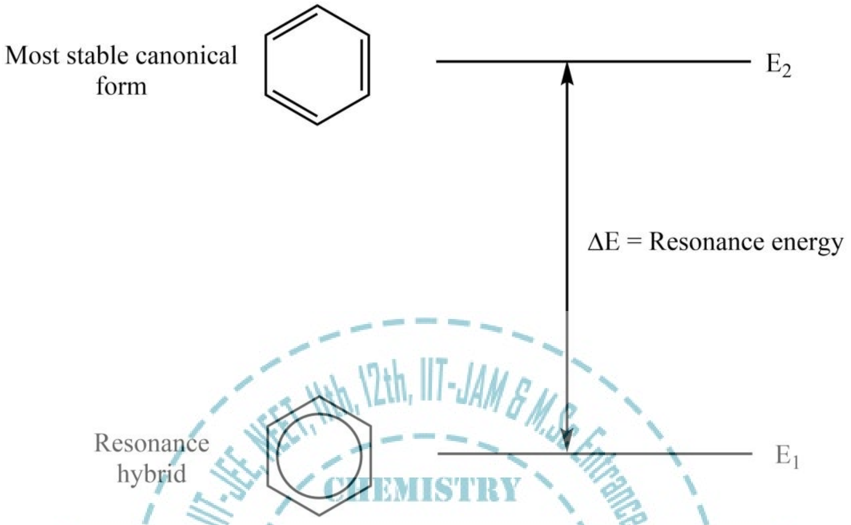
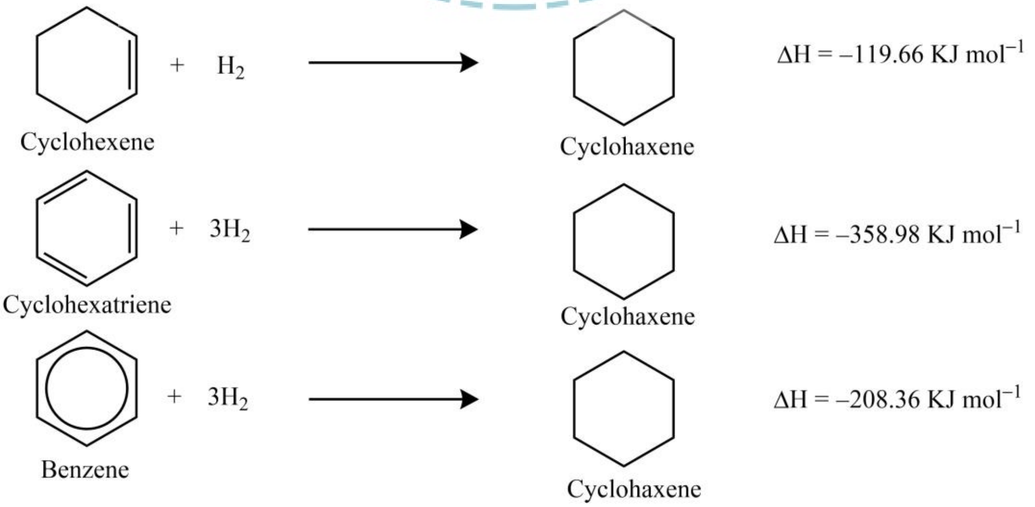


Figure 11. The depiction of resonance hybrid, most stable canonical form, and resonance energy in benzene molecule.

Since the Lewis structures are not real ones, the resonance energy for the benzene molecule can be obtained via two routes as discussed below.

i) From heat of hydrogenation: The hypothetical six-membered cyclic ring system with no resonance would be cyclohexatriene whose heat of hydrogenation should be three times of cyclohexene molecule.



Now since the enthalpy of hydrogenation of the actual benzene molecule is less than its hypothetical localized version (358.98 – 208.36 = 150.62 kJ mol^{-1}), the extra stabilization can be attributed to the phenomena of delocalization easily.

ii) From heat of formation: The hypothetical six-membered cyclic ring system with no resonance would be cyclohexatriene (Kekule structure) whose heat of formation should be the sum of the bond energies of different carbon-carbon and carbon-hydrogen bonds.

$$\begin{aligned}\Delta H_{calculated} &= 6 \times Bond\ dissociation\ energy\ of\ C-H\ bond \\ &+ 3 \times Bond\ dissociation\ energy\ of\ C-C\ bond \\ &+ 3 \times Bond\ dissociation\ energy\ of\ C=C\ bond\end{aligned} \tag{1}$$

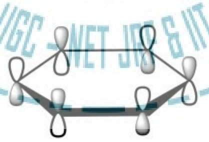
$$\begin{aligned}&= 6 \times 413.3\ KJ\ mol^{-1} + 3 \times 347.7\ KJ\ mol^{-1} + 606.7\ KJ\ mol^{-1} \\ &= 5343\ KJ\ mol^{-1}\end{aligned} \tag{2}$$

Now since the experimental enthalpy of formation of the actual benzene molecule is −5494.84 kJ mol^{-1} which is more than its hypothetical localized version (−5343 kJ mol^{-1}), the extra stabilization of −151.84 kJ mol^{-1} can be attributed to the phenomena of delocalization easily.

Conditions for resonance: In order to show the phenomenon of resonance, the following condition must be satisfied by the molecule under consideration.

1. Different canonical forms of the molecule should differ only with respect to the position of electrons and not the nuclei.

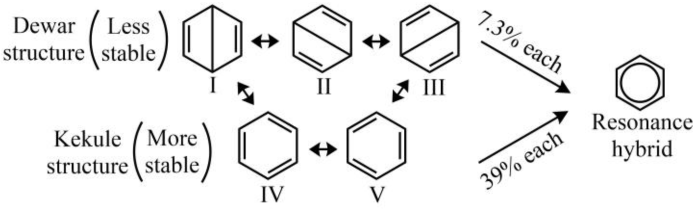
2. All the participating atoms must lie in the same plane.



3. All resonating structures must possess the same number of unpaired and paired electrons.

4. If two resonating structures are having the same energy, they will contribute equally to the resonance hybrid.

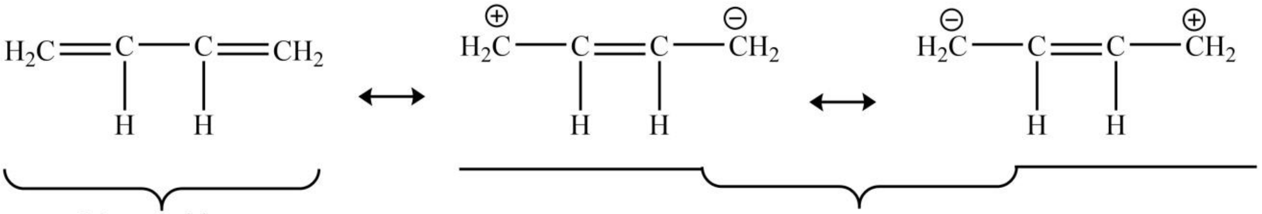
5. More stable resonating structure will contribute higher to the resonance hybrid.



6. Greater is the number of canonical structures, higher will be the stability of corresponding resonance hybrid.

7. The following factors must be taken into consideration before we decide the relative stability of participating canonical structure:

i) Resonating structures with a greater number of covalent bonds will be more stable, and therefore, will show more contribution towards resonance hybrid.



More stable
(more contribution)

Less stable
(less contribution)

ii) Structures with charge separation will be less stable, and therefore, will contribute less towards the resonance hybrid.

More stable
(more contribution)

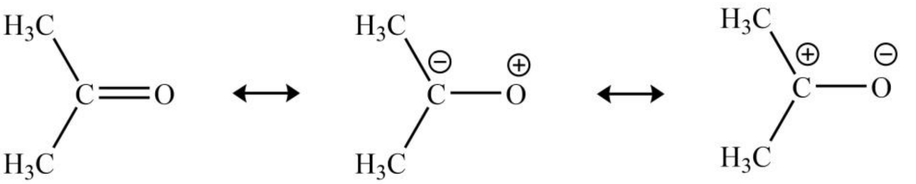
Less stable
(less contribution)

iii) Structures violating the octet rule should not be considered (involving second-period elements).

Stable
(will show contribution)

Highly unstable
(should be discarded)

iv) Resonating structures with the negative charge on a more electronegative atom will be less stable, and therefore, will contribute less to the resonance hybrid.

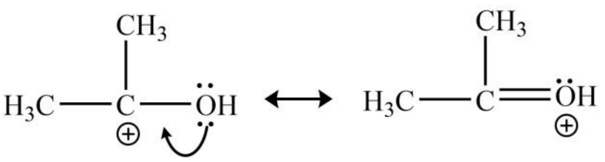


Most stable
(most contribution)

Least stable
(least contribution)

Less stable
(less contribution)

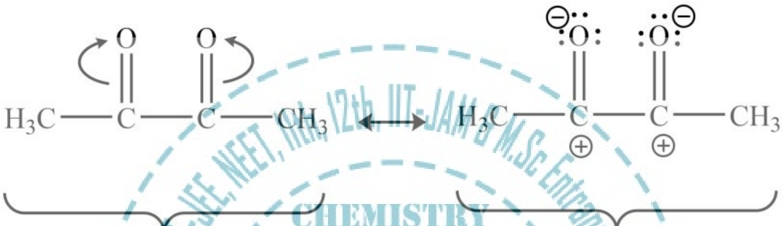
v) If a structure helps to delocalize the positive charge will contribute significantly toward the resonance hybrid even if the positive charge is on the electronegative atom.



Most stable (more contribution)

Significantly stable (significant contribution)

vi) Resonating structures with like charges on adjacent atoms in space will be less stable sterics, and therefore, will contribute less towards the resonance hybrid.



More stable (more contribution)

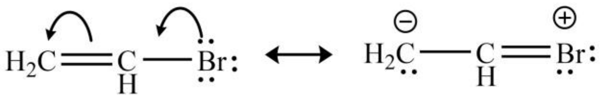
More stable (more contribution)

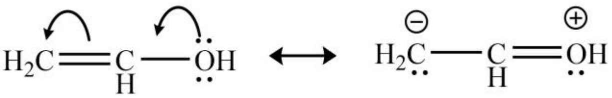
Resonance effect:

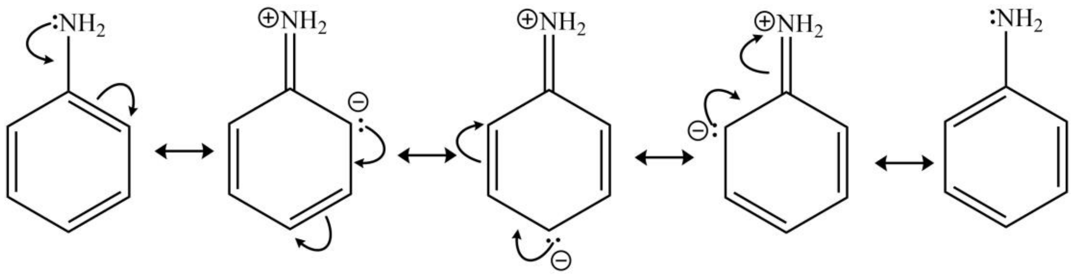
The resonance or mesomeric effect in organic compounds may simply be defined as the polarity produced in the molecule due to resonance phenomena.

The effect is used in a qualitative way and describes the electron-withdrawing or releasing properties of substituents based on relevant resonance structures and is symbolized by the letter R or M. The resonance effect is negative (–R) when the substituent is an electron-withdrawing group and the effect is positive (+R) when the substituent is an electron releasing group. A detailed explanation of the two effects with some typical examples is given below.

i) +R effect: Some groups release the electron density to the multiple bonds through resonance and are said to have a +M or +R effect in general.



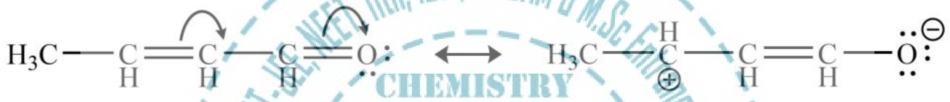


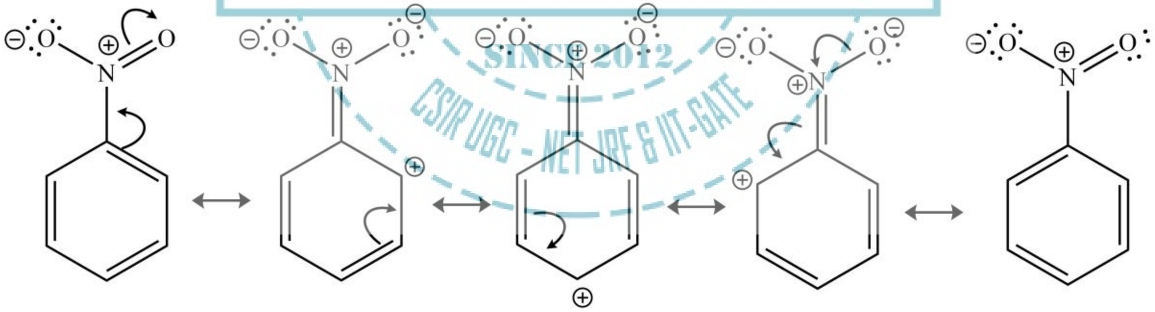


It is also worthy to mention that groups showing the +R effect are having lone pair of the electron that can be put into conjugation with the double of the chain or ring to which it gets attached with. Some of the typical groups showing the +R effect are given below.

$-O^- > -NH_2 > -NHR > -OR > -NHCOR > -OCOR > -Ph > -F > -Cl > -Br > -I$

ii) −R effect: Some groups withdraw the electron density to the multiple bond through resonance, and are said to have −M or −R effect in general.





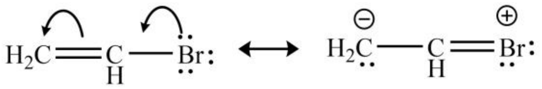
It is also worthy to mention that groups showing the −R effect are having a double bond that can be put into conjugation with the double of the chain or ring to which it gets attached with. Some of the typical groups showing the −R effect are given below.

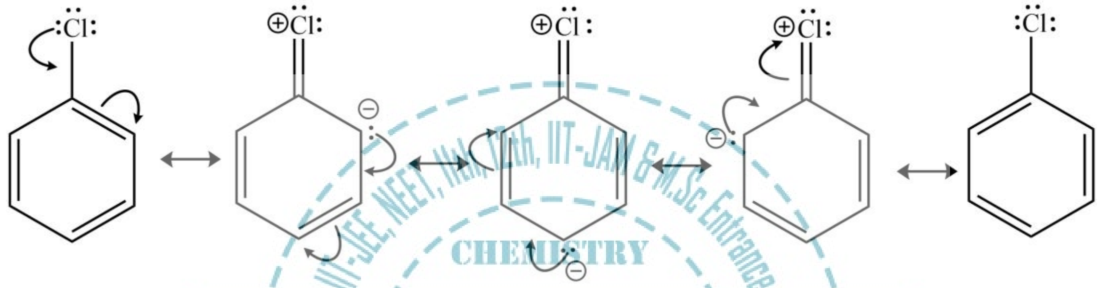
$-NO_2 > -CN > -S(=O)_2-OH > -CHO > -C=O > -COOCOR > -COOR > -COOH > -CONH_2 > -COO^-$

It should also be noted that the resonance is different from the inductive effect and can exert its electron-withdrawing or electron releasing effect in a direction along or opposite to the inductive effect. Unlike inductive effect which can also act in saturated molecules, the resonance effect is observed only in conjugated systems. Furthermore, the inductive effect involves σ-electrons and is operative only up to four carbon atoms, whereas the resonance effect involves unpaired or π-electrons which can get delocalized over longer distances.

Applications of resonance effect: Some of the important applications of the resonance or mesomeric effect that affect the properties to a great extent are given below.

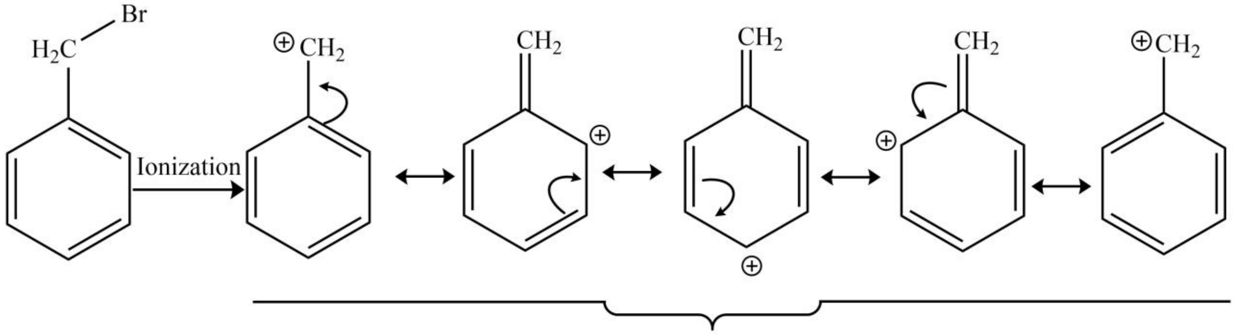
i) Low reactivity of vinyl and aryl halides: The existence of the +R effect in vinyl and aryl halides makes them less reactive towards the nucleophilic substitution reaction due to the partial double character of the carbon-halogen bond as shown below.





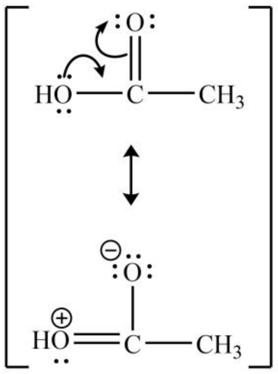
ii) High reactivity of allyl and benzyl halides: The existence of the −R effect in allyl and benzyl halides makes them more reactive towards the nucleophilic substitution reaction due to the formation resonance stabilized cation bond as shown below.

Resonance stablized cation

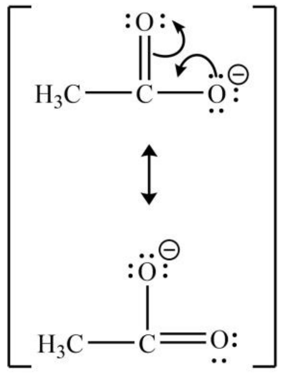


Resonance stablized cation

iii) Acidic character of carboxylic acid: The existence of charge separation in one of the resonating structures of carboxylic acid makes it less stable than the carboxylate anion which is formed by the loss of a proton.



Charge separation
(less stable)

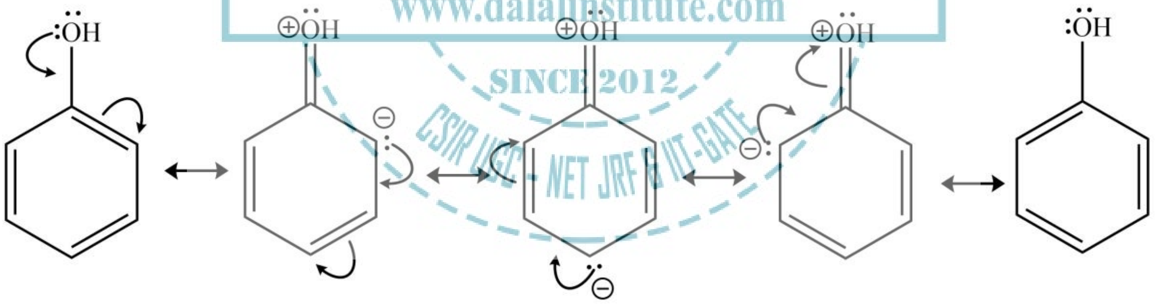


No charge separation
(more stable)

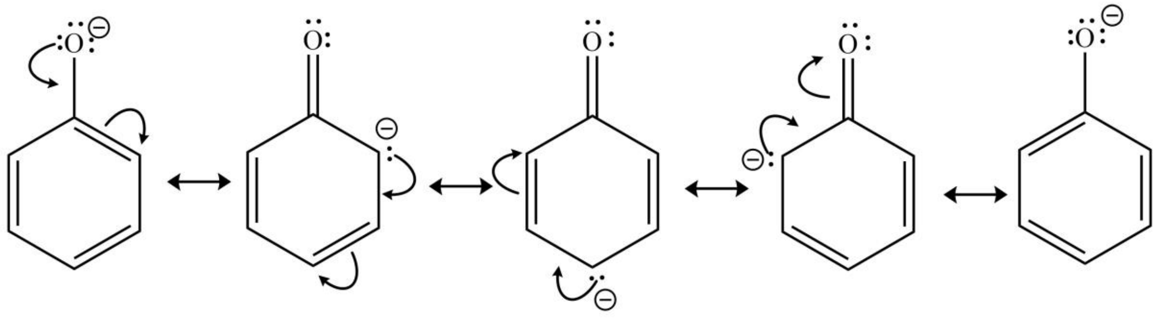
iv) Acidic strength of alcohols and phenols: Alcohols are less acidic than phenols because, unlike alkoxide ion, the phenoxide (formed by the loss of proton) resonance stabilized.

$$R-CH_2-\ddot{O}H \rightleftharpoons R-CH_2-\ddot{O}:^{\ominus}$$

No resonance (less stable)

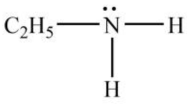


Charge separation (less stable)

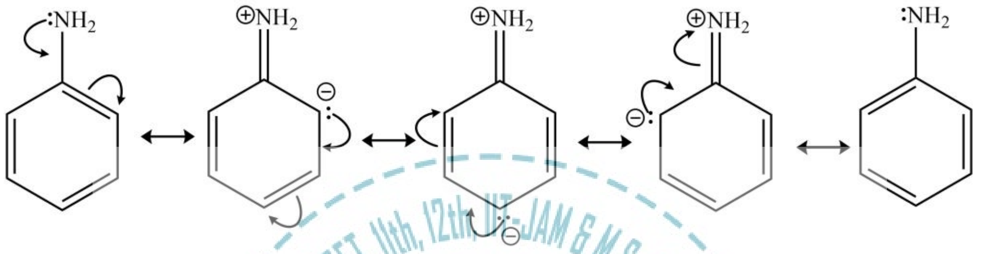


No charge separation (more stable)

v) Basic strength of ethylamine and aniline: Ethylamine is more basic than aniline because the electron pair in aniline is less available for donation due to resonance. On the other hand, the +I effect of the ethyl group increases the electron density on the nitrogen atom making it more basic.

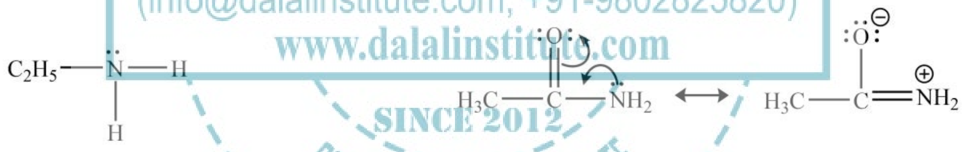


+I effect of -C_2H_5 (more basic)



+R effect (less basic)

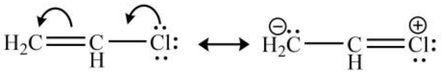
vi) Basic strength of ethylamine and acetamide: Ethylamine is more basic than acetamide because the electron pair in acetamide is less available for donation due to resonance. On the other hand, the +I effect of the ethyl group in ethylamine increases the electron density on the nitrogen atom making it more basic.



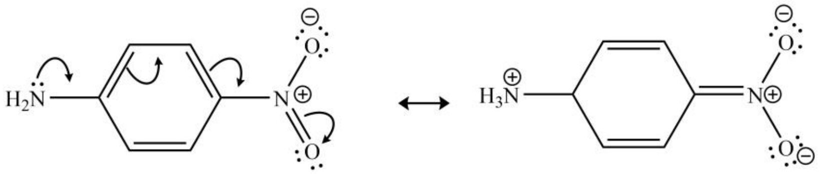
+I effect of -C_2H_5 (more basic)

+R effect (less basic)

vii) Effect on dipole moments: The dipole moments of different organic molecules are also affected by the resonance effect to a very large extent. For instance, the dipole moment of vinyl chloride is found to be only 1.69D which is much less than the value expected from a large inductive effect (2.05D).



Direction of dipole due to –I effect of Cl →
Direction of dipole due to +R effect of Cl ←



Direction of dipole due to –I effect of NO_2 →
Direction of dipole due to –R effect of NO_2 →

❖ Hyperconjugation

The phenomenon of hyperconjugation (or σ-conjugation) may simply be defined as the delocalization of electrons with the participation of bonds of primarily σ-character.

Typically, the phenomenon of hyperconjugation involves the interaction of the σ-electrons from the C–H bond with an adjacent empty nonbonding *p* or antibonding σ^* or π^* orbitals to give a pair of extended molecular orbitals. Nevertheless, antibonding σ^* orbitals, which are low-lying energetically, may also interact with fully-filled orbitals of lone pair character (*n*), which in that case is called as 'negative hyperconjugation'. Increased delocalization of electron density associated with the phenomenon of hyperconjugation raises the stability of the system. Particularly, the new bonding orbital is stabilized, resulting in high overall stabilization of the molecular system. The Baker-Nathan effect, which is also sometimes synonymously used for hyperconjugation, is an explicit application employed to some reactions or structure types.

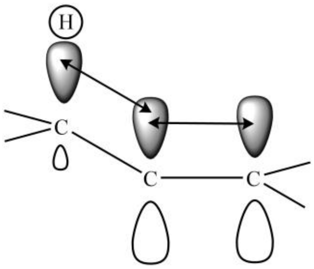
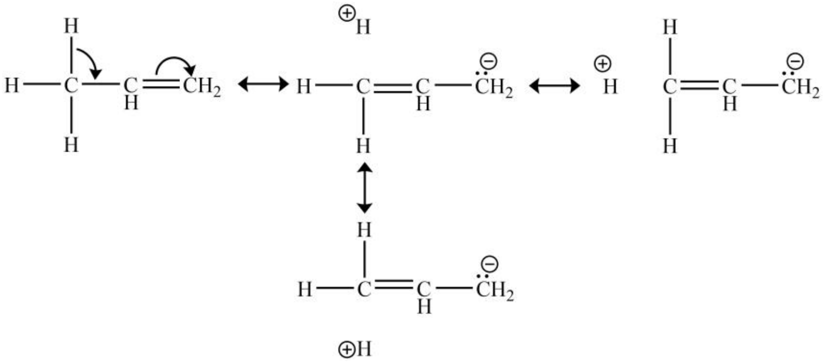


Figure 12. The orbital picture of hyperconjugation.

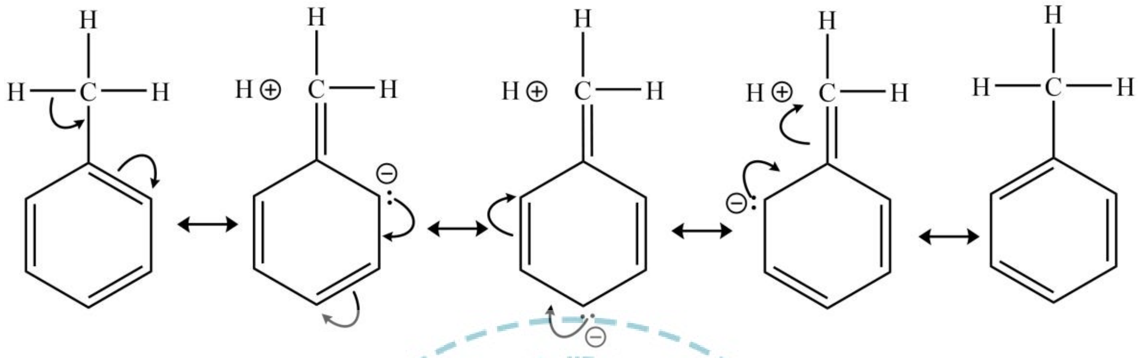
This effect also reverses the order of the +I effect of alkyl groups if they are attached to an unsaturated carbon. The general order of +I effect is $(CH_3)_3C- > (CH_3)_2CH- > CH_3-CH_2- > -CH_3$. However, consider the hyperconjugation after attaching them to unsaturated carbon i.e.



Therefore, the greater the number of hydrogen at the carbon attached to unsaturated carbon, the more will be the number of possible hyper conjugative structures resulting in a larger electron-donating effect. The number of α-hydrogens in $(CH_3)_3C-$, $(CH_3)_2CH-$, CH_3-CH_2- and $-CH_3$ are 0, 1, 2 and 3, respectively; and thus, the new order of electron donating strength becomes is $(CH_3)_3C- < (CH_3)_2CH- < CH_3-CH_2- < -CH_3$.

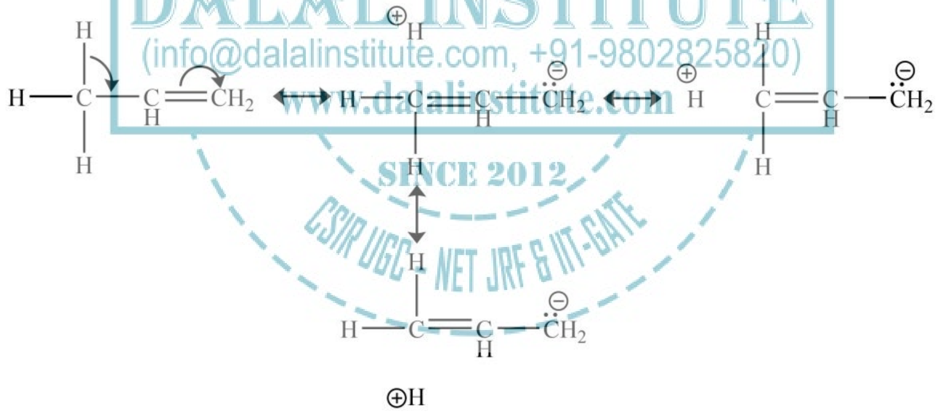
Applications of hyperconjugation effect: Some of the important applications of the hyperconjugation effect that affect the properties to a great extent are given below.

i) Directive influence of alkyl groups: The existence of the hyperconjugation effect can be used to rationalize the *o*- and *p*-directing influence of alkyl groups as shown below.

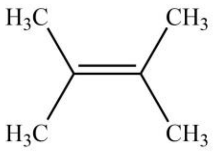


Similarly, six more hyperconjugative structures can also be written for two other H-atoms; and it is obvious that the electron density is increased at *o*- and *p*-sites.

ii) Shortening of C−C bond adjacent to multiple bonds: The existence of hyperconjugation effect can be used to rationalize the shortening of C−C bond adjacent to multiple bonds as shown below.

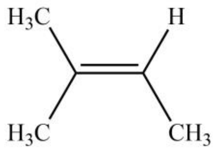


iii) Relative stability of different alkenes: The existence of hyperconjugation effect can be used to rationalize the relative stability of different alkenes as shown below.



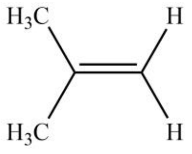
2,3-dimethylbut-2-ene

(12 α hydrogens $\Delta_{H2} = 26.6$ Kcal mol^{-1})



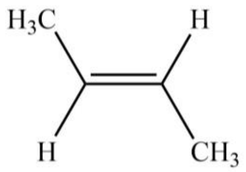
2-methylbut-2-ene

(9 α hydrogens $\Delta_{H2} = 26.9$ Kcal mol^{-1})



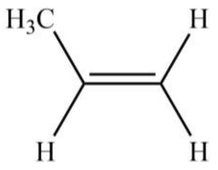
2-methylprop-1-ene

(6 α hydrogens $\Delta_{H2} = 28.6$ Kcal mol^{-1})



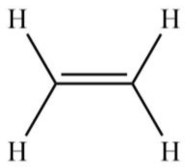
(*E*)-but-2-ene

(6 α hydrogens $\Delta_{H2} = 27.6$ Kcal mol^{-1})



prop-1-ene

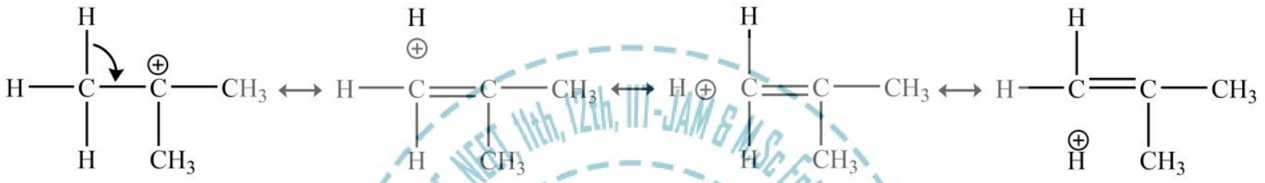
(3 α hydrogens $\Delta_{H2} = 30.1$ Kcal mol^{-1})



ethene

(0 α hydrogens $\Delta_{H2} = 32.8$ Kcal mol^{-1})

iv) Relative stability of different carbocations: The existence of hyperconjugation effect can be used to rationalize the relative stability of different carbocations as shown below.

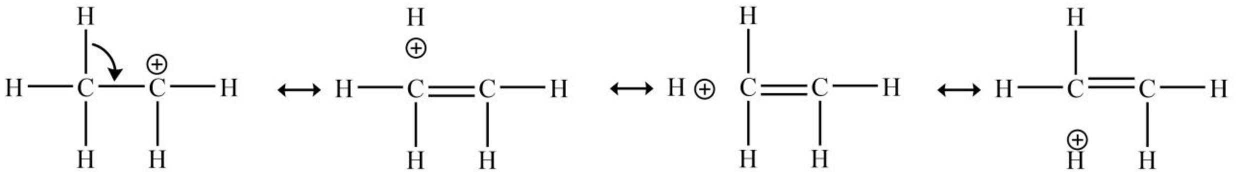


tert-butyl carbocation

(3 hyperconjugative structures for one methyl group Total hyperconjugative structures = 9)

iso-propyl carbocation

(3 hyperconjugative structures for one methyl group Total hyperconjugative structures = 6)

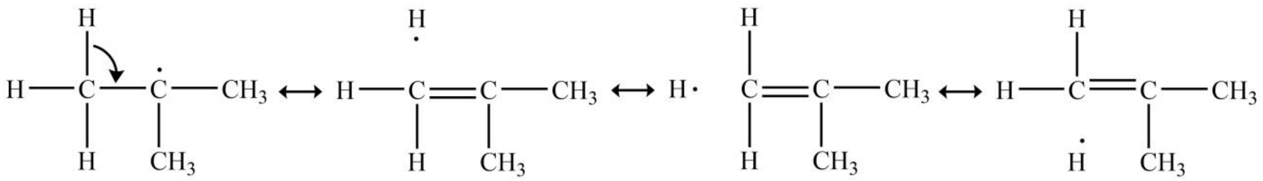


ethyl carbocation

(3 hyperconjugative structures for one methyl group Total hyperconjugative structures = 3)

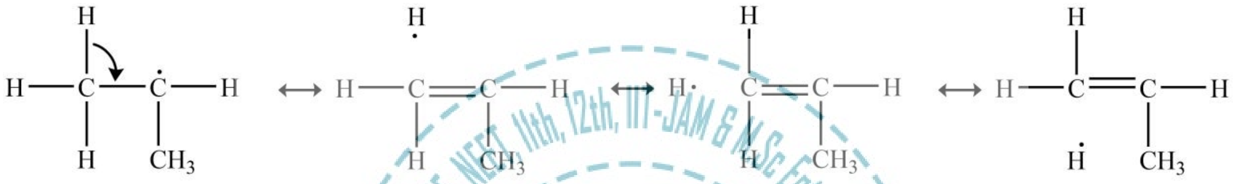
Hence, as far as the number of possible hyperconjugative structures possible is concerned, tertiary carbocation should be more stable than secondary, which in turn should be more stable than primary.

v) Relative stability of different free radicals: The existence of hyperconjugation effect can be used to rationalize the relative stability of different free radicals as shown below.



tert-butyl free radical

(3 hyperconjugative structures for one methyl group
Total hyperconjugative structures = 9)



iso-propyl free radical

(3 hyperconjugative structures for one methyl group
Total hyperconjugative structures = 6)

ethyl free radical

(3 hyperconjugative structures for one methyl group
Total hyperconjugative structures = 3)

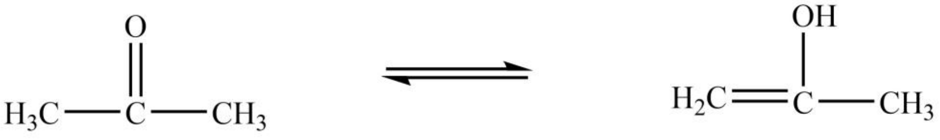
Hence, as far as the number of possible hyperconjugative structures possible is concerned, tertiary free radicals should be more stable than secondary, which in turn should be more stable than primary.

The phenomenon of hyperconjugation can also clarify numerous other effects where explanations may also not be as clear as that for the rotational barrier of C_2H_6. For instance, the Lewis structure for an ammonium ion shows a positive charge on the N atom; though, the hydrogen atoms are more electropositive than is nitrogen atoms, and therefore, are the more genuine carriers of the positive charge. We have known this fact since bases eliminate the protons instead of the nitrogen atom. The matter of the ethane's rotational barrier is not settled by the scientific community till now. An investigation of quantitative molecular orbital theory demonstrates that 2-orbital-4-electron (steric) repulsions are much more dominant over the phenomenon of hyperconjugation. The valence bond theory also put a strong emphasis on the steric significance.

❖ Tautomerism

The phenomenon of tautomerism may simply be defined as the fast interconversion of structural isomers (constitutional isomers) of chemical compounds.

The phenomenon of tautomerism is also called as “desmotropism”. The chemical reaction interconverting the two is called tautomerization. One should not be confused with tautomers at the depictions of 'contributing structures' in typical resonance phenomenon. Tautomers are absolutely different chemical species and can be recognized as such by their distinguished spectroscopic profile, whereas resonating structures are nothing but convenient portrayals and do not have physical meaning. One of the most common examples of tautomerism is the interconversion of the keto- and enol forms of an organic compound.

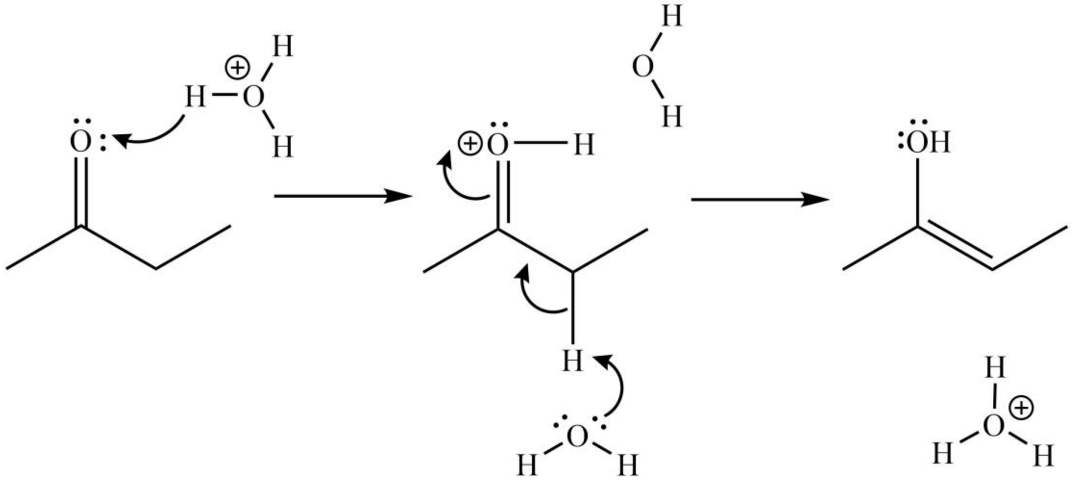


propan-2-one prop-1-en-2-ol

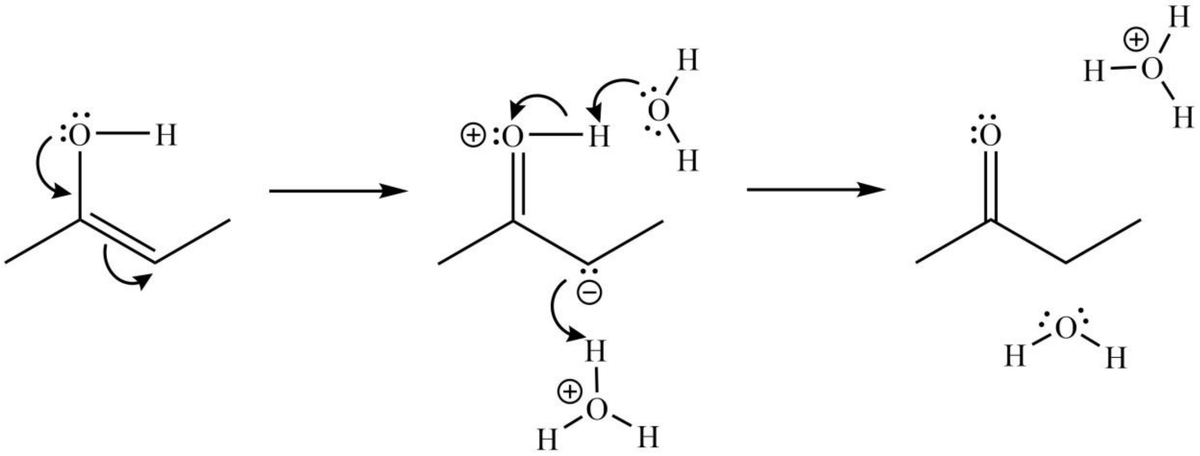
It is also worthy to mention before we discuss the mechanism involved that the phenomenon of tautomerism commonly results in the relocation of a proton.

Mechanism: The phenomenon of tautomerism can occur in the acidic as well as in the basic medium as discussed below.

i) In acidic medium: The most positive species in acidic medium is H^+ ions and the most negative species is the water molecule itself. Therefore, the following mechanism is proposed for keto- to enol conversion.

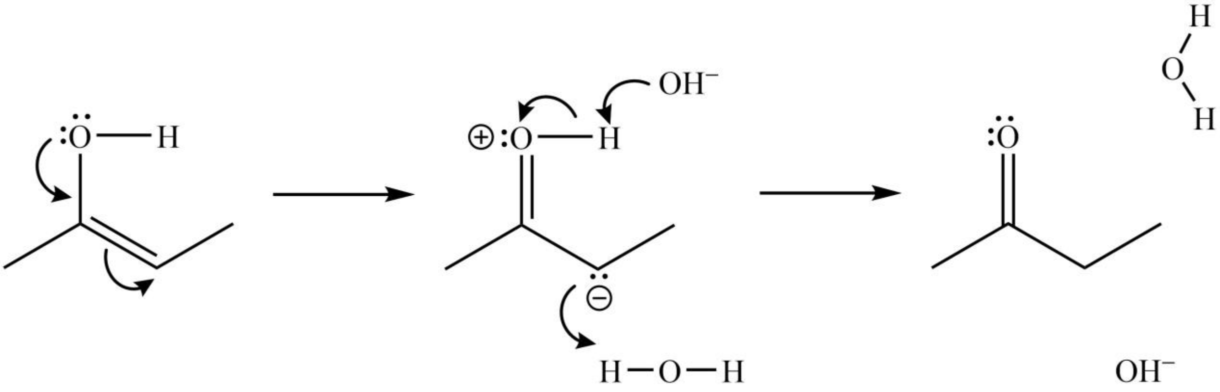


Similarly, the mechanism responsible for enol- to keto conversion is can also be proposed as given below.



ii) In basic medium: The most positive species in a basic medium is H_2O ions and the most negative species is the hydroxyl ion. Therefore, the following mechanism is proposed for keto- to enol conversion.

Similarly, the mechanism responsible for enol- to keto conversion is can also be proposed as given below.



❖ Aromaticity in Benzenoid and Nonbenzenoid Compounds

In order to understand the aromatic character of benzenoid and non-benzenoid compounds, we need to understand the aromaticity first.

The phenomenon of aromaticity in organic chemistry may simply be defined as a special property of planar cyclic geometries with a ring of resonating bonds that gives enhanced stability relative to other connective or geometric arrangements with the same atomic set.

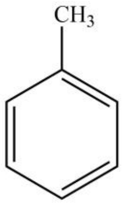
Aromatic compounds are quite stable and don't get fragmented easily to react with other chemical compounds. Organic compounds that don't have aromatic character are categorized as aliphatic compounds, which might be cyclic, but only aromatic rings have low reactivity character. Now because most common aromatic compounds are derived from benzene, the word aromatic generally refers to benzene derivatives. Nonetheless, many non-benzenoids also exist. Alternatively saying, these compounds can mainly be classified into two categories as given below.

➢ *Aromaticity in Benzenoid Compounds*

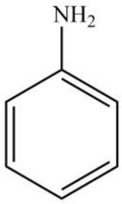
Benzenoid aromatic compounds are the organic molecular species either with isolated benzene rings or with multiple benzene rings which fused to form a more complex structure. Therefore, these compounds can further be classified into monocyclic aromatic compounds and polycyclic aromatic compounds.

i) Monocyclic aromatic compounds:

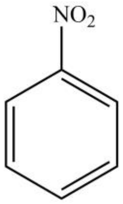

benzene



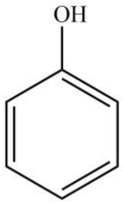
toluene



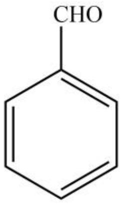
aniline



nitrobenzene

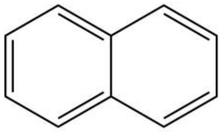


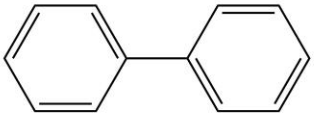
phenol

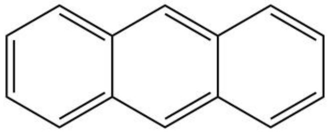


benzaldehyde

ii) Polycyclic aromatic compounds:


naphthalene


1,1'-biphenyl

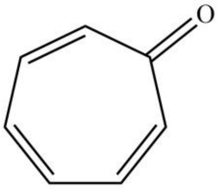

anthracene


1,1':4',1''-terphenyl

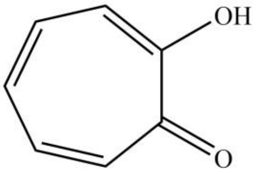
➢ *Aromaticity in Nonbenzenoid Compounds*

Nonbenzenoid aromatic compounds are the organic molecular species either with all carbons in the cycle or with one or more heteroatoms in the rings. Therefore, these compounds can further be classified into homocyclic (carbocyclic) aromatic compounds and heterocyclic aromatic compounds.

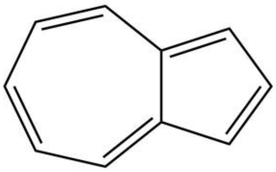
i) Homocyclic aromatic compounds:



tropone



tropolone



Azulene

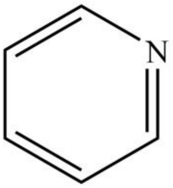
Cyclotetradecaheptaene

ii) Heterocyclic aromatic compounds:

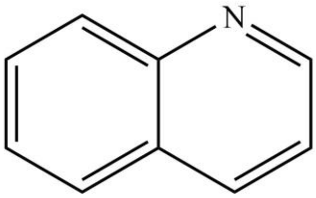
pyrrole

furan

thiophene



pyridine



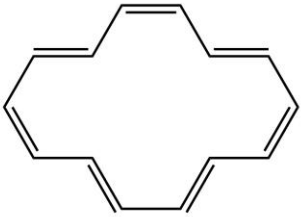
quinoline

❖ Alternant and Non-Alternant Hydrocarbons

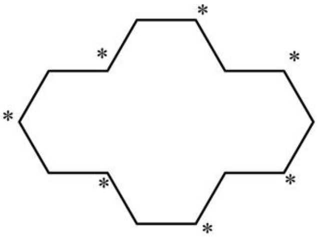
Besides benzenoid and non-benzenoid grouping, all aromatic hydrocarbons can also be classified as alternant and non-alternant hydrocarbons. A general discussion on the two types is given below.

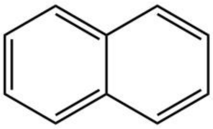
➢ *Alternant Hydrocarbons*

An alternant hydrocarbon is any conjugated hydrocarbon system that doesn't possess an odd-membered cycle. In such cases, it is quite plausible to follow a starring route, where all the C atoms are divided into two groups; in one group, all the carbons are marked with a star in such a way that no two-starred or unstarred atoms are mutually bonded.

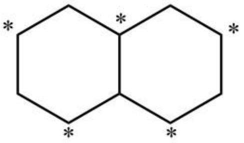


Cyclotetradecaheptaene





naphthalene



In alternate hydrocarbons, the secular determinant in the Hückel approximation has a simpler form, since cross-diagonal elements between atoms in the same set are necessarily 0.

Important properties of alternant hydrocarbons:

i) The coefficients of two paired MOs are the same at the same position, except for a change of sign in the unstarred group.

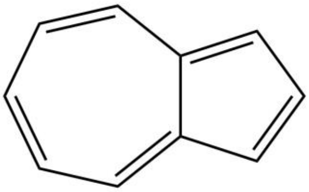
ii) The electron density or population at all sites is equal to 1 in the ground electronic state, so that the distribution of π-electron density is uniform across the entire molecular structure.

iii) The energies of molecular orbitals for the π system are paired, that is for an orbital of energy $E = \alpha + x\beta$ there is one of energy $E = \alpha - x\beta$.

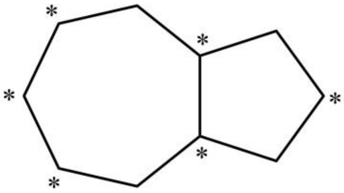
Furthermore, if the alternant hydrocarbon has an odd number of carbon atoms then there must be an unpaired orbital with no bonding energy (i.e., a non-bonding wave function). For this wavefunction, the coefficients on the atomic sites can be given without calculation; the coefficients on all the orbitals belonging to the smaller set are 0, and the sum of the coefficients of the orbitals around them should also be zero. Modest calculations allow the assignment of different coefficients with normalization. This route allows the prediction of patterns of reactivity and can be employed to find Dewar's reactivity numbers for all positions.

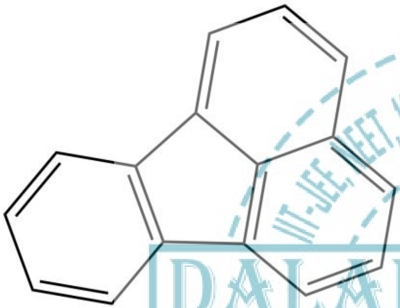
➢ ***Non-Alternant Hydrocarbons***

A non-alternant hydrocarbon is any conjugated hydrocarbon system in which it is not possible to mark all the carbon atoms in a complete alternate fashion.

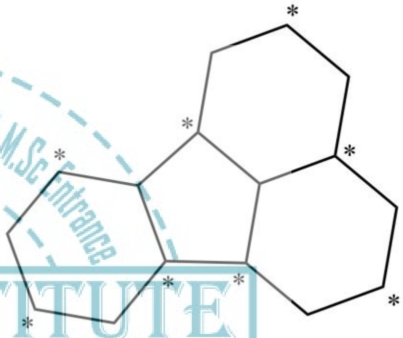


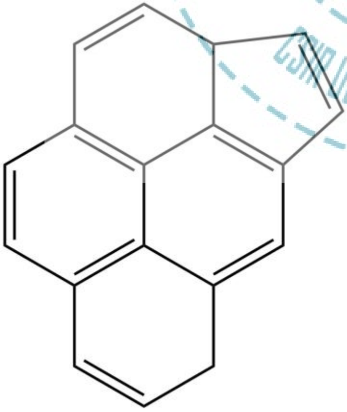
Azulene



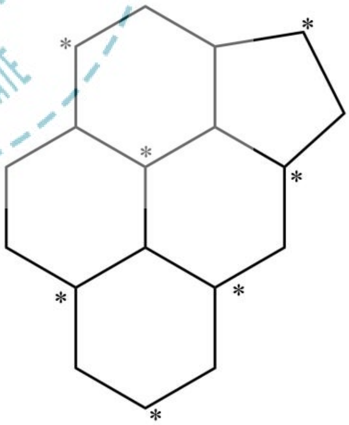


Fluoranthene





2a,6-dihydrocyclopenta[*cd*]pyrene



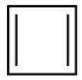
In non-alternate hydrocarbons, the energies of the antibonding and bonding molecular orbitals are not the same and opposite. Furthermore, is also worthy to note that the charge distributions in non-alternate hydrocarbons also are not the same in the anions cations and in radical species.

❖ Huckel's Rule: Energy Level of π-Molecular Orbitals

Huckel's rule states that all the planar and conjugated systems with $4n + 2$ *π-electrons will be aromatic, and therefore, will be more stable than their acyclic conjugates.*

The theoretical basis for Hückel's rule is the Hückel molecular orbital theory (HMO), which was proposed by Erich Hückel in 1930. This theory considers a very simple linear combination of atomic orbitals molecular orbitals method for the determination of energies of molecular orbitals of π-electrons in π-delocalized molecules, such as ethylene, benzene, butadiene, and pyridine.

$4n$+2 π-electrons
(aromatic)



$4n$ π-electrons
(antiaromatic)

➢ *Main Features of Hückel Molecular Orbital Theory*

1. It is limited to conjugated hydrocarbons only.

2. Only π-electron density of MOs is included because these determine much of the spectral and chemical properties of these compounds. The σ-electron density is thought to form the framework of the molecule and σ-connectivity is employed to find whether two π-orbitals interact or not. Nevertheless, the orbitals generated by σ-orbitals are overlooked and presumed not to interact with π-electrons, which is called as σ-π separability. It is defensible by the orthogonality of π and σ orbitals in planar molecular geometries. That's why the Hückel method is only limited to systems that are nearly or completely planar.

3. The theory is based on the variational method to the linear combination of atomic orbitals and makes simple assumptions about the resonance, overlap, and Coulomb integrals of these atomic orbitals. Also, it doesn't try to solve the Schrödinger equation, and neither the functional form of the atomic basis nor particulars of the Hamiltonian involved.

4. For different hydrocarbons, the theory takes atomic connectivity as the only input value; empirical parameters are only required after the incorporation of heteroatoms.

5. The theory successfully predicts the number of energy levels for a given molecule, their degeneracy and it expresses the energies molecular orbital in terms of two parameters, called α, the energy of an electron in an atomic $2p$ orbital, and β which represents the energy of interaction between two $2p$ orbitals. The typical convention makes both α and β be as negative quantities. In order to fully understand and equate systems in a qualitative or semi-quantitative manner, clear numerical values for these parameters are typically not needed.

6. This theory also enables the calculation of charge density for each atom in the π framework, the fractional bond order between any two carbon atoms, and the overall dipole moment of the molecule.

➢ *Energy Level of Some Typical π-Molecular Orbitals*

The exact procedure to determine the energy levels of conjugated π -bonded systems is beyond the scope of this book. However, the results from theory can be concluded in some simple mathematical expressions which can be used to yield the required energy levels. For linear and cyclic systems (with N atoms), general solutions are given below.

1. Linear system (polyene/polyenyl): The energy of different molecular orbitals for these types of systems can be obtained from the expression given below.

$$E_k = \alpha + 2\beta\ Cos\frac{(k+1)\pi}{(N+1)} \qquad (1)$$

Where $k = 0, 1, 2, 3 \ldots N-1$ and N is the number conjugated carbons. Once the energies of different molecular orbitals are obtained, they should be arranged in accenting order on the energy level diagram.

i) Ethylene: In case of ethylene, $N = 2$, we get

for $k = 0$
$$E_0 = \alpha + 2\beta\ Cos\frac{(0+1)\pi}{(2+1)} = \alpha + \beta \qquad (2)$$

for $k = 1$
$$E_1 = \alpha + 2\beta\ Cos\frac{(1+1)\pi}{(2+1)} = \alpha - \beta \qquad (3)$$

The corresponding energy level diagram is given below.

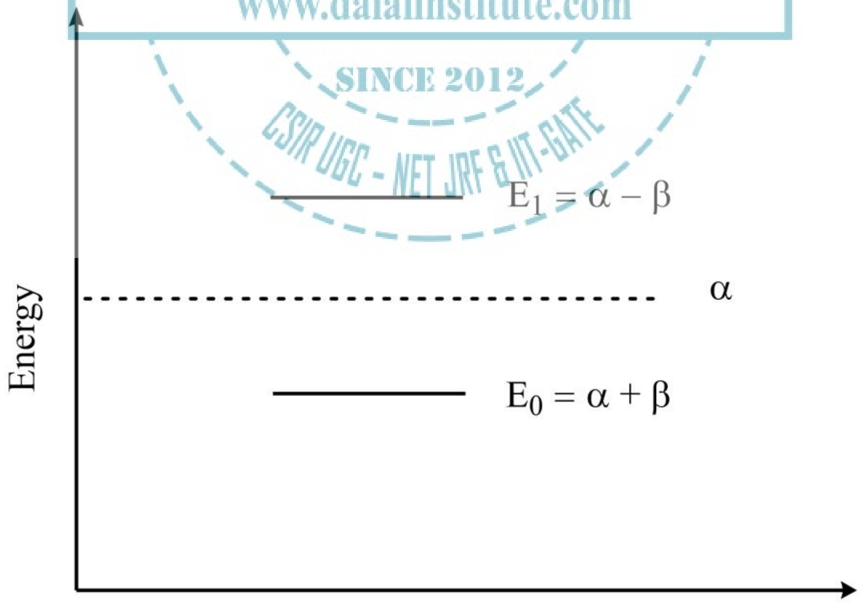


Figure 13. The π-molecular orbital energy level diagram of ethylene.

ii) Allyl: In case of allyl, $N = 3$, we get

for $k = 0$ $$E_0 = \alpha + 2\beta\, Cos\frac{(0+1)\pi}{(3+1)} = \alpha + \sqrt{2}\beta \tag{4}$$

for $k = 1$ $$E_1 = \alpha + 2\beta\, Cos\frac{(1+1)\pi}{(3+1)} = \alpha \tag{5}$$

for $k = 2$ $$E_2 = \alpha + 2\beta\, Cos\frac{(2+1)\pi}{(3+1)} = \alpha - \sqrt{2}\beta \tag{6}$$

The corresponding energy level diagram is given below.

Figure 14. The π-molecular orbital energy level diagram of allyl.

iii) Butadiene: In case of butadiene, $N = 4$, we get

for $k = 0$ $$E_0 = \alpha + 2\beta\, Cos\frac{(0+1)\pi}{(4+1)} = \alpha + 1.618\,\beta \tag{7}$$

for $k = 1$ $$E_1 = \alpha + 2\beta\, Cos\frac{(1+1)\pi}{(4+1)} = \alpha + 0.618\,\beta \tag{8}$$

for $k = 2$ $$E_2 = \alpha + 2\beta\, Cos\frac{(2+1)\pi}{(4+1)} = \alpha - 0.618\,\beta \tag{9}$$

for $k = 3$ $$E_3 = \alpha + 2\beta\, Cos\frac{(3+1)\pi}{(4+1)} = \alpha - 1.618\,\beta \tag{10}$$

The corresponding energy level diagram is given below.

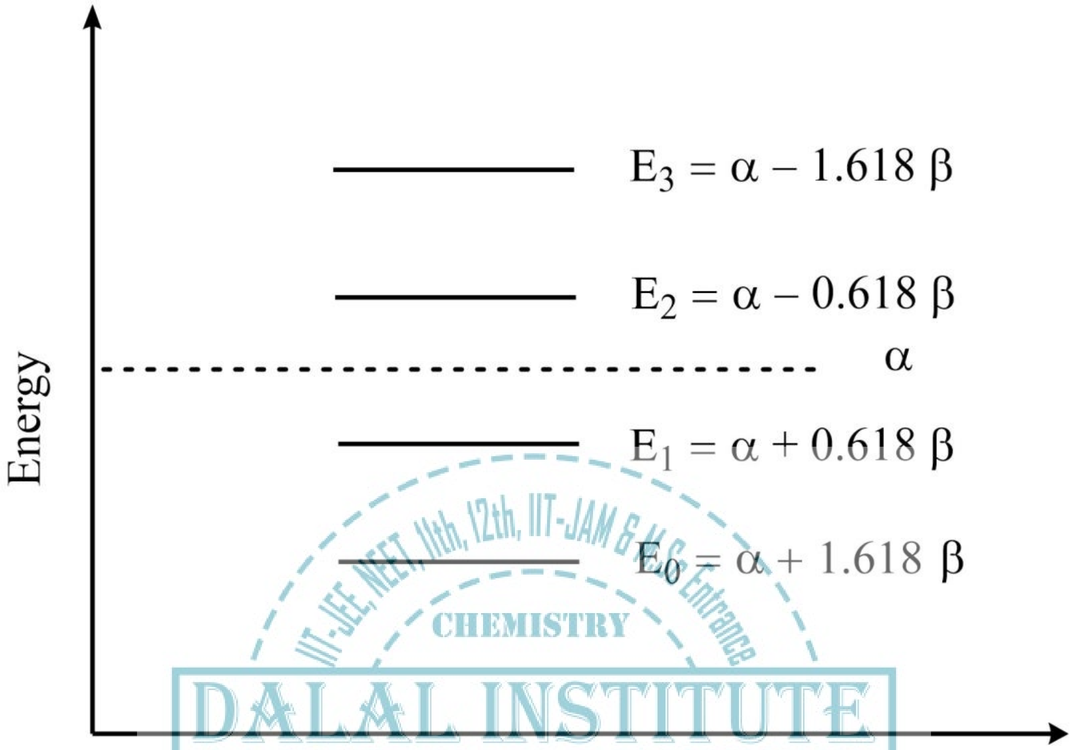


Figure 15. The π-molecular orbital energy level diagram of butadiene.

2. Cyclic system, Hückel topology (annulene/annulenyl): The energy of different molecular orbitals for these types of systems can be obtained from the expression given below.

$$E_k = \alpha + 2\beta\, Cos\frac{2k\pi}{N} \tag{11}$$

Where $k = 0, 1, 2, 3 \ldots N-1$ and N is the number conjugated carbons. Once the energies of different molecular orbitals are obtained, they should be arranged in accenting order on the energy level diagram.

i) Cyclopropenyl: In case of cyclopropenyl, $N = 3$, we get

for $k = 0$

$$E_0 = \alpha + 2\beta\, Cos\frac{2(0)\pi}{3} = \alpha + 2\beta \tag{12}$$

for $k = 1$

$$E_1 = \alpha + 2\beta\, Cos\frac{2(1)\pi}{3} = \alpha - \beta \tag{13}$$

for $k = 1$

$$E_2 = \alpha + 2\beta\, Cos\frac{2(2)\pi}{3} = \alpha - \beta \tag{14}$$

The corresponding energy level diagram is given below.

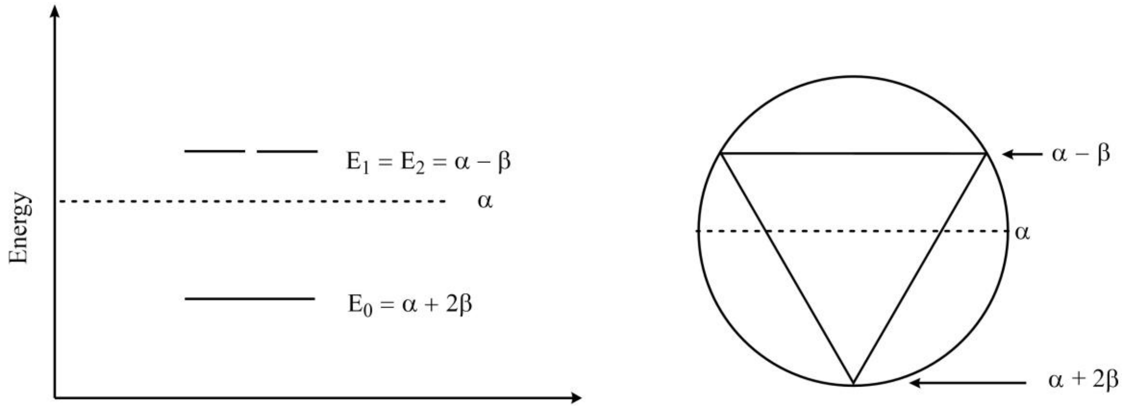


Figure 16. The π-molecular orbital energy level diagram of cyclopropenyl.

ii) Cyclobutadiene: In case of cyclobutadiene, $N = 4$, we get

for $k = 0$
$$E_0 = \alpha + 2\beta \, Cos \frac{2(0)\pi}{4} = \alpha + 2\beta \tag{12}$$

for $k = 1$
$$E_1 = \alpha + 2\beta \, Cos \frac{2(1)\pi}{4} = \alpha \tag{13}$$

for $k = 2$
$$E_2 = \alpha + 2\beta \, Cos \frac{2(2)\pi}{4} = \alpha - 2\beta \tag{14}$$

for $k = 3$
$$E_3 = \alpha + 2\beta \, Cos \frac{2(3)\pi}{4} = \alpha \tag{15}$$

The corresponding energy level diagram is given below.

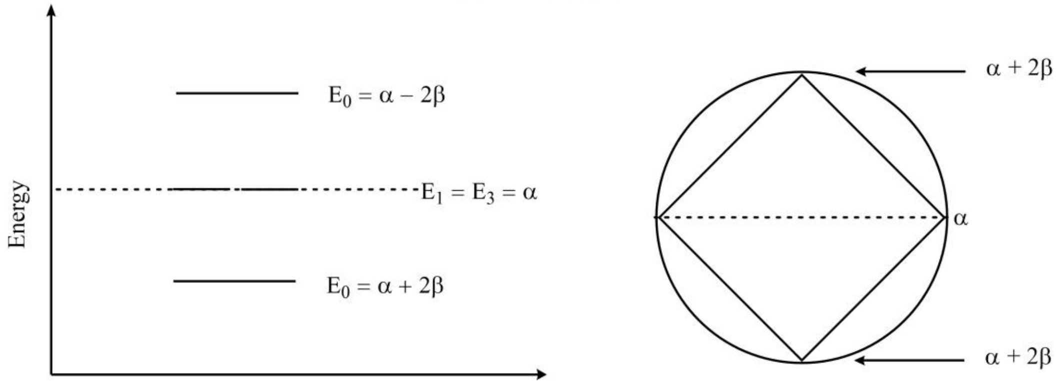


Figure 17. The π-molecular orbital energy level diagram of cyclobutadiene.

iii) Benzene: In case of butadiene, $N = 6$, we get

for $k = 0$
$$E_0 = \alpha + 2\beta \; Cos \frac{2(0)\pi}{6} = \alpha + 2\beta \tag{16}$$

for $k = 1$
$$E_1 = \alpha + 2\beta \; Cos \frac{2(1)\pi}{6} = \alpha + \beta \tag{17}$$

for $k = 2$
$$E_2 = \alpha + 2\beta \; Cos \frac{2(2)\pi}{6} = \alpha - \beta \tag{18}$$

for $k = 3$
$$E_3 = \alpha + 2\beta \; Cos \frac{2(3)\pi}{6} = \alpha - 2\beta \tag{19}$$

for $k = 4$
$$E_4 = \alpha + 2\beta \; Cos \frac{2(4)\pi}{6} = \alpha - \beta \tag{20}$$

for $k = 5$
$$E_5 = \alpha + 2\beta \; Cos \frac{2(1)\pi}{6} = \alpha + \beta \tag{21}$$

The corresponding energy level diagram is given below.

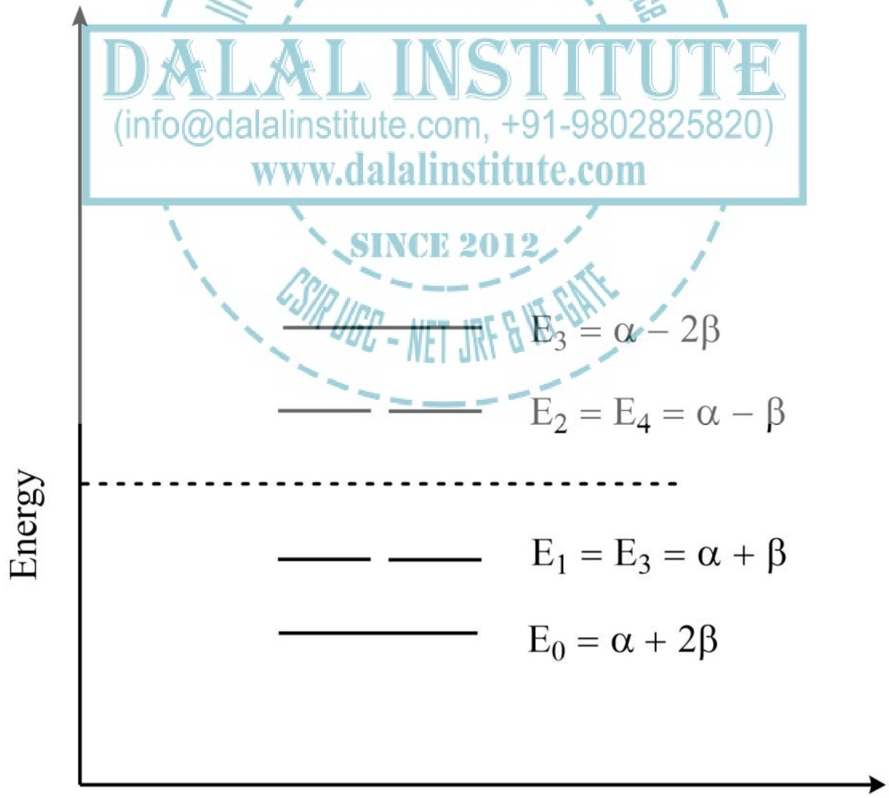
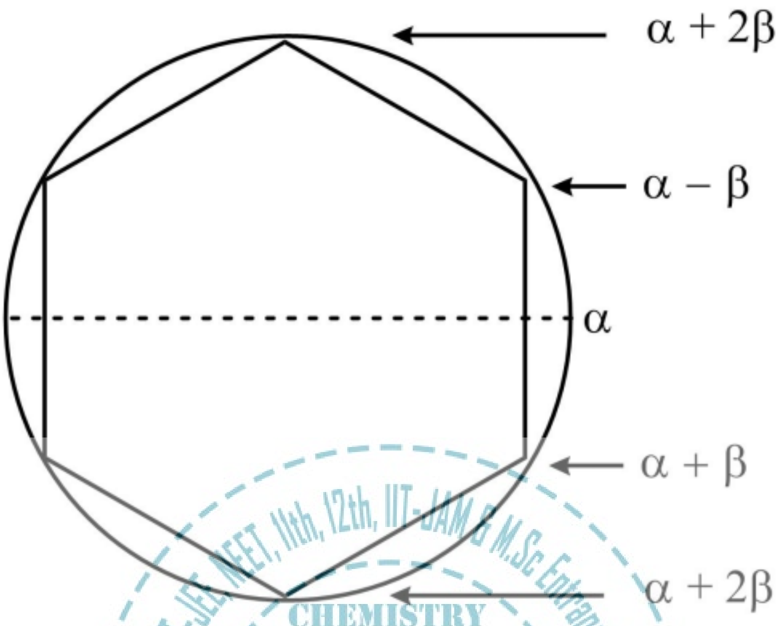


Figure 18. The typical π-molecular orbital energy level diagram of the benzene molecule.

The corresponding Frost circle is given below.



The energy levels for cyclic systems can be obtained using the Frost circle method (named after the American chemist A. A. Frost). A circle with a center at α with a radius of 2β is inscribed with a regular polygon with N sides with one vertex pointing downward; the *y*-coordinate of the vertices of the polygon then shows the energies of different orbital of the [N]annulene/annulenyl system. Corresponding mnemonics exist for Möbius and linear systems. The energy level diagrams of different cyclic systems are assisted with the corresponding Frost cycle.

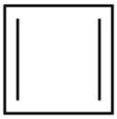
In the later period, it was extended to conjugated molecules with heteroatoms like pyrrole, pyridine, and furan. A more dramatic extension of the method (Huckel molecular orbital method) to include σ-electrons, known as the extended Hückel method (EHM), was developed by Roald Hoffmann.

The Hückel method's extension provides some degree of quantitative accuracy for organic compounds in general and was employed to give computational justification for the famous Woodward-Hoffmann rules. In order to differentiate the original route from Hoffmann's extension, the Hückel method is also well-known as the 'simple Hückel method' (SHM). Even though the method is quite simple, the Hückel route in its original form makes chemically useful and qualitatively accurate predictions for numerous common molecular geometries, and therefore, is a very powerful and widely popular educational toolkit. It is also included in textbooks of preliminary quantum chemistry and physical organic chemistry. Furthermore, many organic chemists, in specific, still apply Hückel theory routinely to find back-of-the-envelope, the very approximate profile of π-interactions.

❖ Annulenes

Annulenes are the monocyclic conjugated polyenes that contain the maximum number of non-cumulated double bonds.

Annulenes have the general formula of C_nH_n (when n represents an even number) or C_nH_{n+1} (when n represents an odd number). The IUPAC nomenclature of annulenes with 7 or more carbon atoms follows as [n]-annulene, where n represents the number of C atoms in their cycle, though the smaller annulenes are referred to using the same notation sometimes (benzene is also an annulene). The first 3 even annulenes include cyclobutadiene, benzene, and cyclooctatetraene. Many annulenes like cyclobutadiene i.e. [4]-annulene, cyclodecapentaene i.e. [10]-annulene, cyclododecahexaene i.e. [12]-annulene and cyclotetradecaheptaene i.e., [14]-annulene, are not stable, with cyclobutadiene at extreme position. Annulenes may be aromatic (benzene, [6]-annulene and [18]-annulene), non-aromatic ([8]- and [10]-annulene), or anti-aromatic (cyclobutadiene, [4]-annulene). Cyclobutadiene or [4]-annulene is the only annulene with considerable antiaromatic character due to unavoidable planarity. With [8]-annulene takes on a tub shape that permits it to evade conjugation of double bonds making it less unstable. [10]-Annulene has very strange geometry to be planar structure; in a planar conformation, ring strain arising from either steric hindrance of internal H atoms (when some double bonds are trans) or the distortion of bond angle (if double bonds are all cis) is unavoidable. hence, it doesn't get appreciable aromatic character.

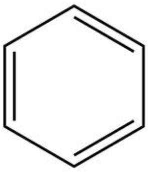


cyclobuta-1,3-diene

[4]-annulene

4 π-electrons, planer

Antiaromatic

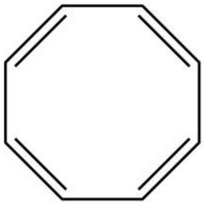


benzene

[6]-annulene

6 π-electrons, planer

Aromatic

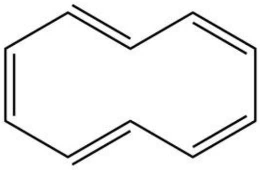


cyclooctatetraene

[8]-annulene

8 π-electrons, non-planer

Nonaromatic

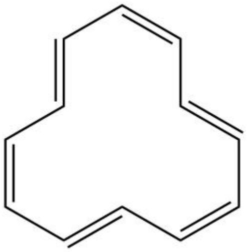


cyclodecapentaene

[10]-annulene

10 π-electrons, non-planer

Nonaromatic



cyclododecahexaene

[12]-annulene

12 π-electrons, planer

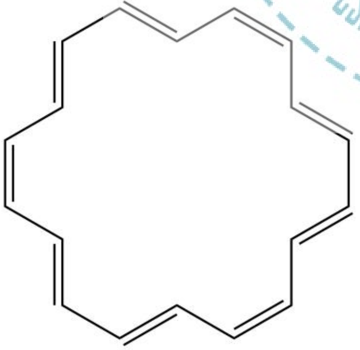
Antiaromatic

cyclotetradecaheptaene

[14]-annulene

14 π-electrons, planer

Aromatic



Cyclooctadecanonaene

[18]-annulene

18 π-electrons, planer

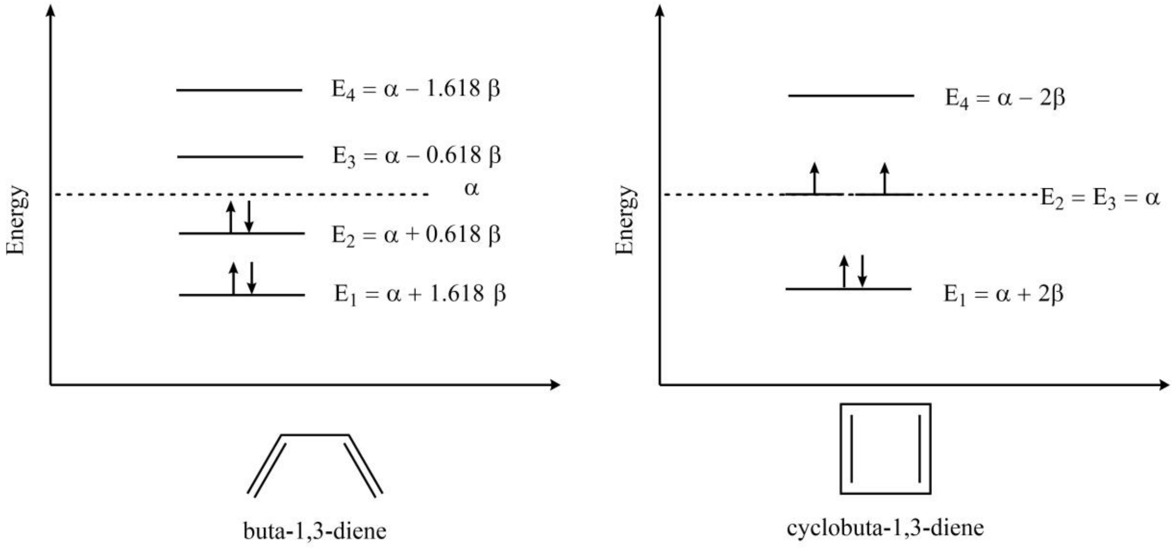
Aromatic

When the annulene is large enough, [18]-annulene, for example, there is enough room internally to accommodate hydrogen atoms without significant distortion of bond angles. [18]-Annulene possesses several properties that qualify it as aromatic. Nevertheless, no bigger annulenes are as stable as [6]-annulene i.e. benzene, as their reactivity resembles closely a conjugated polyene than a hydrocarbon of aromatic nature.

❖ Antiaromaticity

The phenomenon of antiaromaticity in organic chemistry may simply be defined as a property of planar conjugated cyclic structures by which it becomes less stable than its acyclic conjugate.

In order to find whether the compound is antiaromatic or not, it is a necessary pre-condition to confirm that its delocalization energy is less than its acyclic conjugate. After studying a lot of conjugated molecules, it was found that in almost all antiaromatic compounds, the total number of the π-electrons can be fitted by the formula $4n$ delocalized (π or lone pair) electrons in it. Unlike aromatic systems, which are governed by Hückel's rule ($4n+2$ π-electrons) and are very stable compounds, these antiaromatic systems are extremely unstable and very reactive. In order to evade this instability due to antiaromaticity, the compound may transform its shape, becoming a non-planar, and therefore, removing some of the π-interactions. In contrast to the diamagnetic ring current of aromatic systems, antiaromatic molecules have a paramagnetic type ring current, which can be detected by the NMR spectroscopic methods. Common examples of antiaromatic systems are. Pentalene, biphenylene, cyclopentadienyl cation. The archetypal case of antiaromaticity, cyclobutadiene molecule, is widely debated with some scientists saying that antiaromaticity is not the primary factor to its large destabilization.



$$E_\pi = E_{after\ \pi\text{-}bonding} - E_{before\ \pi\text{-}bonding}$$

$$E_\pi = [2\times(\alpha + 1.618\ \beta) + 2\times(\alpha + 0.618\ \beta)] - 4\alpha = 4.48\beta$$

$$E_D = E_\pi - 4\beta = 4.48\beta - 4\beta = 0.48\beta$$

$$E_\pi = E_{after\ \pi\text{-}bonding} - E_{before\ \pi\text{-}bonding}$$

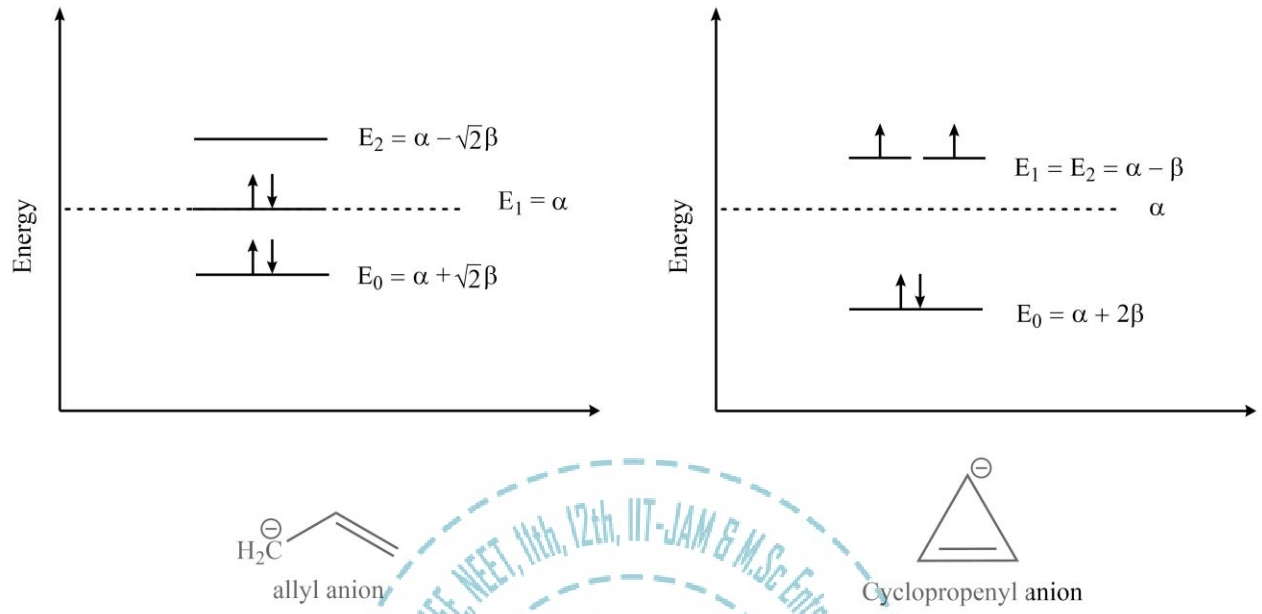
$$E_\pi = [2\times(\alpha + 2\ \beta) + 1\times(\alpha) + 1\times(\alpha)] - 4\alpha = 4\beta$$

$$E_D = E_\pi - 4\beta = = 4\beta - 4\beta = 0.48\beta$$

Figure 19. The π-molecular orbital energy level diagram of cyclobutadiene.

It is obvious that the delocalization energy (E_D) of cyclobutadiene is less than its acyclic conjugate, and therefore, it is antiaromatic in nature.

Similarly, we can prove the antiaromaticity of cyclopropenyl anion as given below.



$$E_\pi = E_{after\ \pi\text{-}bonding} - E_{before\ \pi\text{-}bonding}$$

$$E_\pi = [2\times(\alpha + \sqrt{2}\beta) + 2\times(\alpha)] - 4\alpha = 2\sqrt{2}\,\beta$$

$$E_D = E_\pi - 4\beta = 2\sqrt{2}\,\beta - 2\beta = 0.83\beta$$

$$E_\pi = E_{after\ \pi\text{-}bonding} - E_{before\ \pi\text{-}bonding}$$

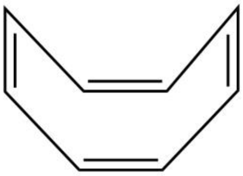
$$E_\pi = [2\times(\alpha + 2\beta) + 1\times(\alpha - \beta) + 1\times(\alpha - \beta)] - 4\alpha = 2\beta$$

$$E_D = E_\pi - 2\beta = 2\beta - 2\beta = 0\beta$$

Figure 20. The π-molecular orbital energy level diagram of cyclobutadiene.

Cyclooctatetraene is the most popular case of a molecule becoming a non-planar geometry to avoid antiaromatic destabilization. Had it been planar, it would have a single 8π-electron system around the cycle, nonetheless, it becomes a boat-like shape with four separate π bonds.


Cyclooctatetraene


Cyclooctatetraene
(Tub conformation)

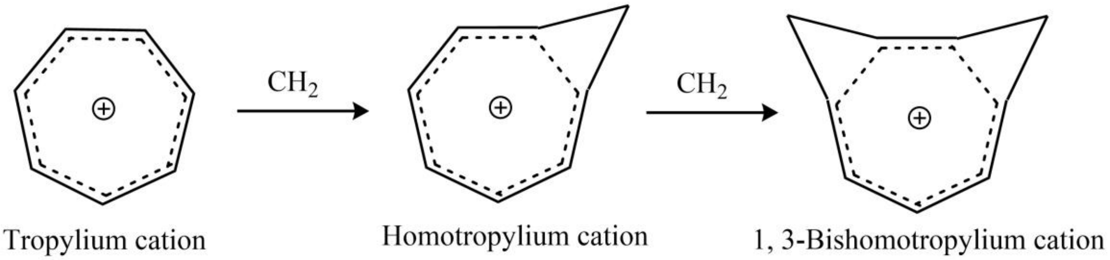
Since antiaromatic systems are usually short-lived and difficult to detect experimentally, the antiaromatic destabilization energy is frequently modeled by computer simulation rather than by actual experiment.

❖ Homoaromaticity

The homoaromaticity in organic chemistry may simply be defined as a special case of aromatic behavior where the normal conjugation is interrupted by a single sp^3-hybridized carbon atom.

Though this sp^3 center disturbs the continuity of overlap between *p*-orbitals, conventionally thought to be a primary need for aromaticity, substantial thermodynamic stability, and many of the magnetic, spectroscopic, and chemical properties related to aromatic compounds are still observed for such molecules. This official discontinuity is bypassed by *p*-orbital overlap, preserving a contiguous cycle of π-electron density that is accountable for its extra stability. The idea of homoaromaticity was proposed by S. Winstein in 1959, encouraged by his analysis of the "tris-homocyclopropenyl" ion. After Weinstein's publication, abundant research has been dedicated to the understanding of these molecules, which embody an additional class of aromatic compounds included broadening the definition of aromatic behavior. Up to the present time, homoaromatic molecules are quite well-known to exist as anionic and cationic species, and some reports support the presence of neutral homoaromatic compounds, nonetheless, these are not so common. It seems that the 'homotropylium' cation ($C_8H_9^+$) is the most studied case of a homoaromatic system.

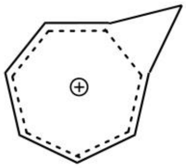
The label "homoaromaticity" originates from the similar structural profile of homoaromatic compounds with analogous homo-conjugated alkenes observed previously. The IUPAC Gold Book needs that bis-, tris-, etc. type prefixes to be used to define homoaromatic compounds where two, three, etc. sp^3 centers separately interrupt the phenomenon of conjugation of the aromatic molecules.



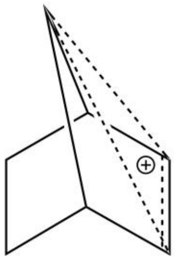
The homoaromatic compounds can simply be divide into three different categories, depending on the nature of the charge on them. A general discussion on all three types is given below.

➢ *Cationic Homoaromatic Compounds*

The most well-known and proven homoaromatic species are cationic entities. As we have earlier mentioned, the homotropenylium cation is the most studied homoaromatic compound. Numerous homoaromatic cationic species act as a basis for a tropylium cation, cyclopropenyl cation, or a cyclobutadiene dication because these species have very strong aromaticity. Additionally, another well-known cationic homoaromatic compound is the norbornen-7-yl cation, which is quite strongly homoaromatic, proven both experimentally and theoretically.



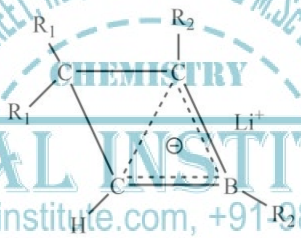
Homotropylium cation



Norbornen 7-yle cation

- ***Anionic Homoaromatic Compounds***

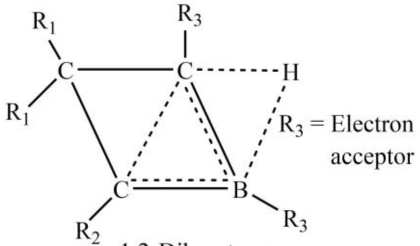
The homoaromatic anions are widely accepted to have "true" homoaromaticity. These anionic species are frequently obtained from their neutral parent molecules via Li-based reduction. 1,2-diboretanide derivatives display strong homoaromatic behavior via their 3-atom (B, B, and C), 2-electron bond, which contains shorter carbon-boron bonds than in the neutral analog. These 1,2-diboretanides can be expanded to bigger ring sizes with different groups and all have some degree of homoaromaticity.



1,2-Diboretanide

- ***Neutral Homoaromatic Compounds***

Numerous classes of neutral homoaromatic compounds have been observed though there is a debate whether they are truly homoaromatic or not. One class of the type of neutral homoaromatics is called monohomoaromatics, including cycloheptatriene. One more example is a 60-carbon fulleroid derivative that has only one methylene bridge. The NMR and UV -visible study has proven that the aromatic character of this modified fulleroid is not disturbed by the addition of a homoconjugate bond, and therefore, this molecule is homoaromatic for sure.



1,2-Diboretane

❖ PMO Approach

The PMO (perturbation molecular orbital) theory is nothing but an extension of the general molecular orbital theory. In this approach, the participating atomic orbitals are considered as the initial state, which in turn, is actually perturbed by the interaction to give the final state i.e. molecular orbitals. Furthermore, the PMO approach can also be applied to molecular orbitals to give new molecular orbitals. Now, depending upon the energy of basis orbitals i.e. unperturbed orbitals, the perturbed molecular orbitals can take two routes as discussed below.

➢ *Perturbed Molecular Orbitals from Degenerate Basis*

The perturbed molecular orbitals are formed by the additive and subtractive interaction of the basis orbitals; and if the unperturbed basis orbitals are degenerate, they equally contribute toward the additive and subtractive interaction.

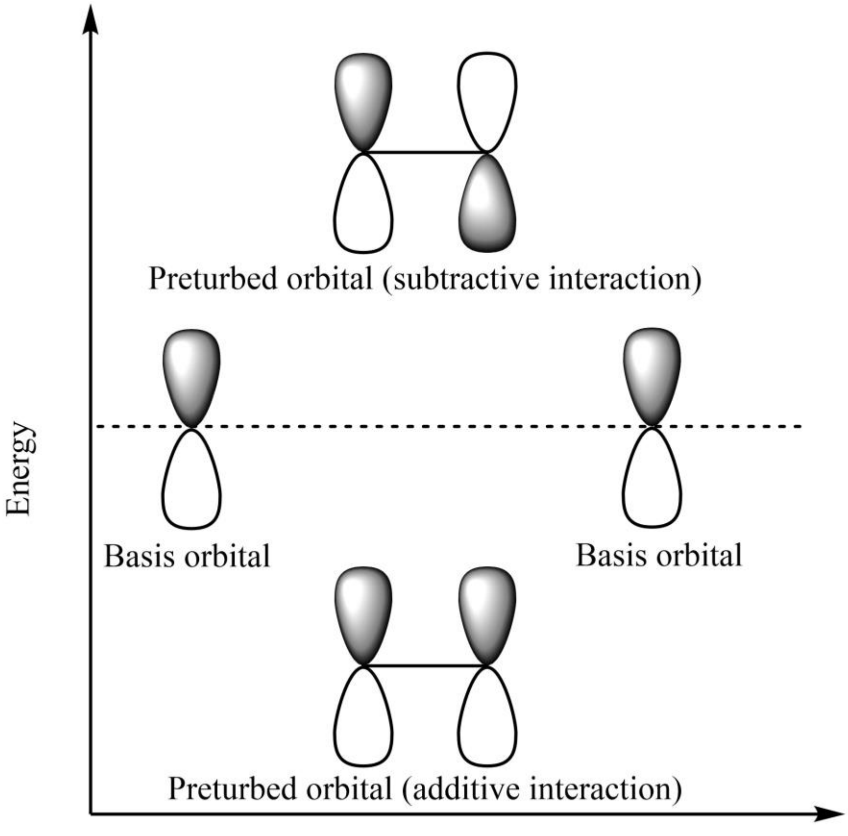


Figure 21. The perturbed molecular orbitals from degenerate basis orbitals.

In other words, the subtractive perturbation increases the energy whereas the additive interaction decreases the total energy of the molecular orbital formed.

- ***Perturbed Molecular Orbitals from Non-Degenerate Basis***

The perturbed molecular orbitals are formed by the additive and subtractive interaction of the basis orbitals; and if the unperturbed basis orbitals are not degenerate, they do not equally contribute toward the additive and subtractive interaction. Consider the two unperturbed basis orbitals ψ_1 and ψ_2 with different energies.

$$\psi_+ = \psi_1 + \lambda\psi_2 \tag{1}$$

$$\psi_- = \psi_2 - \lambda\psi_1 \tag{2}$$

Where the symbol λ whose value varies from 0 to 1. As the energy difference between ψ_1 and ψ_2 increases, the magnitude of λ approaches to zero.

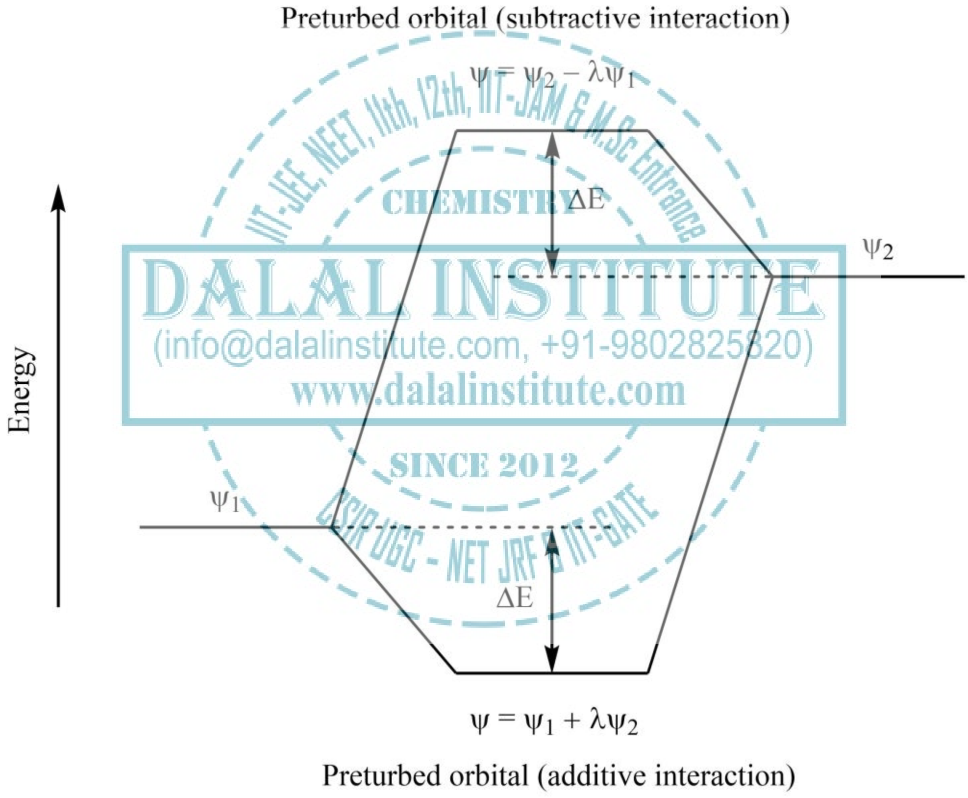


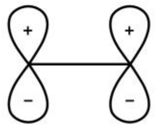
Figure 22. The perturbed molecular orbitals from non-degenerate basis orbitals.

In other words, the subtractive perturbation increases the energy whereas the additive interaction decreases the total energy of the molecular orbital formed. It is obvious from the above energy level diagram that the perturbation made the lower-energy basis orbital to lowered down and higher energy-orbital to rise above in energy further.

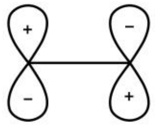
➢ ***Characteristic Features of PMO Approach***

Before we apply the PMO method to draw all the molecular orbitals of different linear and cyclic systems, it is very important to discuss some characteristic features of perturbed molecular orbitals first as given below.

1. Depiction of perturbed molecular orbitals: Unlike conventional MO theory, the molecular orbitals in the PMO approach are portrayed as in terms of basis orbitals rather than the actual shapes. Therefore, every shape with more than one atomic orbital is actually a molecular orbital.



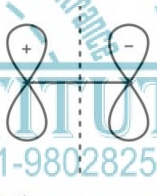
Bonding molecular orbital (BMO)



Antibonding molecular orbital (BMO)

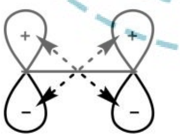
2. Symmetry of perturbed molecular orbitals: If a molecular orbital can be divided into two equal halves, the MO will be said to possess mirror or '*m*' symmetry.

Mirror symmetry present

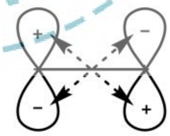


Mirror symmetry absent

Similarly, a molecular orbital has a two-fold symmetry axis, the MO will be said to possess inversion or 'C_2' symmetry.

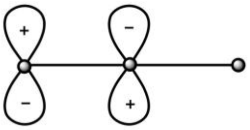


C_2 symmetry absent

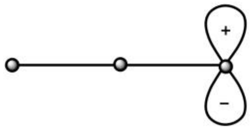


C_2 symmetry present

3. Representation of basis orbitals: The basis orbitals in PMO approach are portrayed combined number of participating atoms. For instance, if the molecular orbital of ethylene and a *p*-orbital are basis orbital, both should be depicted three carbon centres.



Ethylene



p-orbital

➢ *Construction of Perturbed Molecular Orbitals of Linear Conjugated Systems*

The π-molecular orbitals of linear conjugated systems can primarily be classified into two categories, even-numbered systems, and odd-numbered conjugated systems.

1. Molecular orbitals of even-numbered linear conjugated systems: If the number of carbon atoms in the conjugated system is even, half of the molecular orbitals will be bonding and half of the molecular orbitals will be antibonding in nature. The number of vertical nodes in the *n*th molecular orbital will be *n*–1.

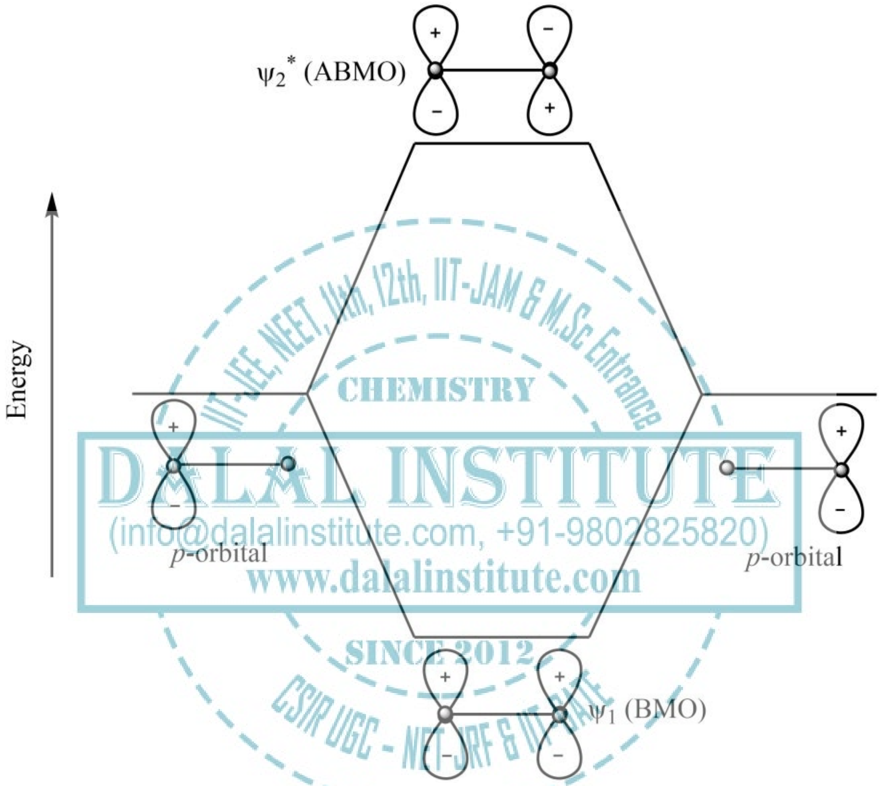


Figure 23. The perturbed molecular orbitals of ethylene.

The nature of the symmetry and number of nodes in the perturbed molecular orbitals (PMO) of ethylene are given below.

Table 1. Symmetry and nodes in different PMOs of ethylene.

PMO	Number of nodes	Mirror symmetry	C_2-symmetry
ψ_1	0	Present	Absent
ψ_2	1	Absent	Present

The nature of the symmetry and number of nodes in the perturbed molecular orbitals (PMO) of other even-numbered π-bonding systems are given below.

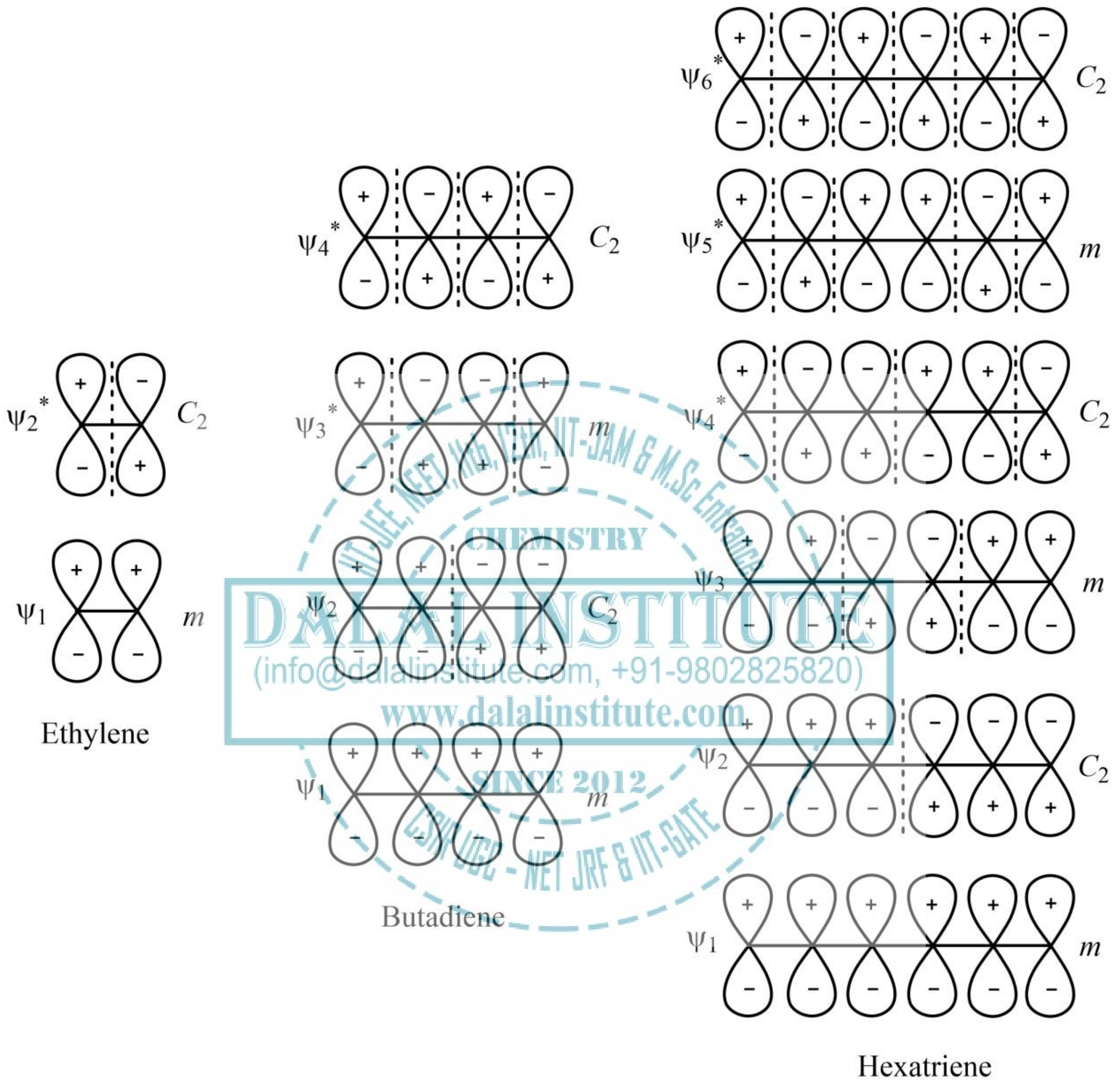


Figure 24. The perturbed molecular orbitals (along with the symmetry) of ethylene, butadiene, and hexatriene.

It is obvious from the above diagram that all the nodes in linear conjugated systems with an even number of carbon atoms pass through in-between the carbon nuclei.

2. Molecular orbitals of odd-numbered linear conjugated systems: If the number of carbon atoms in the conjugated system is odd, say *N*; *N*/2 of the molecular orbitals will be bonding whereas *N*/2 of the molecular orbitals will be antibonding in nature. One perturbed molecular orbital will be non-bonding in nature. The number of vertical nodes in the *n*th molecular orbital will be *n*–1.

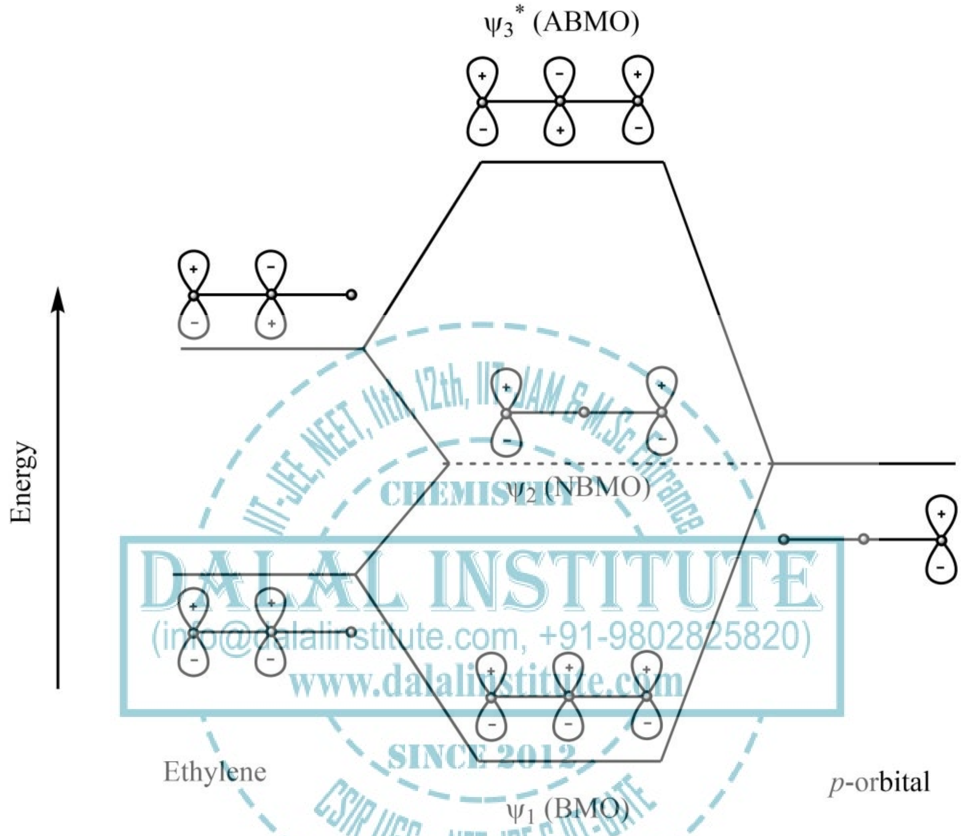


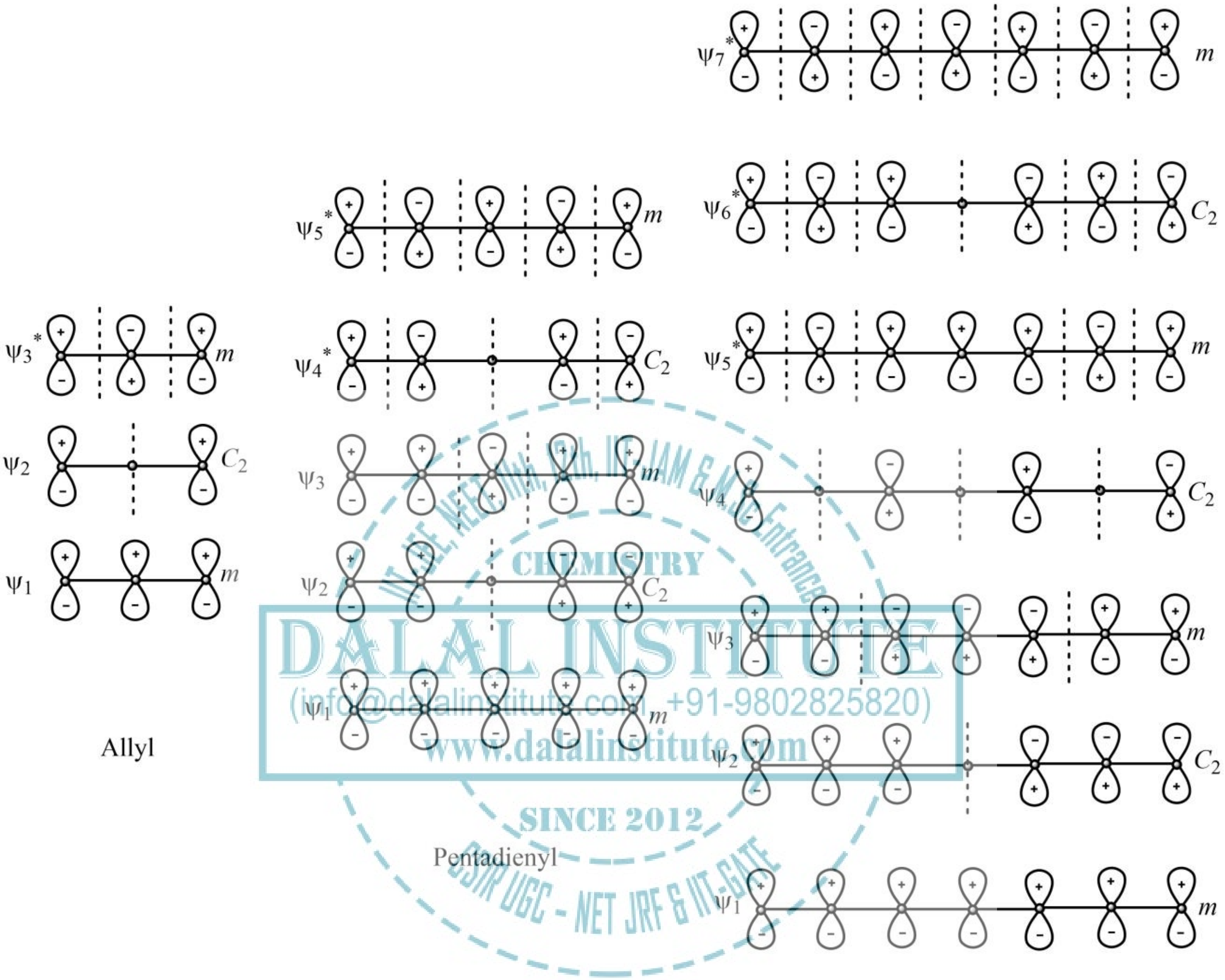
Figure 25. The perturbed molecular orbitals of allyl.

The nature of the symmetry and number of nodes in the perturbed molecular orbitals (PMO) of ethylene are given below.

Table 2. Symmetry and nodes in different PMOs of allyl.

PMO	Number of nodes	Mirror symmetry	C_2-symmetry
ψ_1	0	Present	Absent
ψ_2	1	Absent	Present
ψ_3	2	Present	Absent

The nature of the symmetry and number of nodes in the perturbed molecular orbitals (PMO) of other odd-numbered π-bonding systems are given below.



Allyl

Pentadienyl

Heptatrienyl

Figure 26. The perturbed molecular orbitals (along with the symmetry) of allyl, pentadienyl, and heptatrienyl.

It is obvious from the above diagram that all the nodes in ψ_{odd} pass through in-between the carbon nuclei whereas all nodes in ψ_{even} pass through in-between the carbon nuclei excepting one that passes through the central carbon nucleus. Furthermore, all the nodes in the case of non-bonding molecular orbitals pass through the carbon nuclei.

➢ *PMO Approach for Aromaticity*

One of the most important applications of the PMO approach is that it can also be used to predict the aromatic character of different organic compounds. According to this method, we need to observe the total energy of the conjugated system when it is molded into a ring. If the energy of the cyclic conjugated system becomes less than the open chain counterpart, it will be labeled as aromatic. Contrariwise, If the energy of the cyclic conjugated system becomes greater than the open chain counterpart, it will be labeled as antiaromatic. M. J. Goldstein and Roald Hoffmann wrote a very important paper in 1971 on symmetry, topology, and aromaticity. In their method, a cyclic conjugated system is considered as a derivative of two open-chain fragments that are joined at the ends, something like a donor-acceptor assembly. Now after taking mirror symmetry into consideration, we should expect a stable association if the symmetry of HOMO of one fragment matches with the symmetry of LUMO of the other fragment and vice-versa.

For simplicity, we will study conjugated systems with an even number of π-electrons only. Goldstein and Hoffmann divided these types of systems into two categories; Mode 2 (HOMO symmetric and LUMO antisymmetric) and Mode 0 (HOMO antisymmetric and LUMO symmetric).

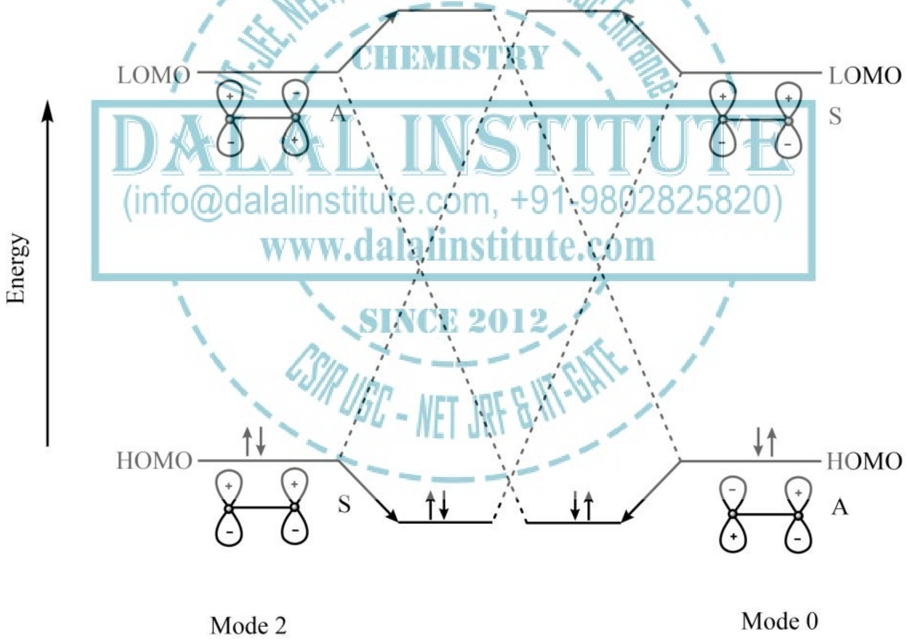


Figure 27. The pictorial depiction of Mode 2 overlap with Mode 0.

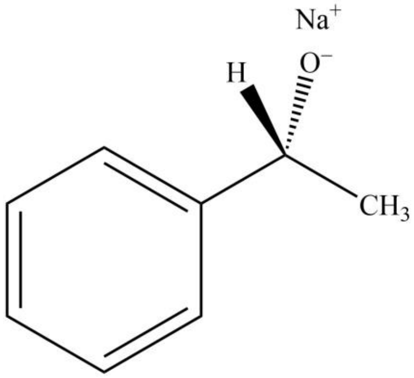
Similarly, if we consider Mode 2 interaction with Mode 2 or Mode 0 with Mode 0, we will get an unstable cyclic system owing to a symmetry disparity. Now since Mode 2 and Mode 0 fragments contain $4n + 2$ and $4n$ π-electrons respectively; the combination of Mode 2 and Mode 0 will create a total of $4n + 2$ π-electrons (aromatic), whereas Mode-2–Mode-2 or Mode-0–Mode-0 will create a total of $4n$ π-electrons (antiaromatic).

❖ Bonds Weaker Than Covalent

The bonds we have studied so far in this chapter possess bond dissociation energy in the range of 200–400 kJ mol^{-1} i.e., covalent bonds. However, there are some bonds with very low bond dissociation energies as well (10–40 kJ mol^{-1}). Therefore, in this section, we will discuss different types of bonds that are weaker than the typical covalent bond and results in supramolecular systems.

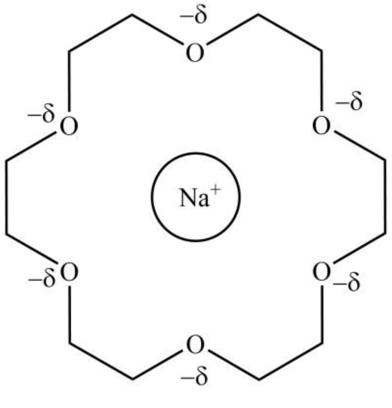
➢ *Ion-Ion Interactions*

Though ionic bonds are stronger than typical covalent bonds, the ion-ion interaction between a cation and organic anion is somewhat weaker than typical covalent interaction because of the bond energy in the range of 100–350 kJ mol.



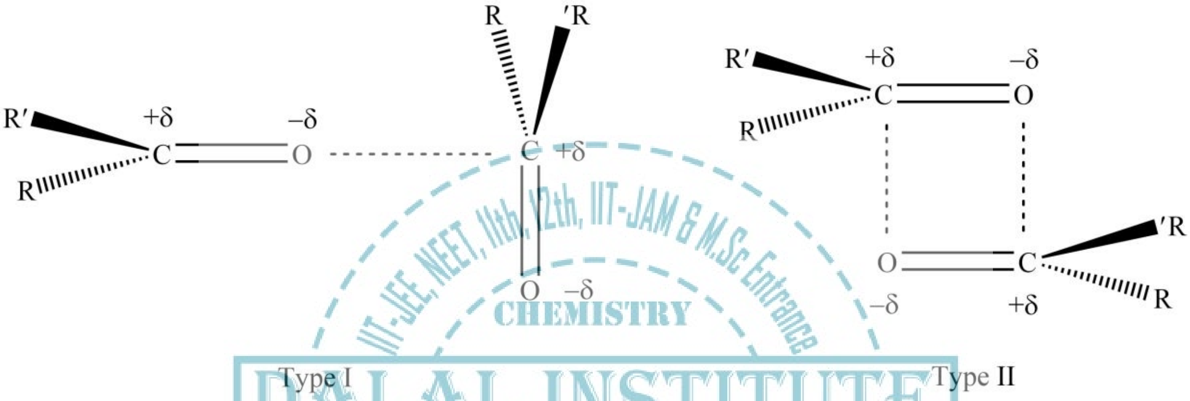
➢ *Ion-Dipole Interactions*

The interaction of an ion (like sodium) with a polar molecule (like water), is the case of ion-dipole interaction, whose bond energy ranges from 50−200 kJ mol^{-1}. This type of interaction is observed both in the solution and in the solid state. The ion-dipole bonding in supramolecular systems of alkali cations' complexes with macrocyclic (large ring) ethers are labeled as crown ethers. The oxygen atoms of the ether play the same role as played by the polar H_2O molecules, though the complex gets its extra stability from the chelate- and macrocyclic effects.



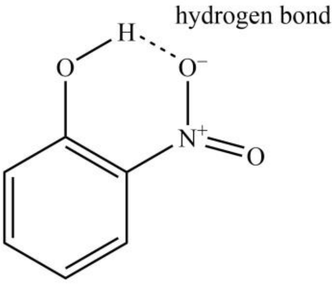
➢ ***Dipole-Dipole Interactions***

The alignment of molecular dipoles with each other can produce substantial attractions. This can be of two types; the first is the matching of a single pair of poles on adjacent molecules, and the second one involves the opposing alignment of one dipole with the other. The bond energy of dipole-dipole interactions ranges from 5–50 kJ mol^{-1}. Many carbonyl derivatives show this type of behavior in the solid state, and studies have proposed that the second type of interactions have energy around 20 kJ mol^{-1}, which is quite comparable to a hydrogen bond of intermediate strength. Nevertheless, the lower boiling point of ketones suggests that dipole-dipole interactions of the second type are relatively weak in solution (acetone's boiling point = 56ºC).

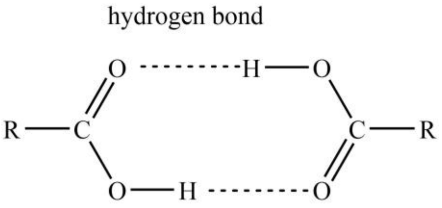


➢ ***Hydrogen Bonding***

The hydrogen bonding or H-bonding may be considered as a special type of dipole-dipole interaction where an H atom is in quite strong attraction with an electronegative atom of the same or neighboring molecule. If the H-bonding takes place within the molecule itself, it is called as intramolecular H-bonding. On the other hand, if the H-bonding takes place between two molecules, it is called as intermolecular H-bonding. The bond energy for H-interactions ranges from 10–120 kJ mol^{-1}. A typical case of H bonding in supramolecular systems is the generation of carboxylic acid dimers. H-bonds are ubiquitous, and are responsible for the overall shape of numerous proteins, recognition of substrates by many enzymes (along with π-π interactions) and also for DNA's double helix structure.



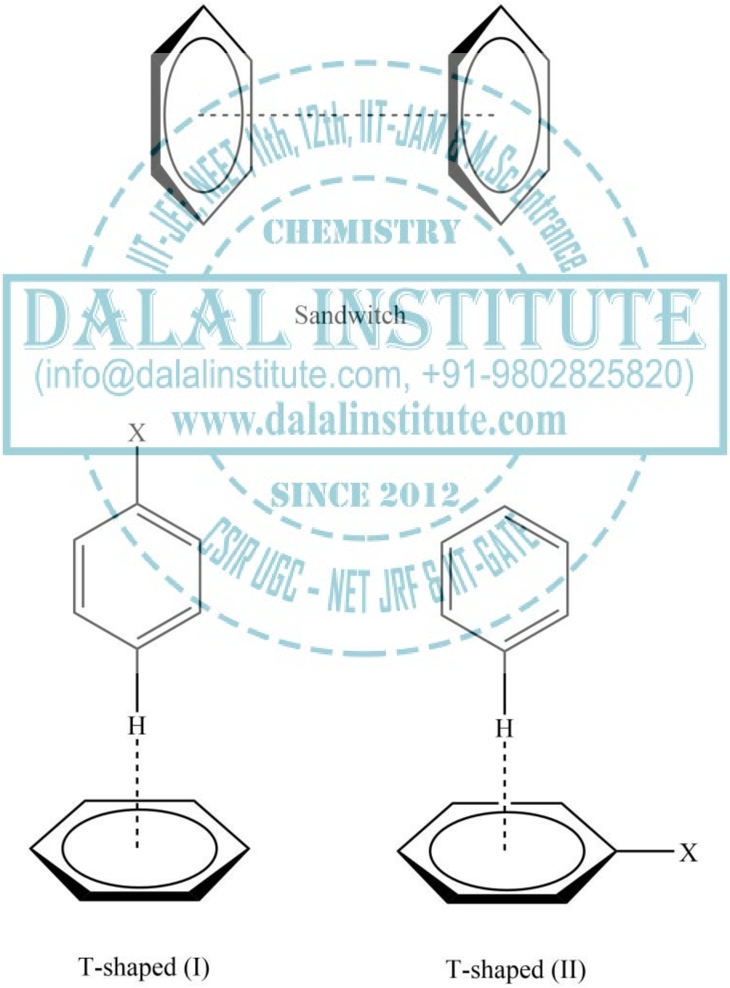
Intramolecular H-bonding



Intermolecular H-bonding

- ***π-π Interactions***

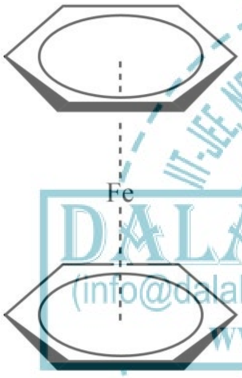
Since π-π interactions happen to be present between aromatic rings, they are also known as aromatic π-π stacking interactions, and generally involve one electron-deficient and one electron-rich species. The bond energy of these types of interactions ranges from 50–500 kJ mol^{-1}. These π-interactions are two kinds; one is face-to-face, and the second one is edge-to-face. The face-to-face π-π interactions are accountable for the slippery nature of graphite and its beneficial lubricant feature. Similar kind of π-π interactions between the aryl rings of nucleobase pairs also helps the DNA double helix to get stabilized. The second type (i.e. edge-to-face interactions) may be considered as weak types of H-bonds between the electron-rich π-cloud of one aromatic ring and the slightly electron-deficient H atoms of another aromatic ring. Hence, they must not be called as π-stacking because no stacking of the π-electron surfaces is present.



The edge-to-face interactions are also accountable for the characteristic herringbone packing in the crystal lattice of a range of small aromatic hydrocarbons (benzene included).

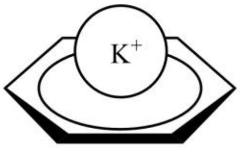
- ***Cation-π Interactions***

Many cations of *d*-block metals (like Fe^{2+}, Pd^{2+}, Pt^{2+}) are known to yield complexes with aromatic and olefinic systems such as ferrocene i.e. $[Fe(C_5H_5)_2]$ and Zeise's salt i.e. $[PtCl_3(C_2H_4)]^-$. The nature of bonding in such systems is quite strong and could not be considered non-covalent, because it is closely linked with the partially filled *d*-orbitals of the metals. For instance, the bond between Ag^+ and C_6H_6 has a significant covalent character. Nevertheless, the bonding of alkali metals' cations or alkaline earth metals' cations with C=C double bonds is quite weak, and therefore, can be considered as non-covalent interaction. These interactions have also been proved to play a significant role in biological systems. For instance, the bond energy of the K^+-benzene bond in the gas phase is around 80 kJ mol^{-1}, which is quite comparable to K^+-water interaction (75 kJ mol^{-1}). This can be attributed to the fact that the K^+ ion is more soluble in water than in C_6H_6 as more water molecules can interact with the potassium ion, but only a few C_6H_6 molecules can fit around it due to bulkier size.



Ferrocene

Zeise's salt



Cation-π interactions in between
K^+ ion and benzene

The bonding of cations of non-metals like RNH_3^+ with double bonds can be regarded as a type of X–H ···π H-interaction.

➢ *Anion-π Interactions*

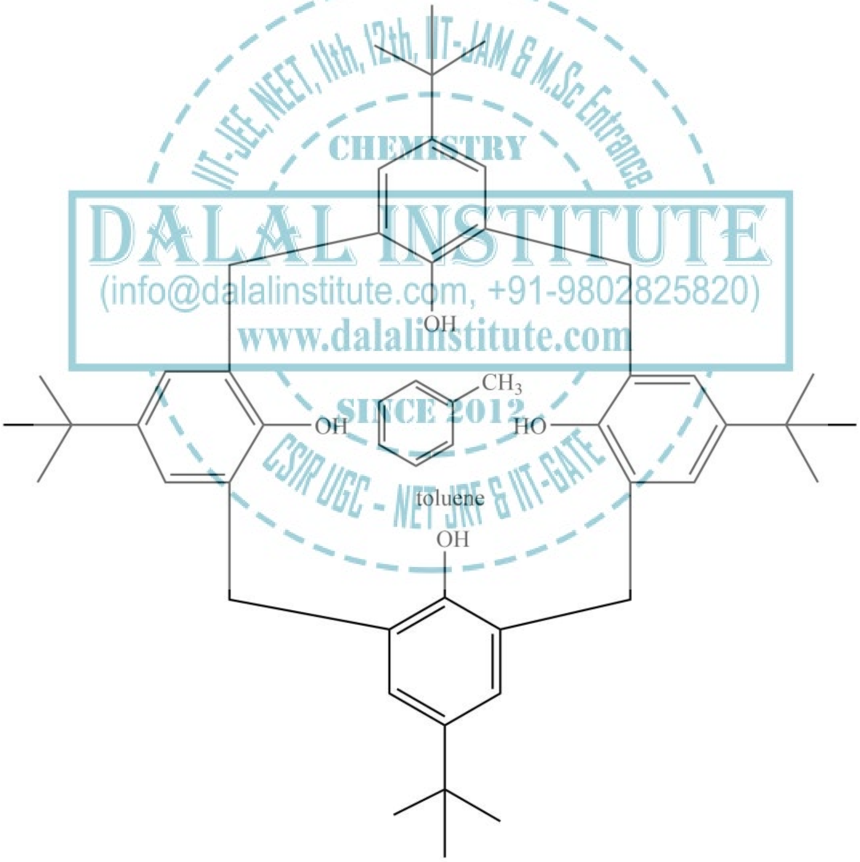
It seems that, unlike cation-π interactions, anion-π interactions should not be favorable as it appears to be repulsive; for instance, the affinity of the aromatic ring with cryptand for halides quickly dopes in the order $F^- >> Cl^- > Br^- \sim I^-$ since repulsions arising from anion-π interaction is more for bigger halides. Nevertheless, there is a difference in the charges between an anion and an overall neutral aromatic ring, and hence, there is a possibility of an electrostatic attraction. These kinds of short anion-π interactions are noted for organometallic calixarene derivatives where the aromatic ring has a substantial positive charge.

Anion-π interaction

The anion-π interactions are also caught up as controlling factors in self-assembly reactions of monovalent silver complexes with π-acidic aromatic rings.

➢ *Van der Waal's Forces*

Van der Waals forces are attractive and arise from the polarization of an electronic cloud by the closeness of an adjacent nucleus, yielding a weak attraction of electrostatic nature. The characteristic range for Van der Waals forces ranges from 0.50–40 kJ mol^{-1}. The Van der Waals forces are non-directional, and therefore, have only restricted scope in designing specific hosts for choosy complexation of specific guest molecules. Generally speaking, van der Waals forces deliver a generic attraction for most 'easily polarisable' (soft) species with the interaction energy relational to the surface area of direct contact. In the case of supramolecular systems, the van der Waals forces are extremely important in the generation of 'inclusion compounds', where very organic molecules small are loosely united within molecular cavities or crystal lattices; for instance, the inclusion of toluene into the molecular cavity of the *p*-tert-butylphenol-based macrocycle. In the case of molecular assemblies in solid-state, the effects of crystal close packing dictate the overall structural arrangement.



toluene in
p-tert-butylcalix[4]arene

The hydrophobic interactions also perform a vital role in supramolecular systems as these are accountable for displacing the H_2O molecules from the host's cavity by an organic molecular guest.

➢ *Closed Shell Interactions*

It is quite a well-known fact that an atom with partially filled electronic shells gives rise to a strong covalent bond. Nevertheless, many ions usually have fully-filled or closed valence electronic shells but feel strong attractions between oppositely charged pairs. Therefore, one might think that closed shell atoms of neutral or like charges should not show any significant interaction; though in some cases, they show significant attraction. These kinds of interactions are labeled as closed shell interactions and involve some secondary bonding interactions; one is halogen bonding and the other is metalophilic interactions. As far as the strength is concerned, these interactions are quite comparable to moderate H-bonds. These interactions are considered to originate from electron correlation effects, which are further strengthened by relativistic effects in the case of heavy metals like gold (i.e., aurophilic interactions). These interactions are very noticeable for heavy metals with electron configurations ranging from d^8 to $d^{10}s^2$.

Closed Shell Interactions

Furthermore, it is also worthy to note the fact that the overall strength of halogen bonding decreases in the following order.

$$I > Br > Cl >> F$$

❖ Addition Compounds: Crown Ether Complexes and Cryptands, Inclusion Compounds, Cyclodextrins

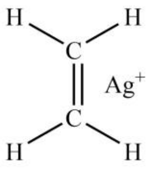
In this section, we will discuss some organic compounds in which the strength of the bonds is less than a typical covalent bond. One of the major types of compounds having weak non-covalent interaction is addition Compounds. An adduct, or addition compound, may simply be defined as the product of the direct addition of two or more distinct molecules, resulting in a single reaction product containing all atoms of all components. Now there are many types of addition compounds but we will confine our discussion only on adducts with bonds weaker than covalent such as electron donor-acceptor complexes.

➢ *Electron Donor-Acceptor Complexes*

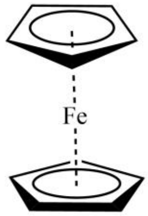
An electron donor-acceptor complex, or simply the charge-transfer complex (CT complex), is an association of two or more molecular entities, or of different parts of one big molecule, where a fraction of electronic charge is transferred from one molecular entity to another.

The resulting electrostatic force of attraction delivers a stabilizing drive for the molecular adduct so formed. The source molecule from which the charge is transferred is called the electron donor whereas the charge receiving species is labeled as the electron acceptor. These electron donor-acceptor complexes usually have spectra that different from the sum of the spectra of the individual participating molecules. There are two primary types of electron donor-acceptor complexes.

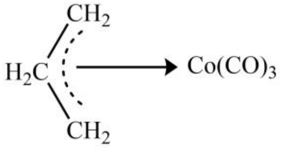
1. When the acceptor is a metal ion and the donor is an aromatic ring an alkene: Some of the typical examples of charge transfer complexes where the donor is an alkene or an aromatic ring and acceptor is a metal ion are given below.



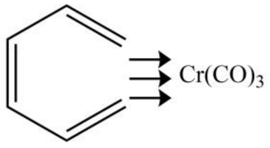
Alkene to metal charge transfer



Ring to metal charge transfer

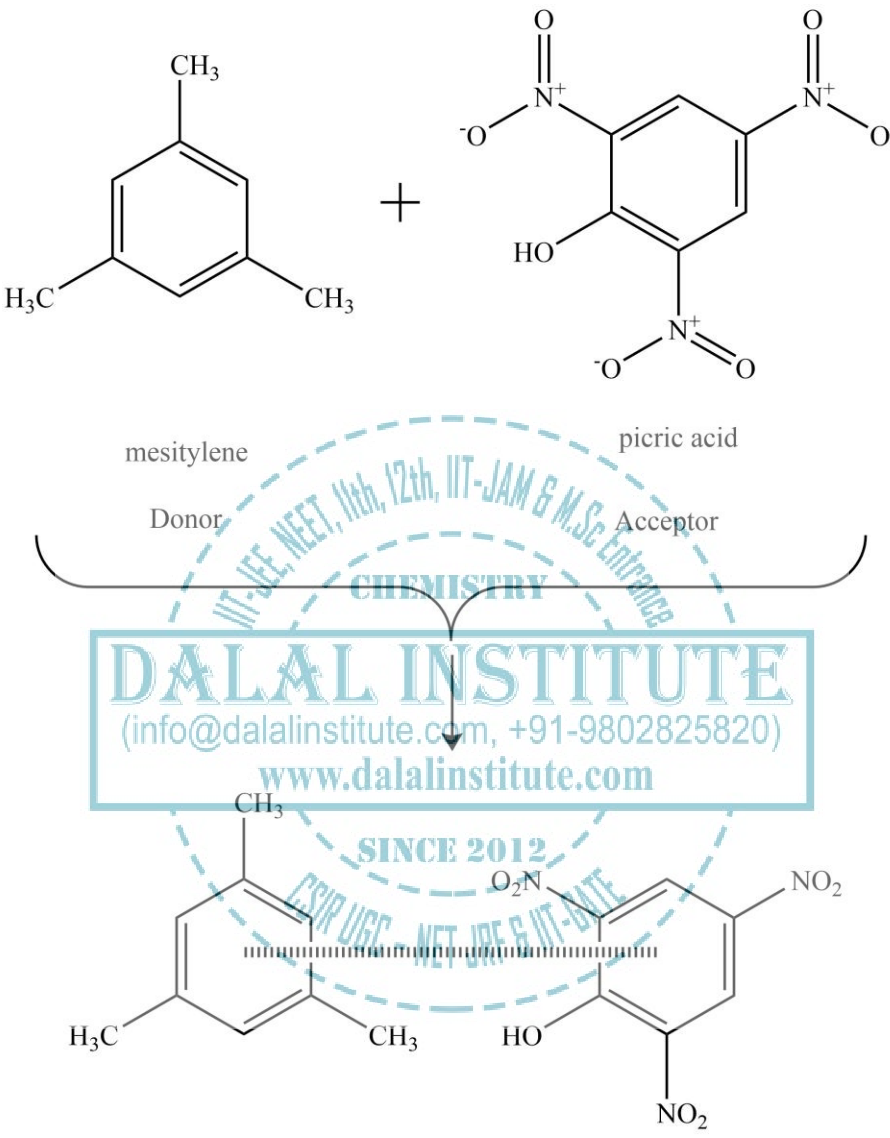


Allyl to metal charge transfer



Open chain to metal charge transfer

2. When the Acceptor is an organic molecule: Some of the typical examples of charge transfer complexes where the acceptor entity is an organic molecule are given below.



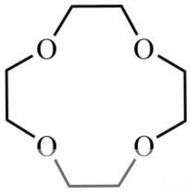
π-complex
(Picrate)

It is also worthy to note that owing to the very small energy gap between the ground and excited states, electron donor-acceptor complexes show absorption peaks in the visible or near-UV region, and therefore, usually show color in sunlight.

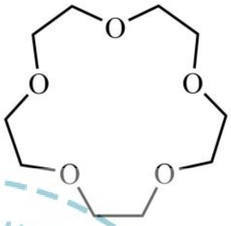
➢ *Crown Ether Complexes and Cryptates*

More typical examples of addition compounds are crown ether complexes and cryptands. A general discussion on both these types is given below.

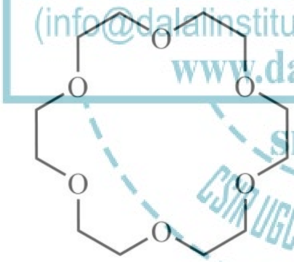
1. Crown ether complexes: Crown ethers may simply be defined as the cyclic compounds that are consisted of a ring with several ether groups. Some of the most common examples of crown ethers are cyclic oligomers of ethylene oxide, where ethyleneoxy is the repeating unit. Chief members of this Crown ethers' series are the hexamer (*n* = 6), the pentamer (*n* = 5), and the tetramer (n = 4).



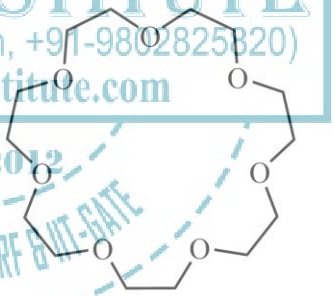
12-crown-4



15-crown-5



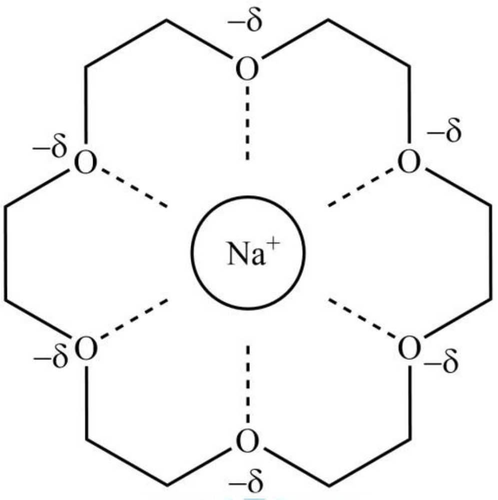
18-crown-6



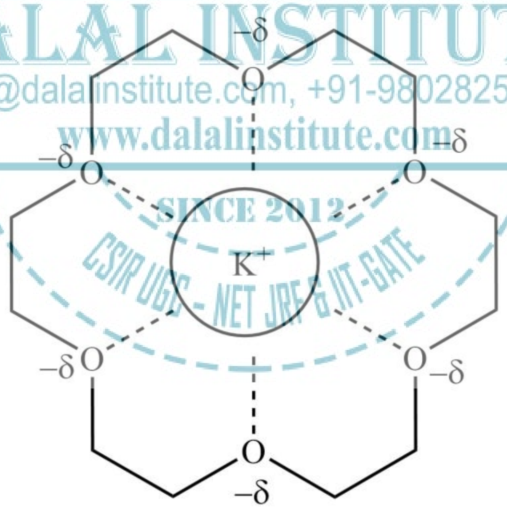
21-crown-7

Here the label "crown" means the resemblance with the structure of a king's crown. As far as the nomenclature is concerned, the first number means the number of atoms in the cycle, and the 2nd number means the number of oxygen atoms. Crown ethers are much broader than the oligomers of ethylene oxide; a very important class that is catechols' derivative.

These compounds have a very strong tendency to bind with certain cations, and therefore, generating complexes. The O atoms are well placed to bind with a certain cation situated within the ring, while the ring's exterior remains hydrophobic. The cations thus produced generally form salts that are solvable in non-polar solvents, and therefore, crown ethers are very valuable in the application of phase transfer catalysis. The polyether's denticity affects the affinity of the crown ether for different cations. For instance, 18-crown-6 has more affinity for K^+, 15-crown-5 for Na^+, and 12-crown-4 for Li^+ ion. The very high affinity of 18-crown-6 for K^+ cation is primarily responsible for its toxic character.



Less stable

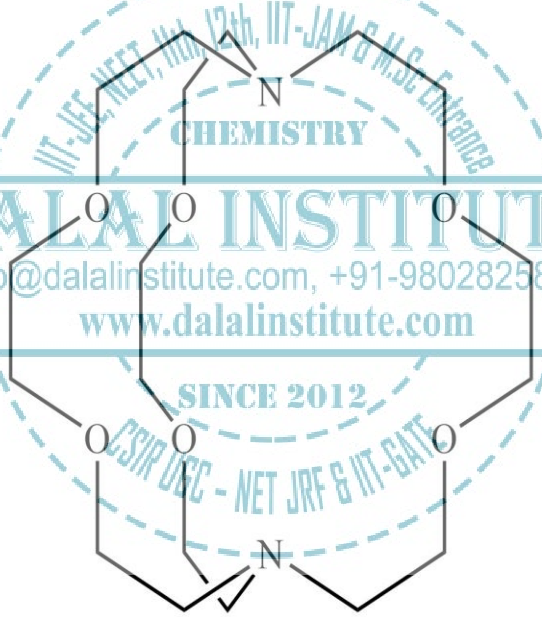


More stable

It is also worthy to note that crown ethers aren't the only macrocyclic ligands that capable of binding with K^+ cation. Some ionophores like valinomycin also show a very strong preference for the K^+ ion over other cationic species. These compounds have also been known to bind with Lewis acids via σ-hole (i.e., halogen bond) interactions, electrostatic interactions; in other words, bonding takes place between the electrophilic Lewis acid center and the Lewis basic oxygen atoms of the crown ether.

2. Cryptands: Cryptands may simply be defined as a family of synthetic bicyclic and polycyclic multidentate ligands that are capable of binding with a range of cationic species. In 1987, Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen got the Nobel Prize in chemistry for the discovery and finding uses of cryptands and crown ethers, and therefore, starting a novel field of supramolecular studies. The label cryptand means that this ligand gets attached to the substrates in a crypt, burying the guest. These molecular systems are 3-dimensional analogs of crown ethers, nevertheless, are more choosy and have a stronger tendency for complex formation giving lipophilic assemblies.

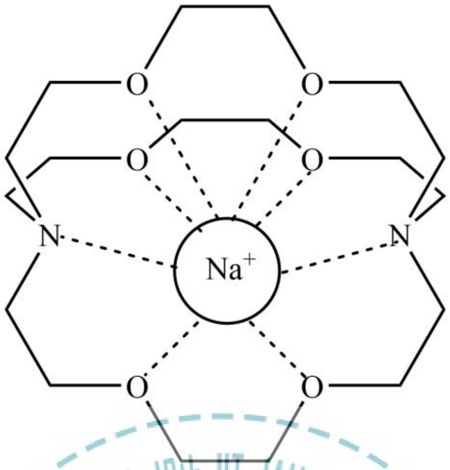
One of the most commonly studied and important cryptand is $N[CH_2CH_2OCH_2CH_2OCH_2CH_2]_3N$; whose IUPAC name is 1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane. This cryptand is labeled as [2.2.2]cryptand, with numbers inferring about the number of ether groups (and so the binding positions) in each bridge between the nitrogen sites. Numerous cryptands are available commercially by the tradename of Kryptofix. Furthermore, almost all of the amine cryptands show a very high affinity for alkali metal ions, which in turn, made the isolation of salts of K^- possible.



2.2.2]Cryptand

Also, the 3-dimensional void of a cryptand gives a binding site for guest ions, which means it acts as the host for the addition compounds. The complex formed between the guest cation and the cryptand is labeled as a cryptate. These ligands give rise to complexes with numerous hard cations (ammonium ion included), lanthanoids, alkaline earth metals, and alkali metals. Unlike crown ethers, cryptands get attached to the guest ions via both oxygen, as well as, nitrogen sites. This kind of 3-dimensional encapsulation bonding tells us about size-selectivity and enables us to distinguish different alkali ions like K^+ or Na^+ cation.

Cryptands are quite expensive and very problematic to synthesize, nevertheless, very valuable because of better strength and selectivity than their crown ethers counterparts.



More stable Cryptate

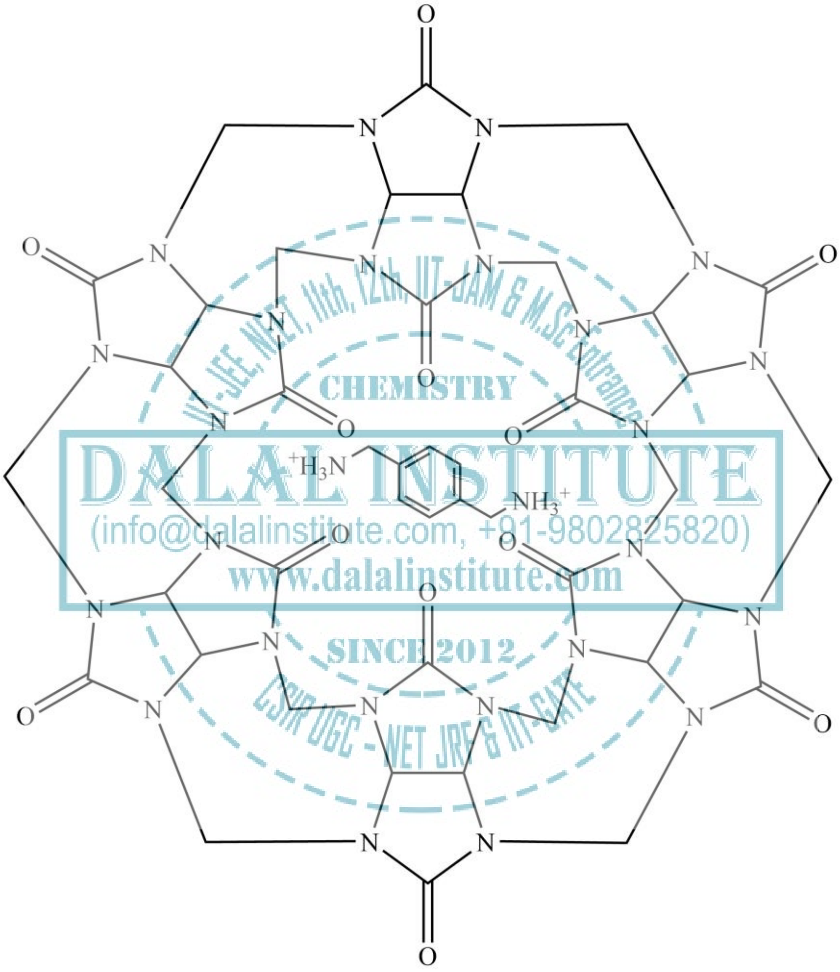
Less stable Cryptate

It is also worthy to note that cryptands are also capable of binding with insoluble salts into the organic phase, making them quite useful as phase transfer catalysts like crown ethers. These ligands enabled the preparation of the electrides and alkalides, and have also been employed to crystallize Zintl ions like Sn_9^{4-}.

- ***Inclusion Compounds***

An inclusion compound in host-guest chemistry may simply be defined as a complex where one compound provides a void to accommodate the other.

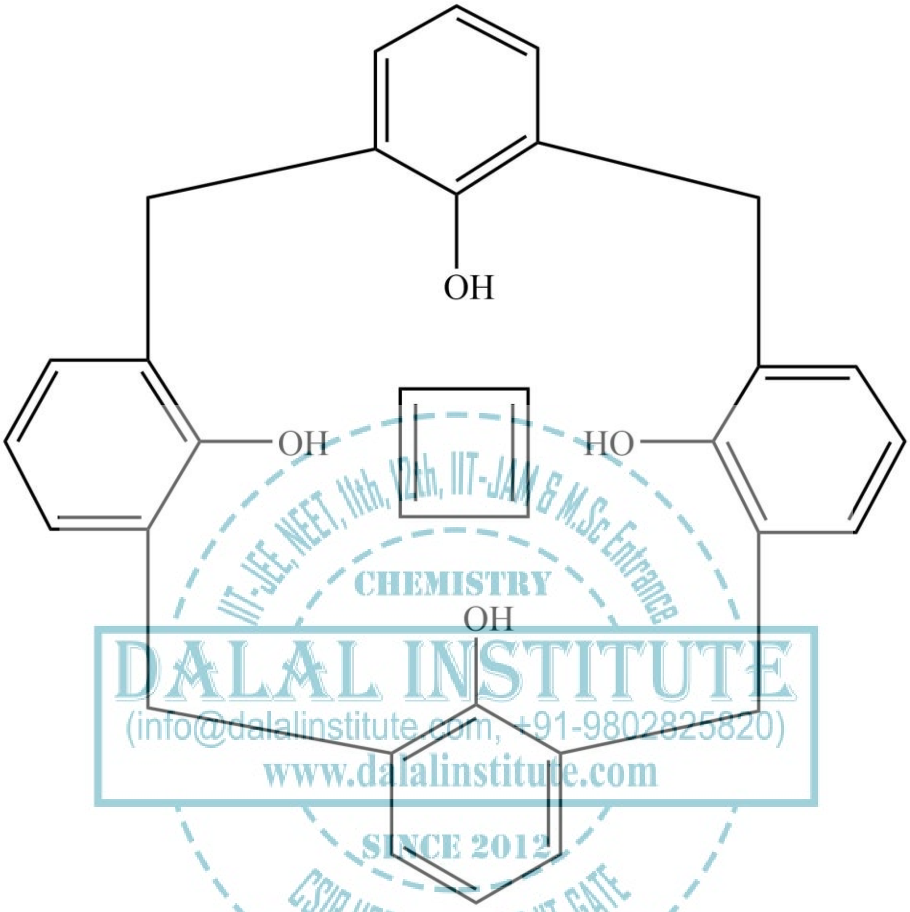
The bonding between the guest and host molecules is purely van der Waals interactions. The idea of inclusion compounds is quite broad, including the channels created between molecules in a crystal lattice where the guest molecules are acceptable.



Inclusion compound consisting of a
p-xylylenediammonium bound
within a cucurbituril

Calixarenes and associated formaldehyde-arene condensates form an important class of host molecules that can give inclusion compounds. One of the most popular examples is the cyclobutadiene adduct, which would be is unstable otherwise. Cyclodextrins are quite proven hosts for the generation of inclusion compounds. For instance, the ferrocene can be inserted into the cyclodextrin at 100 °C if conditions are hydrothermal.

Cyclodextrin also gives inclusion compounds when treated with fragrances. Consequently, the fragrance molecules have a reduced vapor pressure and become more stable to the exposure to air and light.



Cyclobutadiene adduct
with

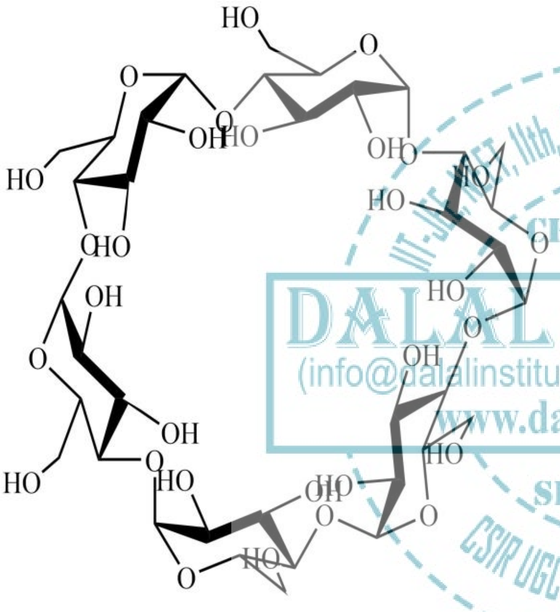
Calix[4]arene-25,26,27,28-tetrol

Furthermore, if incorporated into textiles the fragrance lasts for a longer period because of the slow-release process. Also, crown ethers and cryptands generally don't give inclusion compounds because the guest is bound by attraction forces that are stronger than van der Waals interactions.

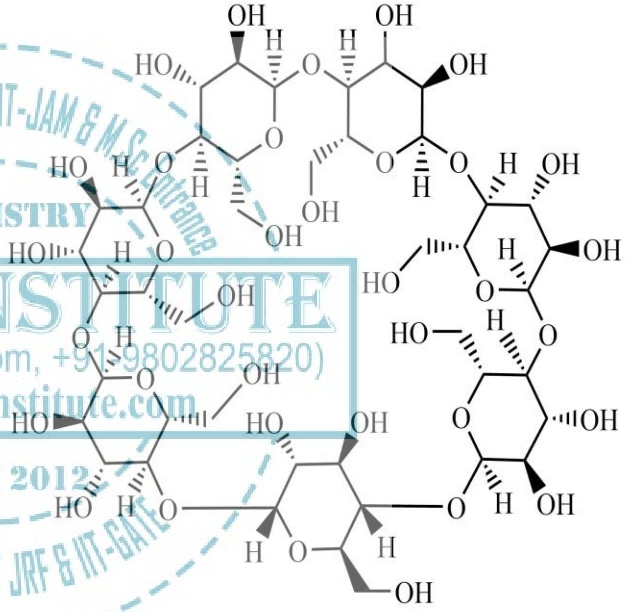
It is also worthy to note that if the guest is surrounded in such a way that it is 'trapped', the compound class is known as a clathrate, which is different from than inclusion complex. This encapsulation at the molecular level traps a guest molecule inside another molecule.

- ***Cyclodextrins***

Cyclodextrins may simply be defined as a family of cyclic oligosaccharides which are consisted of a macrocyclic ring having glucose subunits united by α-1,4 glycosidic linkage. These compounds are generated by the enzymatic conversion from starch. Cyclodextrins are quite useful in pharmaceutical, food, chemical industries, and drug delivery, as well as environmental and agriculture engineering. These compounds are made up of 5 or more α-D-glucopyranoside units which are joined at 1->4, like in amylose (a starch's fragment). The biggest cyclodextrin molecule has 32 1,4-anhydroglucopyranoside units, whereas as a poorly characterized mixture, 150-membered cyclic oligosaccharides have also been proved. Archetypal cyclodextrin molecules have several glucose monomer units ranging from 6 to 8 parts in a cycle, giving rise a cone shape structures.



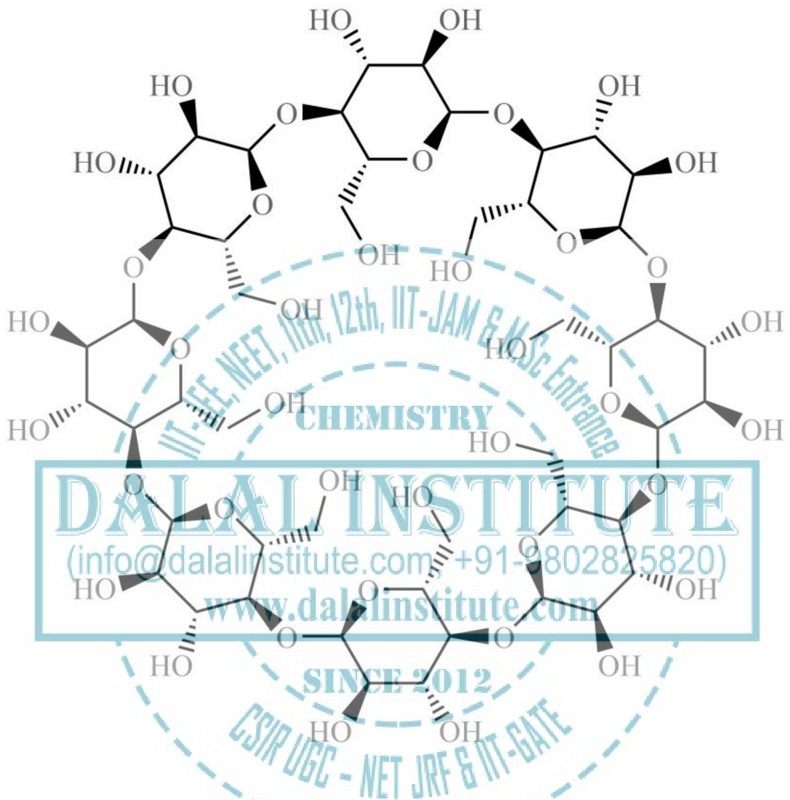
α-cyclodextrin



β-Cyclodextrin

With a hydrophilic exterior and hydrophobic interior, these molecules give rise to complexes with hydrophobic systems. The FDA-approved compounds are α-, β-, and γ-cyclodextrin that have been employed for delivery of different kinds of drugs, including prostaglandin, hydrocortisone, itraconazole, nitroglycerin, chloramphenicol. These compounds confer stability and solubility to these drugs. The inclusion complexes of cyclodextrins with hydrophobic fragments can penetrate tissues, and therefore, can be used to release biologically important compounds under explicit conditions. In many cases, the mechanistic behavior of controlled decay of such compounds is based upon the pH change of aqueous solutions, yielding the loss of ionic or hydrogen bonds between the guest and host systems. The other means for the disturbance of the compound take benefit of enzymatic or heating action which is capable to break the α-1,4 bond between glucose monomeric units. These compounds have also been shown to improve mucosal penetration of different kinds of drugs.

Cyclodextrin compounds are synthesized by the enzymatic reaction on starch. Normally cyclodextrin glycosyltransferase is used along with α-amylase. The starch is liquified first either via heating action or by employing α-amylase, then cyclodextrin glycosyltransferase is added for the enzymatic treatment. cyclodextrin glycosyltransferase gives rise to the mixtures of different kinds of cyclodextrins, and therefore, the three main types of cyclic compounds are produced, where the ratios are strongly dependent on the enzyme employed. Also, each cyclodextrin glycosyltransferase has its characteristic ratio of α:β:γ yield.



γ-cyclodextrin

The distillation of the 3 kinds of cyclodextrins takes the benefit of their dissimilar water solubility; β- cyclodextrins is very poorly soluble in water and can be easily obtained via crystallization whereas the more soluble α- and γ- cyclodextrins are typically obtained by using expensive and time-consuming techniques of chromatography. Alternatively, some complexing agents (like acetone toluene, or ethanol) can also be added in the course of the enzymatic treatment step to yield a complex with the desired cyclodextrin, which in turn, can easily be precipitated subsequently. The formation of the complex drives the transformation of starch into the generation of the precipitated cyclodextrin, and so enriching its amount in the final products. W. Chemie practices some dedicated enzymes, that can yield α-, β- or γ-cyclodextrin explicitly. This is quite important particularly in food engineering because the only α-, β- or γ-cyclodextrin can be consumed without any limit on the daily intake.

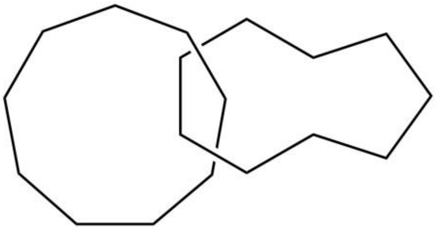
❖ Catenanes and Rotaxanes

Besides the addition compounds, some compounds contain two or more sovereign parts which are linked but without any valence forces. A more general discussion on these two types of organic compounds is given below.

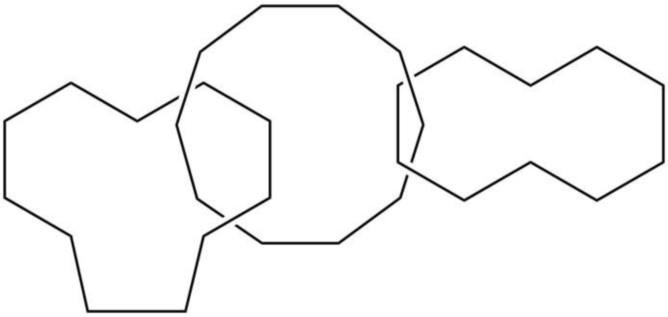
➢ *Catenanes*

A catenane may simply be defined as a mechanically interlocked molecular construction that is consisted of two or more macrocycles, i.e. a molecular assembly having two or more intertwined cycles.

These interlocked cycles cannot be parted without the cleavage of covalent bonds of one of the macrocycles. These compounds are obtained their name from the Latin word 'catena' which literally means 'the chain'. Catenanes can be abstractly associated with other mechanically interlocked molecular constructions, like rotaxanes, molecular Borromean rings, or molecular knots.



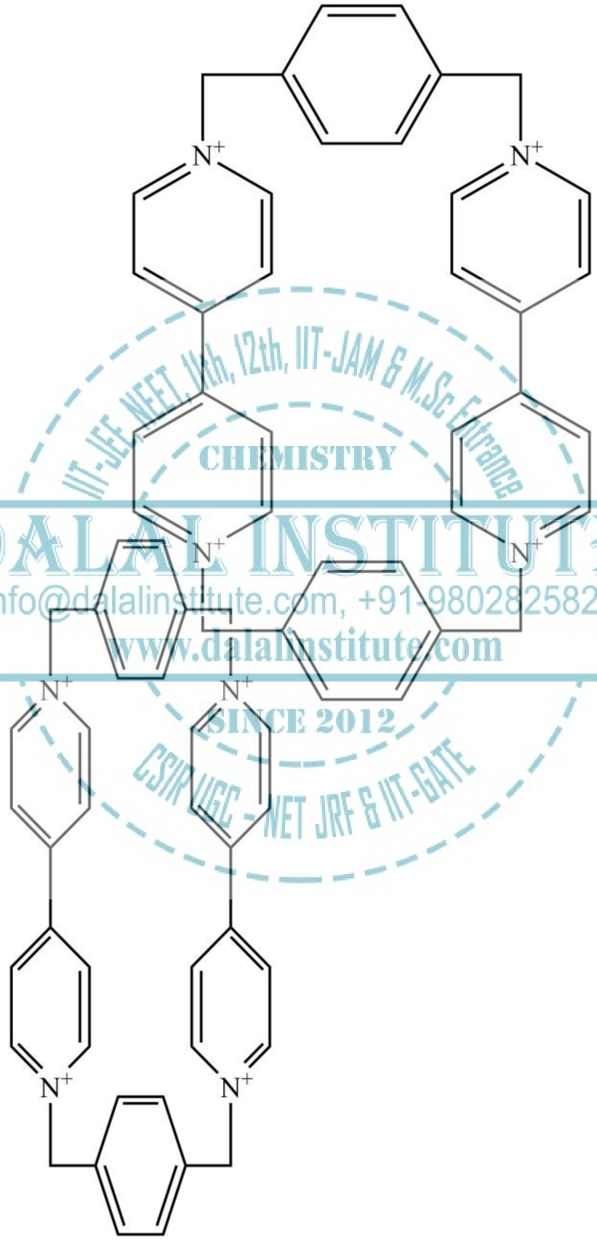
A [2]-Catenane



A [3]-Catenane

In recent years, the term "mechanical bond" has been devised that defines the correlation between the macrocycles of a single catenane.

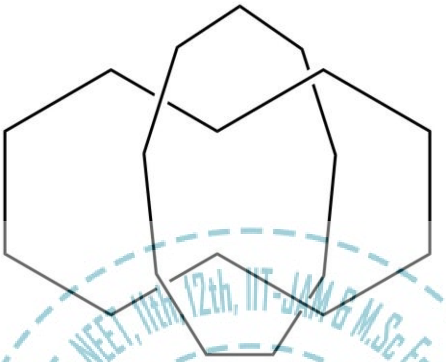
Catenanes can be synthesized via two different routes; the first one is the statistical synthesis, whereas the second one is called as the template-directed method. The first approach is to simply carry out a ring-closing reaction and hoping that some of the reactnt will be generated around other cyclic system yielding the required catenane produce. This approach is very inefficient, needing high dilution of the closing ring and a huge excess of the pre-formed ring, and therefore, this methos is used in rare cases.



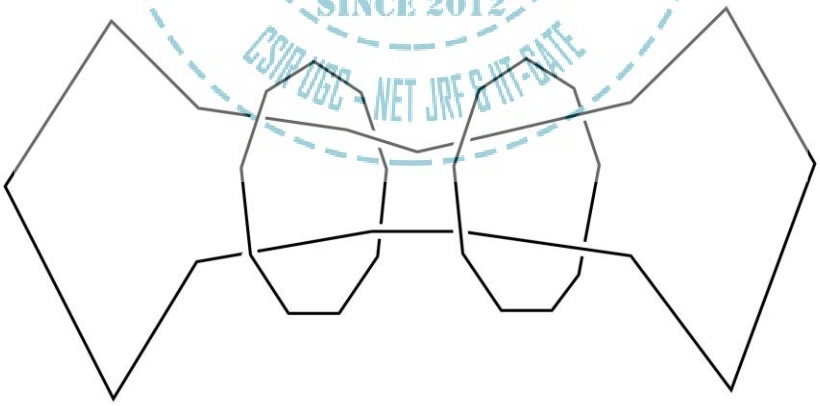
The 2nd approach depends upon the supramolecular preorganization of the macrocyclic reactants by employing properties like metal coordination, hydrogen bonding, coulombic interactions, or hydrophobic effect.

- ***Rotaxanes***

A rotaxane may simply be defined as a mechanically interlocked molecular assembly that is consisted of a dumbbell-shaped molecule, which is threaded through a macrocycle. These compounds got their name from the Latin word wheel (rota) and axle (axis). Rotaxane's two components are kinetically trapped because the dumbbell's ends are bigger than the internal diameter of the cycle, and therefore, forbid the dissociation of the components as it would need a huge magnitude of distortion of the covalent interactions.



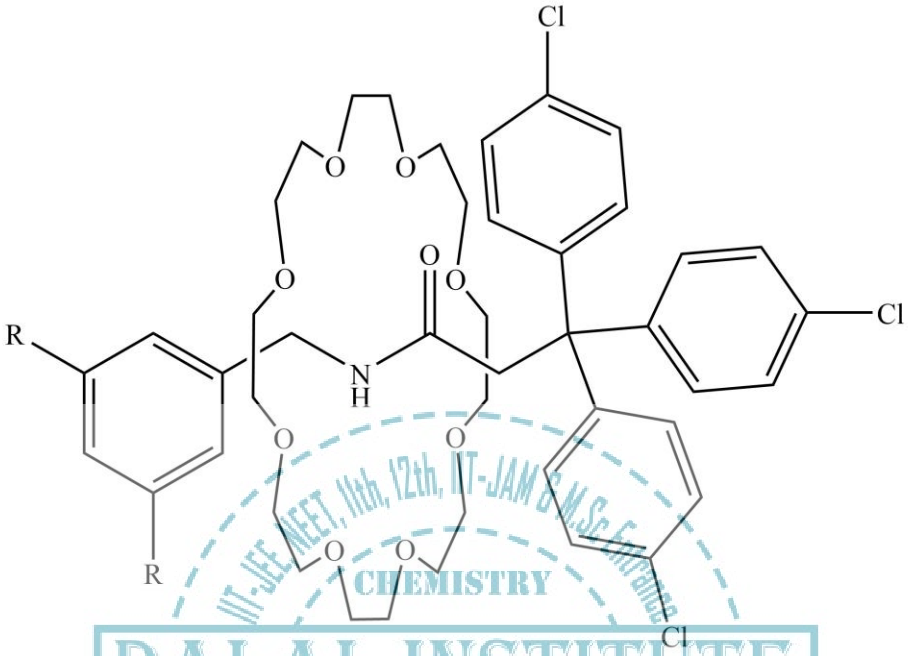
A [2]-rotaxane



A [3]-rotaxane

Also, most of the research about rotaxanes has been focused on their efficient preparation or their use as artificial machines at the molecular level.

Nevertheless, many rotaxane examples have been found in naturally occurring substances like peptides (i.e. cyclotides or lasso-peptides and cystine knot peptides).



A [2]-rotaxane formed by crown ether

❖ Problems

Q 1. Define the delocalized chemical bond in the valence bond framework with a suitable example.

Q 2. What is resonance? How is it different from tautomerism?

Q 3. What is hyperconjugation? How can it be used to rationalize the relative stability of carbocations?

Q 4. Write a short note on alternate and non-alternate hydrocarbons.

Q 5. Define aromaticity with special reference to the benzenoid compounds.

Q 6. What is the Huckel rule of aromaticity? Discuss its theoretical foundation.

Q 7. Comment on the aromatic character of different annulenes.

Q 8. What are homoaromatic compounds?

Q 9. Discuss the 'perturbed molecular orbital' approach for aromaticity.

Q 10. What are antiaromatic compounds? How they can be rationalized in terms of planarity.

Q 11. Discuss the bonds weaker than covalent with special reference to Crown ether complexes.

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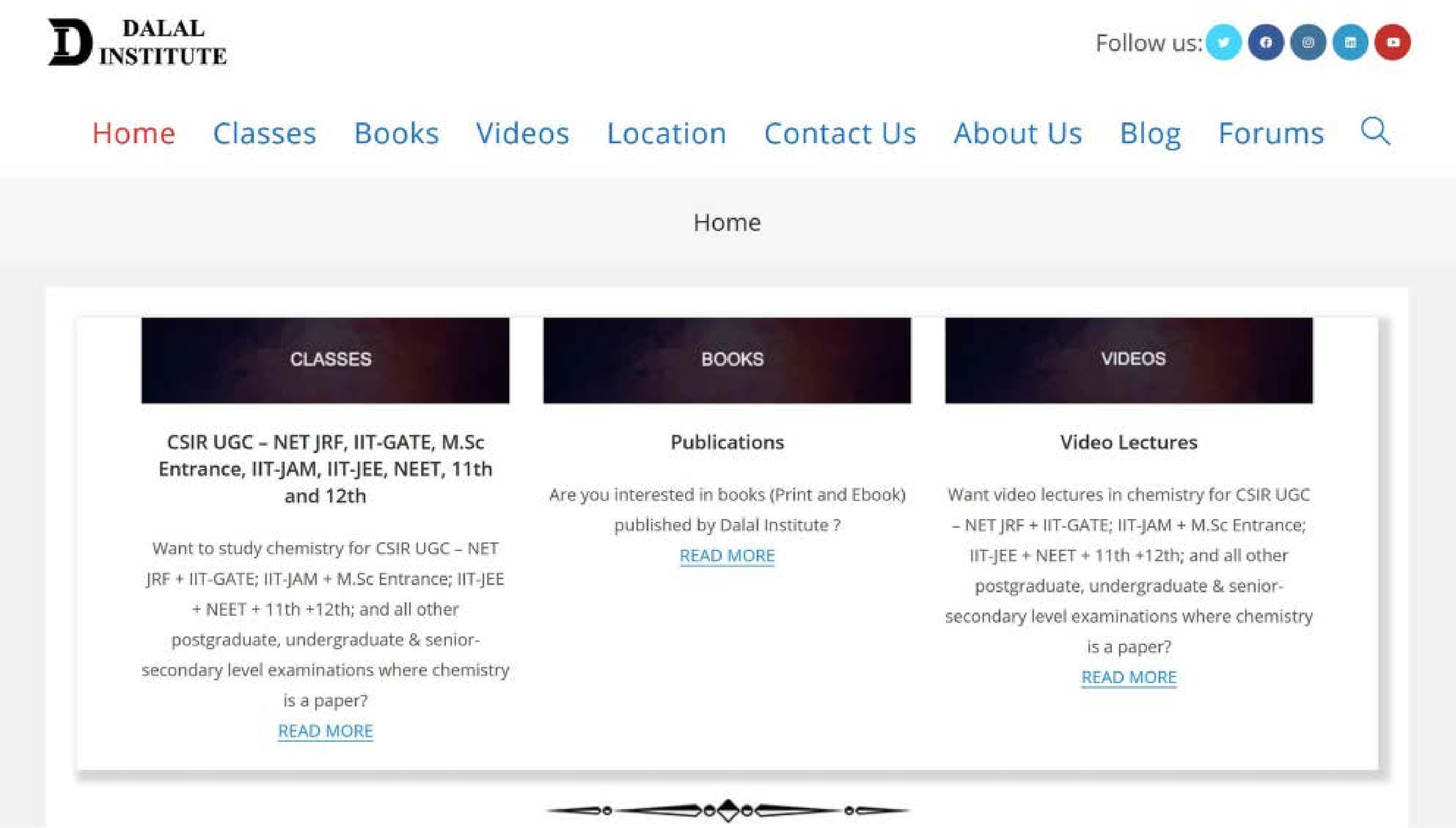

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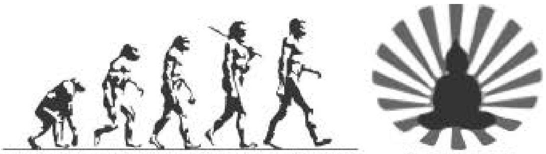

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