❖ 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.

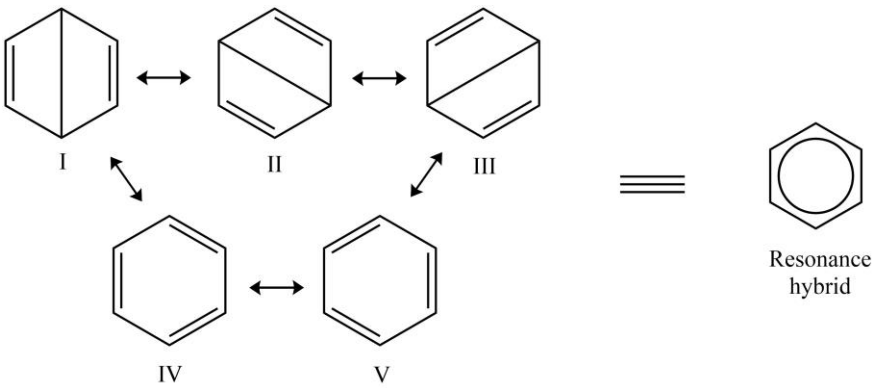


Figure 9. Different resonating structures of the benzene molecule.

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.

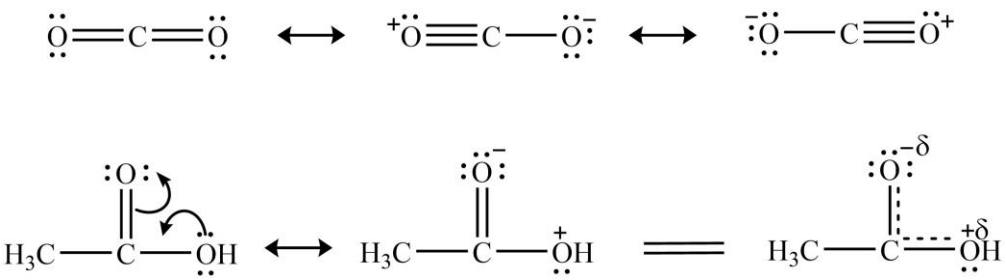


Figure 10. Resonance phenomena in carbon dioxide and acetic acid.

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.

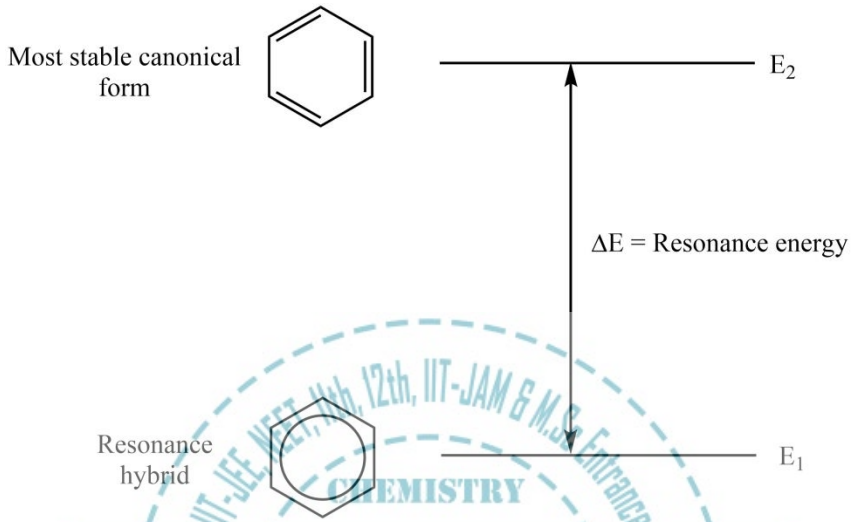
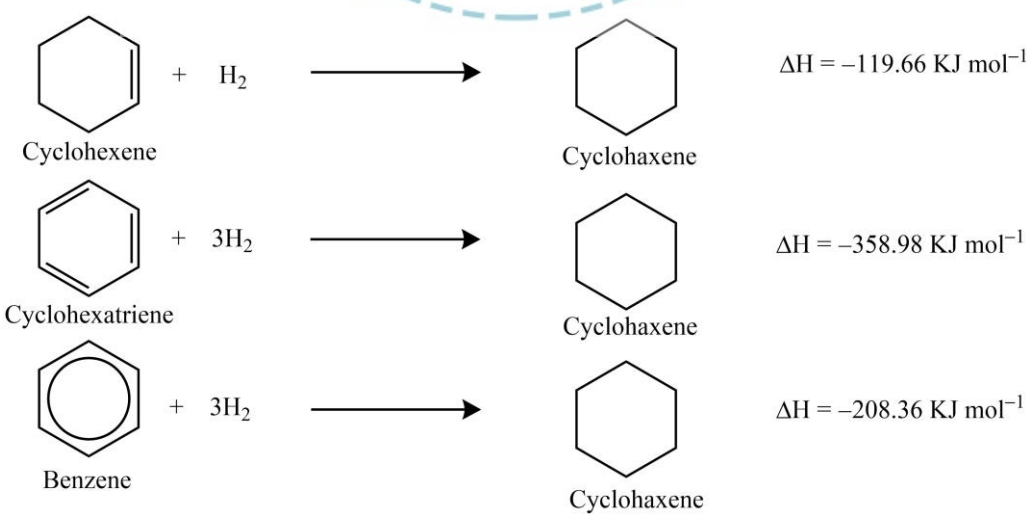


Figure 11. The depiction of resonance hybrid, most stable canonical form, and resonance energy in benzene molecule.

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.

$$\Delta H_{calculated} = 6 \times Bond\ dissociation\ energy\ of\ C-H\ bond + 3 \times Bond\ dissociation\ energy\ of\ C-C\ bond + 3 \times Bond\ dissociation\ energy\ of\ C=C\ bond \quad (1)$$

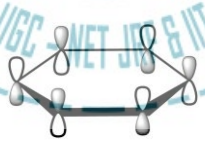
$$= 6 \times 413.3\ KJ\ mol^{-1} + 3 \times 347.7\ KJ\ mol^{-1} + 606.7\ KJ\ mol^{-1} = 5343\ KJ\ mol^{-1} \quad (2)$$

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.

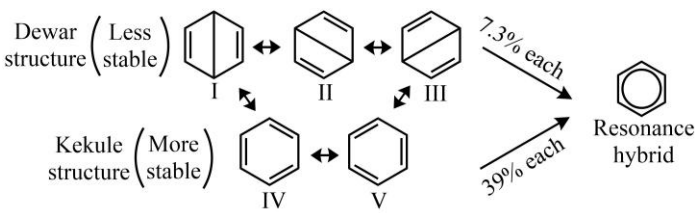
2. All the participating atoms must lie in the same plane.



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.

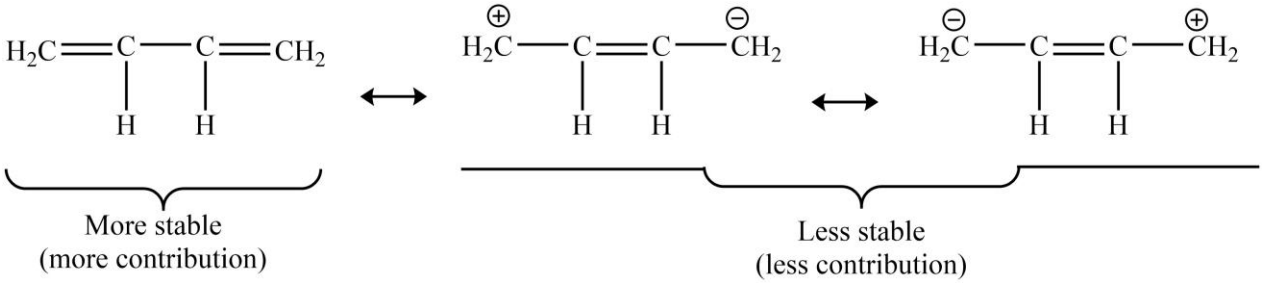
5. More stable resonating structure will contribute higher to the resonance hybrid.



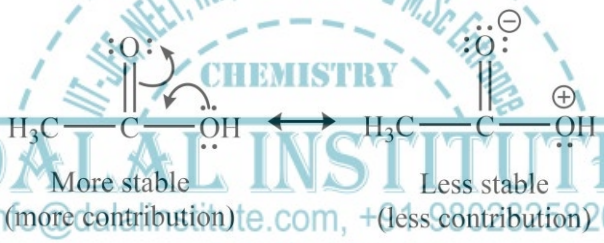
6. Greater is the number of canonical structures, higher will be the stability of corresponding resonance hybrid.

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

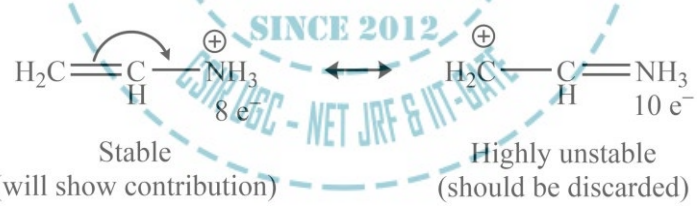
i) Resonating structures with a greater number of covalent bonds will be more stable, and therefore, will show more contribution towards resonance hybrid.



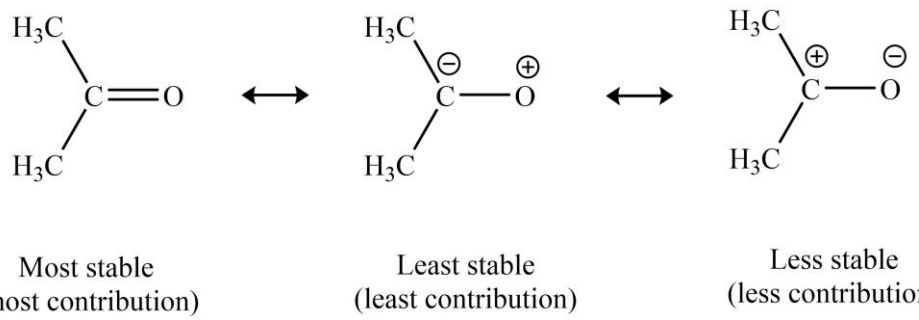
ii) Structures with charge separation will be less stable, and therefore, will contribute less towards the resonance hybrid.



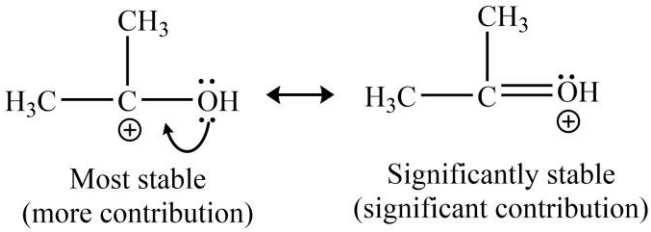
iii) Structures violating the octet rule should not be considered (involving second-period elements).



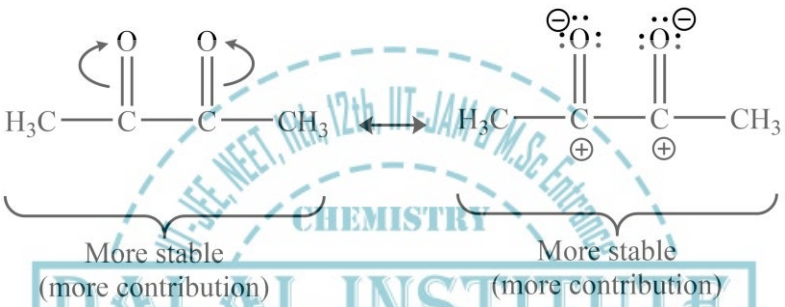
iv) Resonating structures with the negative charge on a more electronegative atom will be less stable, and therefore, will contribute less to the resonance hybrid.



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.



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.

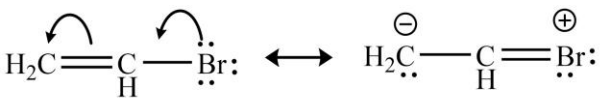


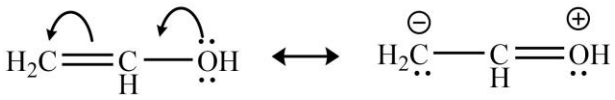
Resonance effect:

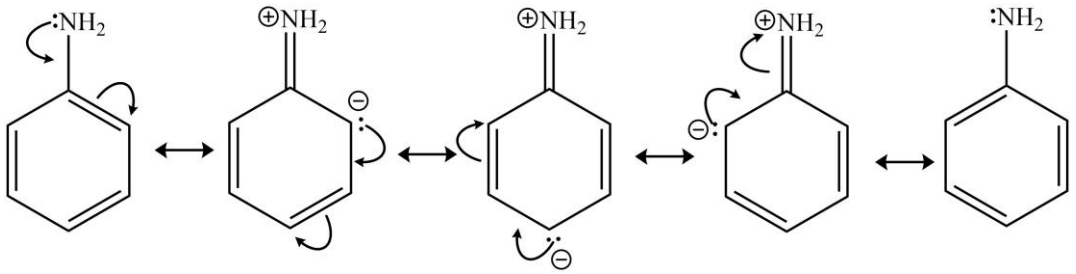
The resonance or mesomeric effect in organic compounds may simply be defined as the polarity produced in the molecule due to resonance phenomena.

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.

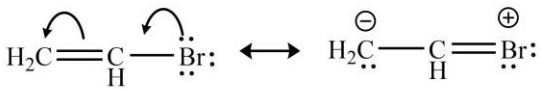
It is also worthy to mention that groups showing the −R effect are having a double bond that can be put into conjugation with the double of the chain or ring to which it gets attached with. Some of the typical groups showing the −R effect are given below.

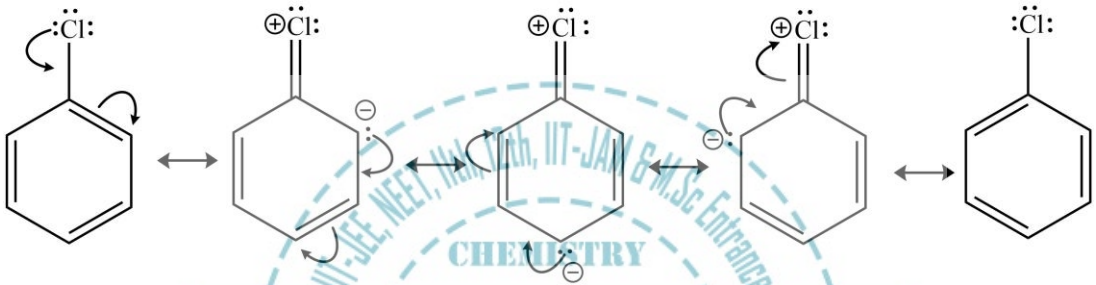
$$-NO_2 > -CN > -S(=O)_2{-}OH > -CHO > -C{=}O > -COOCOR > -COOR > -COOH > -CONH_2 > -COO^-$$

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.

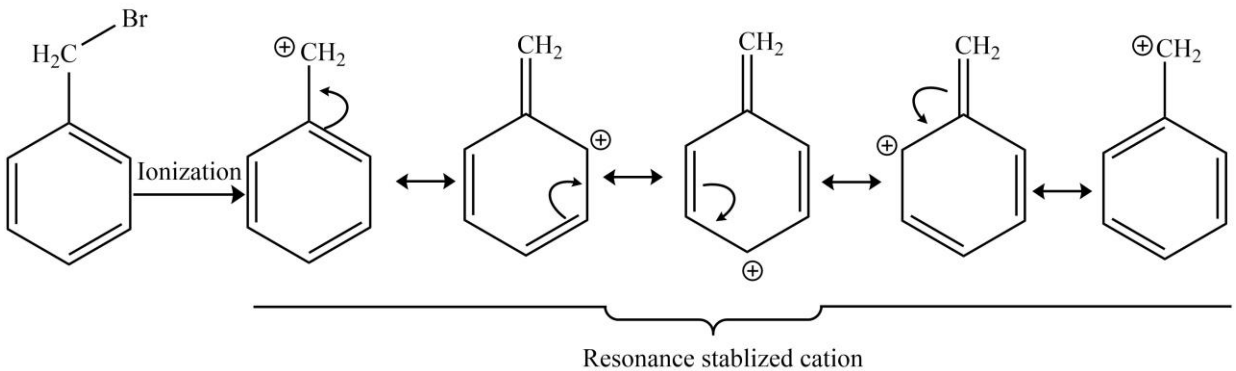
Applications of resonance effect: Some of the important applications of the resonance or mesomeric effect that affect the properties to a great extent are given below.

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.

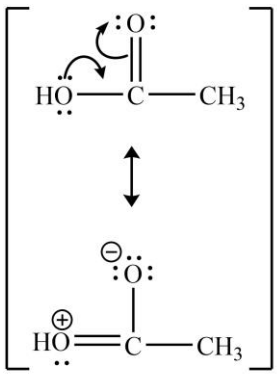




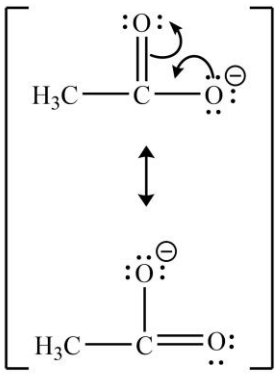
ii) High reactivity of allyl and benzyl halides: The existence of the −R effect in allyl and benzyl halides makes them more reactive towards the nucleophilic substitution reaction due to the formation resonance stabilized cation bond as shown below.



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.



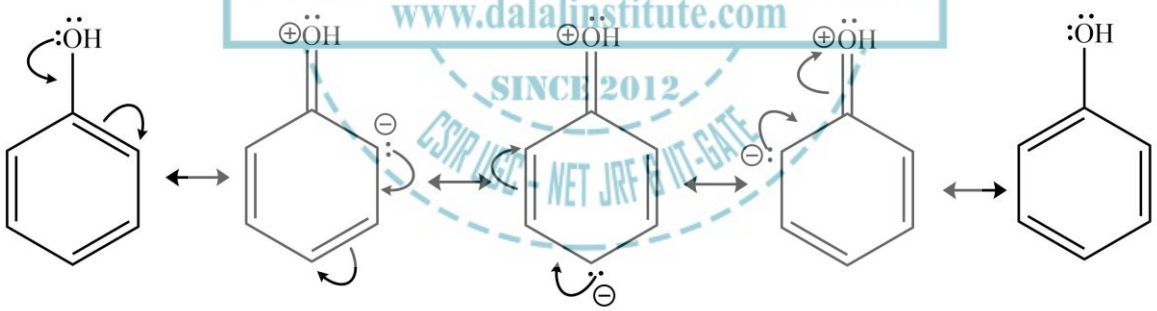
Charge separation (less stable)



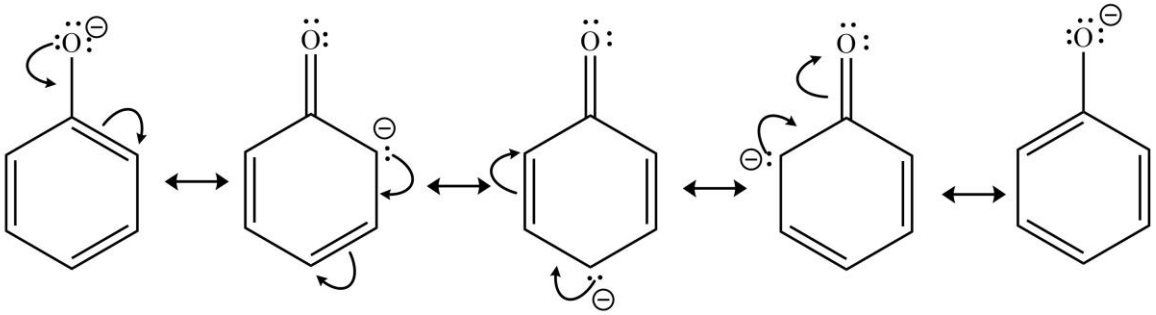
No charge separation (more stable)

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.

No resonance (less stable)

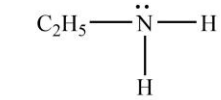


Charge separation (less stable)

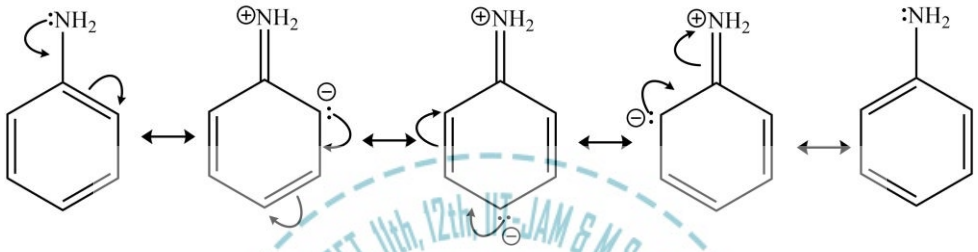


No charge separation (more stable)

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)

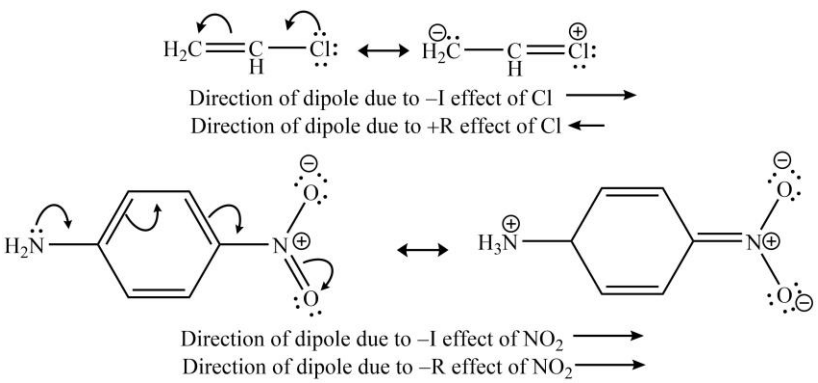


+R effect (less basic)

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 →

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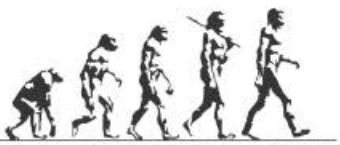

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