Effect of phenyl substitution on the aromatic ring: (para-substitution)

$$+E^{+} \longrightarrow +E^{+} \longrightarrow +$$

- Effect of withdrawing and donating group:

Examples:

Electrophilic substitution of disubstituted benzene ring:

Two or more substituent produces a combine effect on the reactive of an aromatic ring.

a- Di donating groups:

$$\begin{array}{c} \text{CH}_3 \\ \text{H}_2\text{SO}_4 \\ \text{HNO}_3 \end{array} \begin{array}{c} \text{CH}_3 \\ \text{NO}_2 \\ \text{m-xylene} \end{array}$$

$$H_2SO_4$$
 H_2SO_4
 H_2SO_4
 H_2SO_4
 H_2SO_4
 H_1NO_3
 H_2SO_4
 H_1NO_3

b- **Donating and withdrawing groups:**

$$E^+$$
 E^+
 E^+

- The presence of groups substituted, one of them *meta* position and the other to be the one donate electrons and the other withdrawing electron shown here *ortho* effect for the group withdrawing.

Examples:

c- Di donating and withdrawing groups:

Examples:

Substitution reaction of polynuclear aromatic hydrocarbons:

Although **naphthalene**, **phenanthrene** and **anthracene** resemble benzene in many respects, they are **more reactive** than benzene in both **substitution** and **addition reaction**.

Orientation of naphthalene:

Orientation in the substitution of naphthalene can be complex, although the 1- position or alpha position(α) is the more reactive, substitution usually occurs more readily at the 1-position (alpha -position) than at the 2-position (beta-position (β)) because the intermediate for alpha-substitution in more stable than that the (beta -position). The reason in that the most favorable resonance structure for either intermediate is those that have one fully aromatic ring.

5 resonsnce structures. Two structures (A, B) have full benzene rings

4 resonsnce structures. One structure (F) has full benzene ring

Example:

a- Di donating group:

b- Withdrawing group:

Electrophilic Substitution in heterocyclic compounds [pyrrole ,furan ,thiophen ,pyridine]:

Like other aromatic compounds these **five** and **six member heterocyclic** undergo nitration, sulfanation, and all reaction. These compounds **more active from benzene**.

a-five member heterocyclic (O, N, S) inter electrophilic substitution in2 postion:

b-six member heterocyclic inter electrophilic substitution in 3 postion:

Why five member heterocyclic inter electrophilic substitution in 2 postion?

Examples: