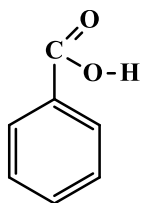


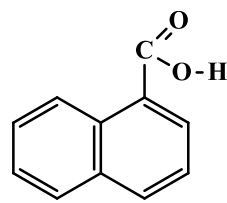
## AROMATIC ACIDS

1. Aromatic acids are compounds in which one or more carboxyl groups (-COOH) attached directly to the aromatic ring.
2. Aromatic carboxylic acids are of two types-
  - i. Those in which the carboxyl group is attached directly to aromatic nucleus.

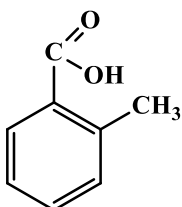
Eg.-



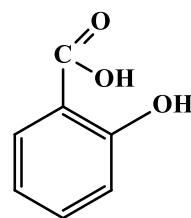
Benzoic acid



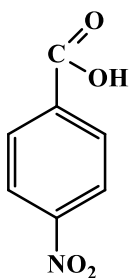
$\alpha$  - Naphthoic acid



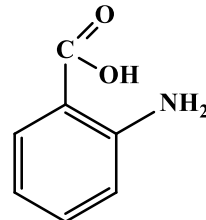
*o*-Methylbenzoic acid  
(*o*-Toluic acid)



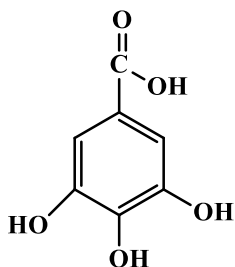
*o*-Hydroxybenzoic acid  
(Salicylic acid)



*p*- Nitrobenzoic acid

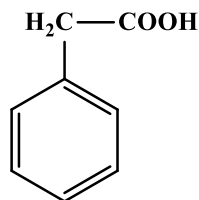


2-Aminobenzoic acid  
(Anthranilic acid)

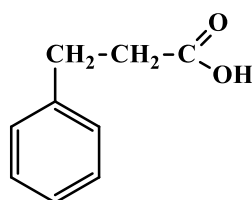


3,4,5-Trihydroxybenzoic acid  
(Gallic acid)

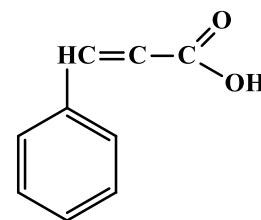
- ii. Those in which the carboxyl group is attached to the side chain.



Phenyl ethanoic acid  
(Phenylacetic acid)

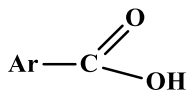


3-Phenylpropanoic acid



3-Phenylpropenoic acid  
(Cinnamic acid)

3. Generally represented by the formula-

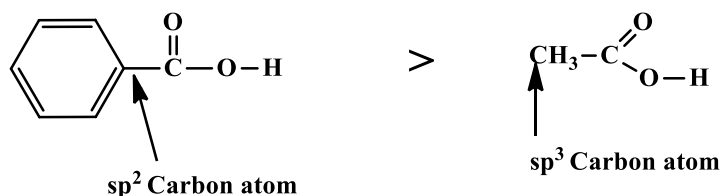


### Acidity of Aromatic acids and effect of substituent on Acidity

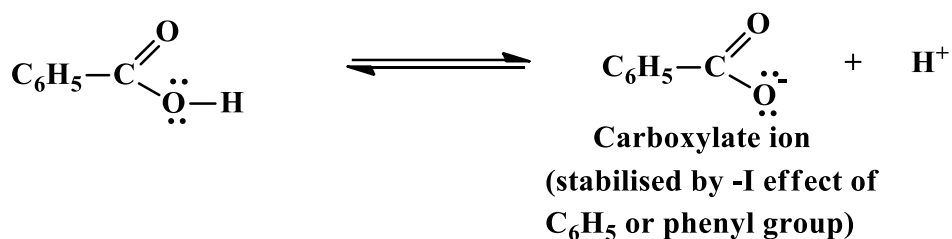
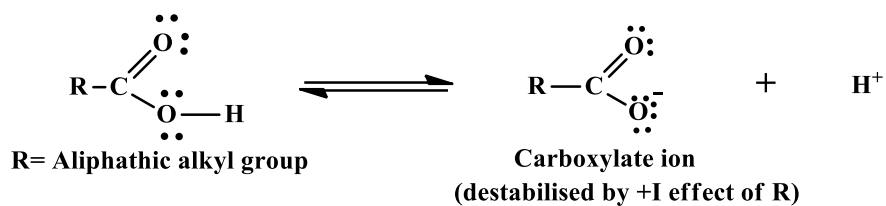
1. Aromatic carboxylic acids are stronger acids than aliphatic carboxylic acids (eg. benzoic acid, has pK<sub>a</sub> of 4.2 and is slightly stronger acid than acetic acid, pK<sub>a</sub>= 4.8).

Note:  $K_a \propto 1/pK_a$ ,  $K_a \propto \text{Acidity}$   
 $pK_a \propto 1/\text{Acidity}$

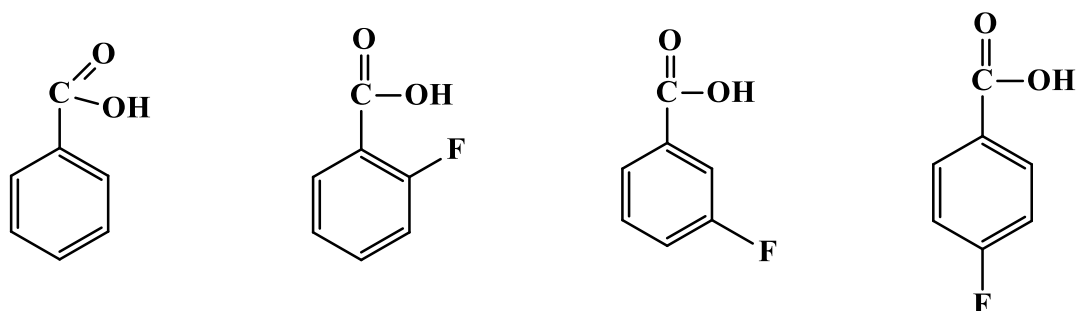
- In benzoic acid, carboxylic group is bonded an sp<sup>2</sup> hybridised carbon atom, which is more electronegative than sp<sup>3</sup> hybridised carbon atom of acetic acid.



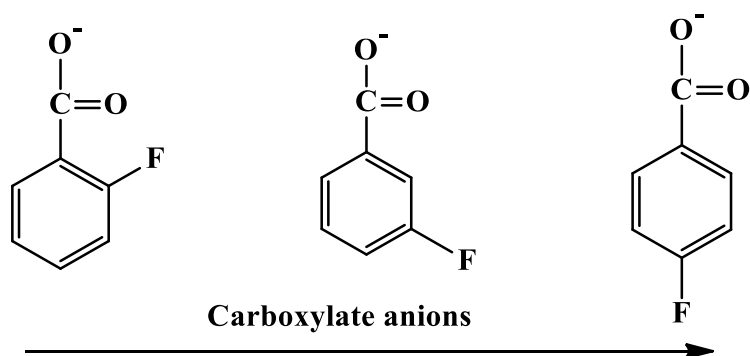
- The greater electronegativity of sp<sup>2</sup> hybridised carbon atom is used to explain the resultant or apparent electron withdrawing inductive effect that the phenyl group demonstrates in stabilising the carboxylate anion.



- Acidity of substituted benzoic acids depends on the nature and position of the substituents.
- All the fluoro benzoic acids are more acidic than benzoic acid.

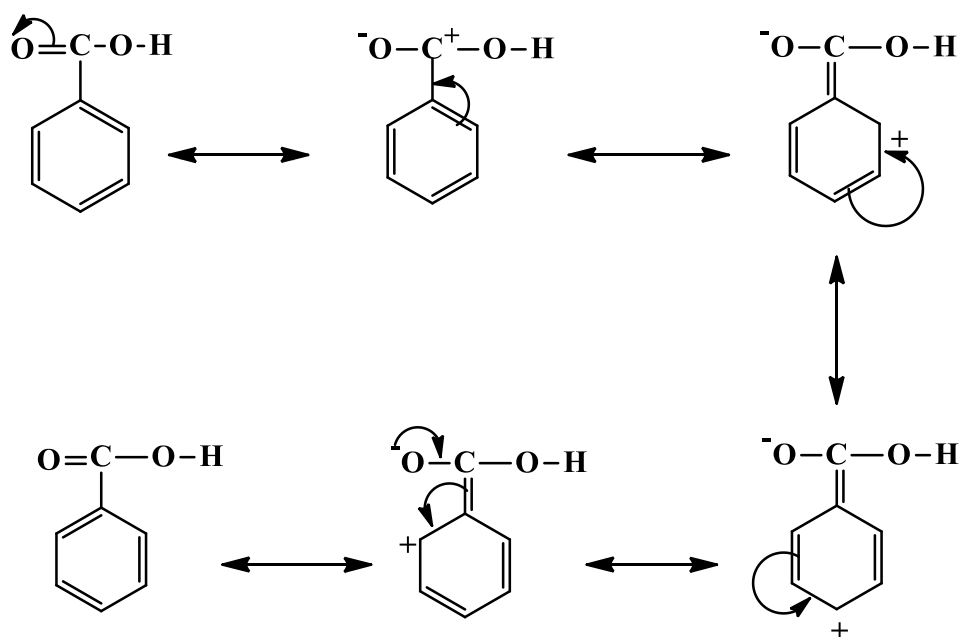


- *o*-fluorobenzoic acid, in which the F-atom is nearest to the carboxylic acid, is the strongest acid of the four, *p*-fluorobenzoic acid, in which the the F-atom is farthest from carboxylic acid, is only slightly more acidic than benzoic acid. The electronegative F-atom exerts/maintains its effect through the bonds and through space, withdrawing  $e^-$  density from the vicinity of the carboxylic group and hence, stabilizes the carboxylate anion.



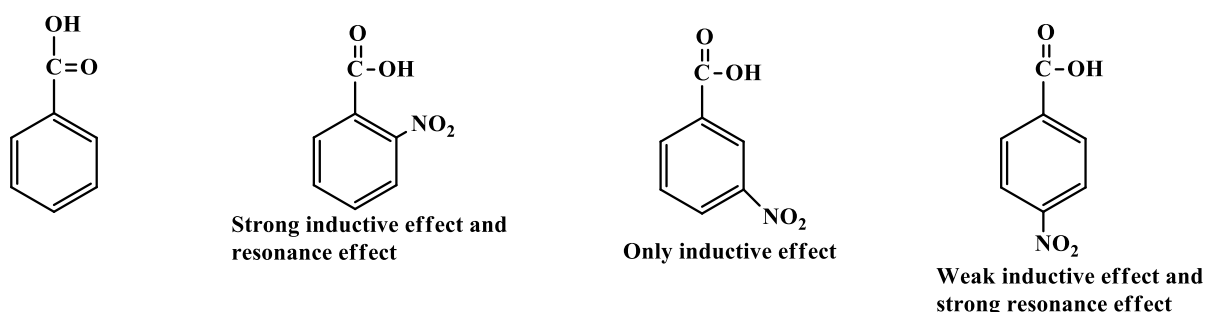
1. increase in the distance between COO<sup>-</sup> and F
2. decrease in -I effect of F
3. decrease in stability
4. decrease in acidity of conjugate acid

**Note:**



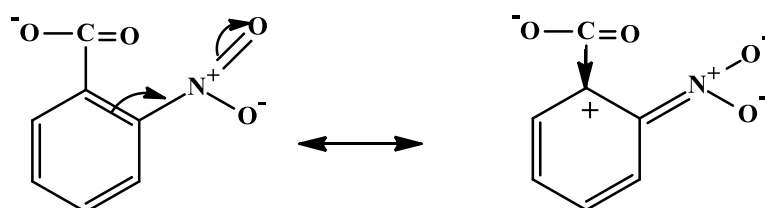
.Hence, the acidity of these four acids can only be explained by the consideration of inductive powers (-I) of group.

For some substituents, the inductive effect is not sufficient to explain the experimental observations. *p*-Nitrobenzoic acid is stronger than *m*-nitrobenzoic acid. This observation contrast with the observed acidity for fluorobenzoic acid for which acid strength decreases as electron withdrawing group is moved further away from carboxylic acid.

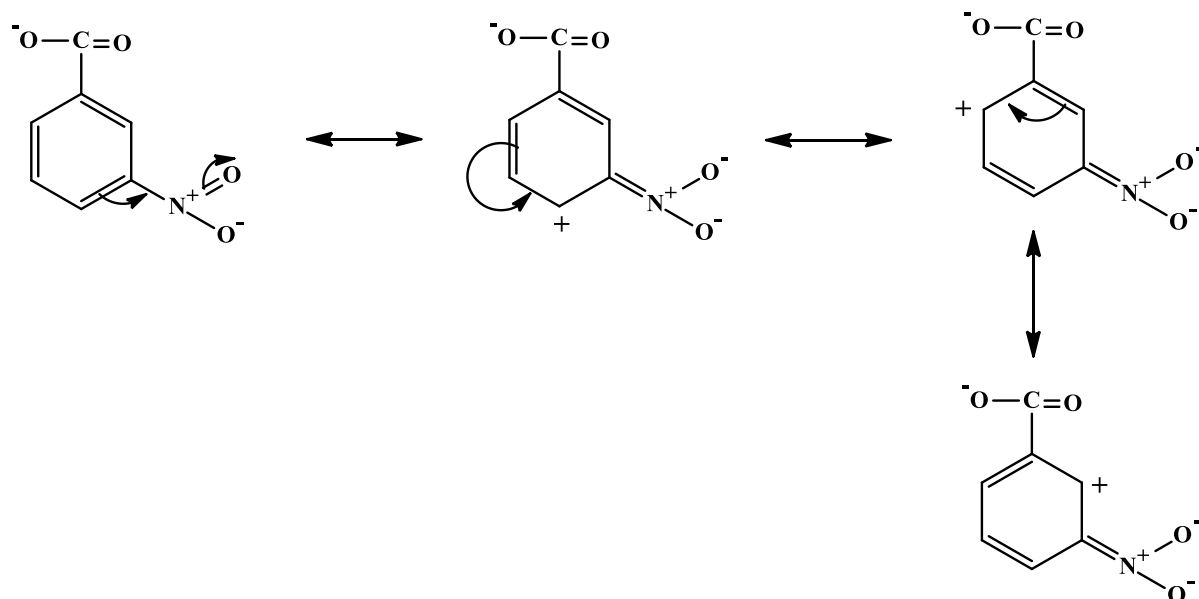


Resonance contributors having positive charge at carbon atom containing the carboxylate anion can be written for ortho and para isomers of nitrobenzoic acid, whereas the nitro group in meta position exert/maintain mainly an inductive effect. The carboxylate anion in each case is stabilised by combination of withdrawing effect. All the nitrobenzoic acids are stronger than benzoic acid. In *o*-nitrobenzoic acid, the strongest acid of three isomers, the inductive effect is stronger and a resonance effect is also present. In *p*-nitrobenzoic acid, a resonance effect is observed but inductive effect is weak.

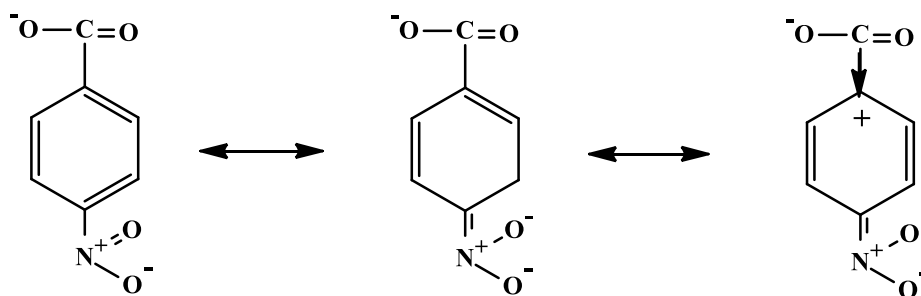
**Ortho:**



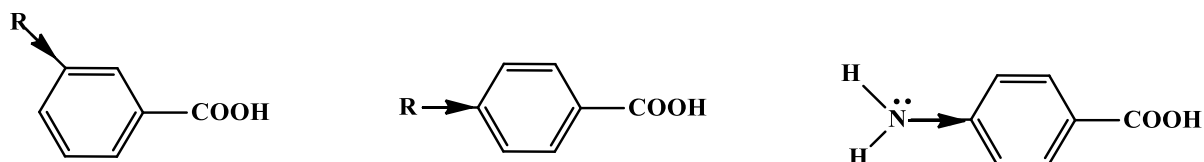
**Meta:**



**Para:**



- *m*-Nitrobenzoic acid is weaker than *p*-nitrobenzoic acid, reconfirm that when the resonance effect operates, it is more important than inductive effect.



An electron releasing substituent i.e. meta or para to the carboxylic group decreases the acid strength of a carboxylic acid derivatives. By releasing electron, the substituent stabilises the unionised acid and destabilises the anion.

Therefore, substituents (-NH<sub>2</sub>, -OH) that activate the aromatic ring towards electrophilic aromatic substitution, decreases acidity because they donate electron through inductive effect. Substituents (-NO<sub>2</sub>) that deactivate the aromatic ring towards electrophilic substitution, increases acidity because they withdraw electron from usually through the inductive effect.

**Note:** ERG (decreases acidity)

EWG (increases acidity)

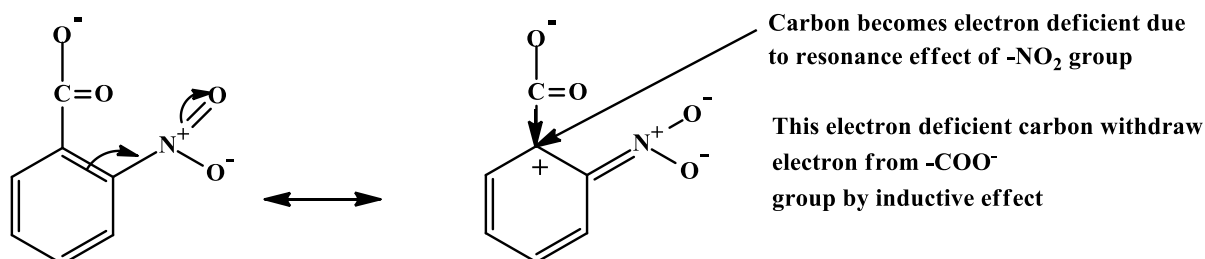
The ortho substituted benzoic acids (electron releasing or electron withdrawing) are considerably stronger than meta and para. This effect is known as ortho effect. The reasons for this are not entirely known although there may be steric effect from having two substituents ortho to one another.

### Acidity of substituted acids:

*o*-substituted benzoic acids are always stronger acid than meta and para derivatives due to the ortho effect.

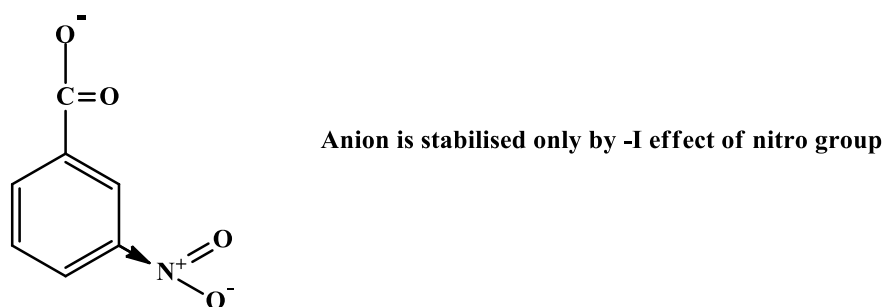
**Case 1:** When group is  $-R$  and  $-I$ .

a)

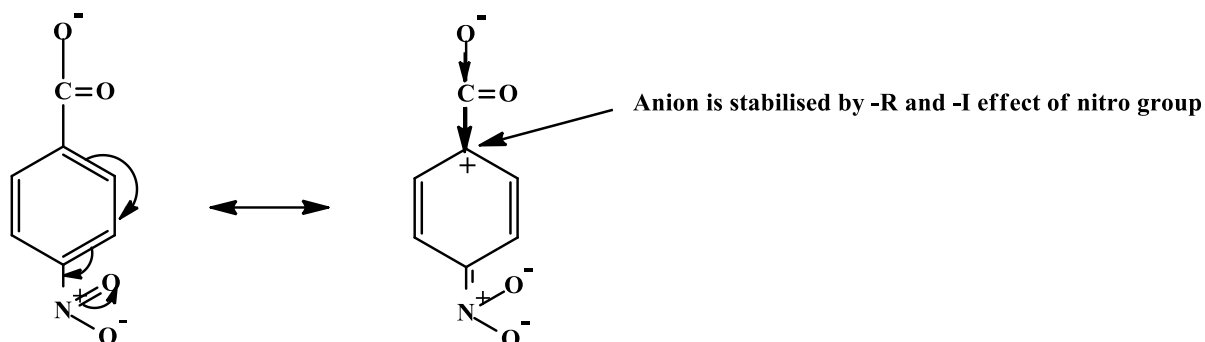


Therefore, anion is stabilized by  $-R$  and  $-I$  and  $-I$  power is maximum.

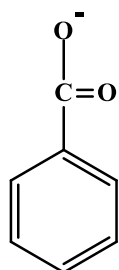
b)



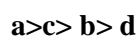
c)



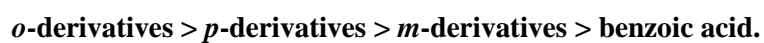
d)



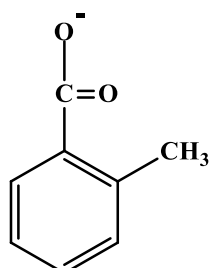
Hence, decreasing order of stability of these anion is as follows-



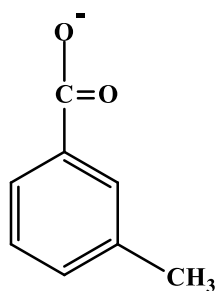
We know that ortho derivative is most acidic, therefore decreasing order of acidity of these acids is as follows-



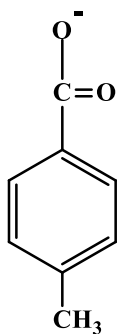
**Case 2:** When group has +R and +I.



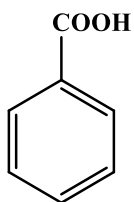
***o*-derivative will be most acidic due to ortho effect**



**Anion is destabilised due to -I effect**



Anion is destabilised by +R and +I effect and +I power is minimum



Acidity:

**Benzoic acid > *o*-derivatives > *m*-derivatives > *p*-derivatives.**

**Case 3:** If group is a halo group, then acidity depends only on inductive effect (-I effect).

Acidity:

***o*-derivatives > *m*-derivatives > *p*-derivatives > benzoic acid.**