### Aromaticity

From VBT point of view aromatic compounds like benzene is stable due to delocalisation of p electrons by resonance. The two Kekule RSs can be drawn to show the delocalisation. But the unusually high stability of benzene (Resonance Energy of 36 kcals/mole) cannot be explained by Resonance alone. MOT will explain this. Let us first realise to what extent benzene is stable from the heat of hydrogenation values.

\[
\begin{align*}
\text{Conjugated cyclohexa-1,3-diene} & \text{ is more stable than its unconjugated isomer cyclohexa-1,4-diene by 2.0 kca}\text{l. The latter produces almost the double of cyclohexene. If benzene would contain 3 localised C=C, then it would have given 85.8 kca}\text{l}(3 \times 28.6). \text{ But actually benzene is evolving 49.8 kca}\text{l/mole of heat. So it is stabilised by 36 kca}\text{l/mole from calculated value. Very interestingly benzene having 3 pi- bonds is releasing less energy than cyclohexa-1,3-diene. Resonance of two C=C is giving a resonance energy of 2 kca}\text{l/mole. So can we expect the resonance of 3 C=C will result a stability energy of 36 kca}\text{l/mole ???. Definitely, resonance alone cannot explain the unusual stability of benzene and other aromatic compounds. For benzene and aromatic compound, it should be called Stability Energy in stead of Resonance Energy.}
\end{align*}
\]

**Conjugation and Stability**: Conjugation can be quantified by the difference in energy between the cyclic and acyclic forms. The cyclic form is generally more stable due to delocalisation of π-electrons.

**Annulenes**: Cyclic compounds having conjugated C=C are called annulenes. The number of carbon atoms in the ring, is given as its prefix number eg. [4], [6], [8] etc. Benzene can be called [6]Annulene.

If resonance would be the only credible electronic effect to provide stability to all compounds including cyclic, then cyclobutadiene (can be called [4]Annulene) would have been stable. In reality, it is so much unstable that it has never been isolated even at room temperature. It readily dimerises, once it is formed, even at low temperature. It is much less stable than its acyclic conjugated buta-1,3-diene. It is therefore called an anti-aromatic compound i.e opposite of aromatics. About cyclooctatetraene, we shall discuss later. Only we can tell this much about it that it has the same stability as its acyclic partner. It readily undergoes addition reaction with Br₂. Therefore such type of compound is called non-aromatic, i.e looking like aromatic or anti-aromatic, but

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behaving like an acyclic analouge. This failure of Resonance, will be overcome by MOT, which we shall discussed a bit later. But one thing we know now, there are three types of annulenes, i.e cyclic compounds having conjugated C=C.

(a) Aromatics: more stable than their acyclic analogue
(b) Anti-aromatics: less stable than their acyclic analogue
(c) Non-aromatic : equally stable as their acyclic analogue

**Aromatics:**

Let's see, how benzene shows stability in chemical reactions as compared to alkenes (say cyclohexene)

\[ \text{Br}_2 \quad \text{Br}_2 \quad \text{Br} \quad \text{Br} \]

An alkene, when reacts with \( \text{Br}_2 \) in \( \text{CCl}_4 \), the red colour of bromine vanishes and we get vicinal dibromide(1,2-dibromocyclohexane). But benzene does not react with the same reagent. So addition reactions do not take place easily in benzene like alkenes.

One unique quality of benzene and hence all aromatic compounds, is that they can undergo substitution reaction (later we shall know that it is electrophilic substitution) reactions easily which an alkene cannot.

\[ \text{Br}_2/ \text{FeBr}_3 \quad \text{Br} \quad + \quad \text{HBr} \]

Such a reaction is not shown by cyclohexene.

**Huckel Rule of Aromaticity:**

For a compound to be aromatic, it should

(a) cyclic
(b) planar, or nearly planar and
(c) should contain \((4n+2)\) conugating \(\pi\)-electrons (peripheral conjugating pi-electrons) where \(n = 0, 1, 2, 3, \ldots\) (any positive whole number including zero)

Annulenes to be aromatic, it should have \((4n+2)\) conjugating \(\pi\)-electrons. This is the **Huckel’s rule of aromaticity.**

**Examples:**

2\(\pi\)-electron systems:

\(n = 0;\) \((4n +2) = 2 \pi\) electrons:

cycloproenyl carbocation(cyclopropenium ion)

\(\text{cyclopropenyl cation} \quad (C_3H_3^+)\)

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6π-electron systems:
\[ n = 1; \quad (4n + 2) = 6 \pi \text{ electrons} \]

About benzene, we have already discussed.

1. Cyclopentadienyl ion (cyclopentadienide ion) qualifies to be aromatic as there are 6 conjugating π-electrons, in 5 orbitals, of course. One of the orbital carries a lone pair. Note that in this case, all the C-atoms are sp²-hybridised, contrary to the prediction of VSEPR theory that a Steric Number of 4 makes the hybridisation sp³. Due to delocalisation of the charge, it is spread to all the carbon atoms and we can dare write \(-\frac{1}{5}\) charge on each carbon atom, as all the RSs are equivalent. See the RSs.

Is this not interesting? Don’t be surprised to find 5 RSs in a species having 3 conjugating units like benzene. It’s not always true that the number of RSs is equal to number of conjugating units plus one. This we have told in ‘chemical bond’ chapter, while introducing resonance. But there are a large number of exceptions to this, as you find in benzene, having two contributing RSs and cyclopentadienyl anion having 5 RSs.

Cyclopentadiene has a pKₐ of 16 close to H₂O(15.7), that means it is almost as much acidic as water and hence readily loses a H⁺ ion by a strong base like tert-butoxide ion(t-BuO⁻K⁺) and forms stable salt(potassium cyclopentadienide), in which the cyclopentadienide ion is aromatic.

Note that a stronger acid can displace a weaker acid in an acid-base reaction of BL type. Also note that cyclopentadienide ion is not as much stable as benzene. It is fairly reactive and acts as nucleophile in many reactions. But it is more stable than its acyclic counterpart; i.e penta-1,4-dien-3-yl anion.
(2) Cycloheptatrienyl cation (tropylium ion):
Here there are 6-\(\pi\) electrons in seven p-orbitals. One orbital is vacant to carry +ve charge. So for cycloheptatrienyl cation, you can draw 7 equivalent RSs and can say that each carbon in the hybrid acquires a charge of \(-\frac{1}{7}\). We avoid writing the 7 RSs here and simply write the resonance hybrid.

Tropylium ion is easily prepared from cyclohepta-2,4,6-trien-1-ol by treating with acid like HBr at pH <3.

Note that tropylium bromide can be prepared and preserved with appropriate conditions. Also note that tropylium ion, due to its aromaticity, though more stable than other carbocations, including its acyclic analogue and hence less reactive, cannot be thought to be as much stable as benzene.

(3) Heteroaromatics:

Furan and thiophene provide only one lone pair for conjugation and the other lone pair on the heteroatom is in a hybrid orbital. In pyrrole, furan and thiophene, we have to believe that the hybridisation of heteroatom is sp\(^2\) and one unhybridised p-orbital carries the lone pair for conjugation. In pyridine, the lone pair is in a hybrid orbital and the unhybridised p-orbital carries an unpaired electron for conjugation. Should I show you the RSs of at least one from the five membered heteroaromatics and a six membered heteroaromatic (pyridine)?

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Pyrrole has five RSs like cyclopentadienide ion, but they are not equivalent and hence we write -δ charge on each carbon atom and +δ on N atom. For furan and thiophene, the RSs are similar to pyrrole.

For pyridine, the last three RSs being polar contribute very little to the hybrid. The most contributing RSs are the first two analogous to benzene. However, if we take the contribution of the polar RSs, then the hybrid will carry +δ charge on position 2, 4 and 6 w.r.t N- atom. Pyridine is quite stable having Resonance Energy of 27 kcals/mole (as against 36 kcals/mole for benzene) and therefore does not undergo addition reactions easily, rather undergoes substitution reactions easily like benzene. Additionally pyridine has basic property for the N-atom. Interestingly when it forms salt (conjugate acid) i.e pyridinium ion by accepting H⁺ ion from some acid, it still continues to be aromatic as the lone pair present in a hybrid orbital is used for protonation and does not take part in conjugation. Still the hybridisation is sp².

N.B: You can, in the similar way, rationalise the aromaticity of other heteroaromatics discussed before and to be discussed later.

10 π-electron Aromatics:

\[ n = 2; \quad (4n + 2) = 10 \pi \text{ electrons} \]

\[ \text{naphthalene} \quad \text{azulene} \quad \text{cyclooctatetraenyl dianion} \]

\[ \text{indole} \quad \text{quinoline} \]

All the above have 10 conjugating p-electrons and are aromatics. Cyclooctatetraenyl dianion is easily formed by treating cyclooctatetraene (which is nonaromatic: to be discussed later) with potassium metal. Cyclononatetraenyl anion is also aromatic (structure not drawn).

Resonance in Naphthalene:
C\textsubscript{1}-C\textsubscript{2}, C\textsubscript{3}-C\textsubscript{4}, C\textsubscript{5}-C\textsubscript{6} and C\textsubscript{7}-C\textsubscript{8} are equivalent having bond order of \( \frac{5}{3} \) while all the rest have a bond order of \( \frac{4}{3} \). Hence in naphthalene two different bond lengths have been determined by x-ray diffraction method, the former ones having greater bond order have a bond length 1.36Å while the latter ones having bond length of 1.42Å. Resonance energy in naphthalene is 61 kcals/mole i.e 30.5 kcals per benzene ring, which is less than benzene(36 kcals).

14 \( \pi \)-electron Aromatics:

\[
\begin{align*}
\text{n} = 3; & & (4n+2) = 14 \ \text{\( \pi \) electrons}
\end{align*}
\]

In pyrene, the internal pi-bond is not in conjugation with the peripheral pi-electrons and hence the two electrons are not counted for aromaticity. That is why, in the definition, we wrote, the number of peripheral pi-electrons should be \((4n+2)\). So far all the examples cited had only peripheral pi-electrons. The first example of pyrene we studied, has two internal non-conjugating pi-electrons, so to be ignored. So pyrene comes under 14 \( \pi \)-electron aromatics category.

Resonance in Anthracene:

\[
\begin{align*}
\text{C1-C2; C3–C4, C5–C6, C7–C8 have greater bond order of } \frac{7}{2} \text{ (lower bond length) while the rest of C–C bonds have lower bond order of } \frac{5}{2} \text{ (greater bond length). Resonance energy of anthracene is 83 kcals/mole i.e 27.7 kcals per benzene ring which is still less than naphthalene. Phenanthrene has 5 RSs and is more stable than anthracene. Its RE is 91 kcals/mole.}
\end{align*}
\]

18 \( \pi \)-electron Aromatics:

\[
\begin{align*}
\text{n} = 4; & & (4n+2) = 18 \ \text{\( \pi \) electrons}
\end{align*}
\]

Similarly we have pentacene(22 \( \pi \)-electron aromatic), hexacene(26 \( \pi \)-electron aromatic) and so on.

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Other examples of aromatic species:

These above species also are aromatics. In imidazole, the lone pair on NH nitrogen will conjugate like pyrrole. The lone pair on other N will remain isolated to exhibit basicity. In pyrimidine too, both the lone pairs will exhibit basicity as they are not part of conjugated system. In the third example too, there are 6p conjugating pi-electrons as one lone pair on O-atom will remain in a hybrid orbitals and not take part in conjugation.

Antiaromatics:
We already know that cyclobutadiene is unstable although there are two conjugated C=C and we can draw two RSs, but for no use. Those annulenes which are less stable and more reactive than their acyclic analogues are called antiaromatic. Their instability cannot be explained by resonance(what an irony !!!). Here the VBT(resonance theory) fails completely. MOT will explain its instability. Wait a bit for details.

Huckel’s Rule of Antiaromaticity:
A species to be called antiaromatic, it should be
(a) cyclic
(b) planar
(c) should have ‘4n’ conjugated \(\pi\)-electrons: where; \(n = 0, 1, 2, 3, \ldots\)

So 4\(\pi\), 8\(\pi\), 12\(\pi\) electron cyclic systems are antiaromatics, and these are less stable and more reactive than their acyclic analogues.

4\(\pi\) electron antiaromatics:

Cyclopropenyl anion(cyclopropenide ion) and cyclopentadienyl cation(cyclopentadienium ion) have 4\(\pi\) electrons like cyclobutadiene and are planar cyclic compounds. They are also less stable than their acyclic counterparts as shown below.

Stability Order:

Allyl carbanion is truly stable due to resonance so also the penta-1,4-dien-3-yl cation. But the 4p cyclic systems are antiaromatics and unstable. No resonance will explain their instability. Wait a bit.

N.B: You can draw 5 RSs for cyclopentadienyl cation like we did for cyclopentadienyl anion(aromatic). In such case, each carbon atom of the hybrid will carry +1/5 charge. Should i draw the RSs for fun ? But what is the gain ?????? Will it be stable ? No. Then why to waste
energy and net space ??!!!! Therefore cyclopentadienyl cation is not formed in a chemical reaction of cyclopenta-2,4-dien-1-ol with sulphuric acid, as we get a stable tropylium ion in a similar reaction.

\[ \pi \text{ electron antiaromatics:} \]

\[ \text{C}_7\text{H}_7^- \quad \text{cycloheptatrienyl anion} \]
\[ \text{C}_8\text{H}_6 \quad \text{pentalene} \]

pentalene (bicyclic compound) is unstable and so also cycloheptatrienyl anion. They are antiaromatics. Note that tropylium ion was aromatic, but its corresponding anion is antiaromatic. Both are planar. In all these, RSs can be drawn, but we won’t. It will be like ridiculing such a great theory (Resonance) which has countless applications we have already learnt and many yet to learn. Ya, in the case of antiaromaticity, it fails.

\[ \pi \text{ electron antiaromatics:} \]

\[ \text{heptalene} \]
\[ \text{s-indacene} \]

**Non-aromatics:**

Cyclic compounds which appear like aromatics or antiaromatics in terms of number of \( \pi \)-electrons i.e either \((4n+2)\) for aromatics or ‘4n’ for antiaromatics, but not having proper conjugation due to lack planarity or otherwise are called non-aromatics.

Nonaromatic compounds are as much stable as their acyclic analogue.

Examples:

Cyclooctatetraene:

\[ \text{cyclooctatetraene} \]

\( \text{(tub-shaped molecule)} \)

Cyclooctatetraene appears like antiaromatic compound having 8 \( \pi \)-electrons. But actually it a tub-shaped molecule (not planar), which violates the Huckel’s rule. It has stabilised by deviating from planarity. Had it been planar, it would have been highly unstable (antiaromatic). Large size rings which have ‘4n’ conjugated \( \pi \) electrons always pucker out to 3D shape to prevent instability. This compound behaves like an unconjugated alkene and undergoes addition with \( \text{Br}_2 \) easily.

\[ [10] \text{- and } [12] \text{ annulenes:} \]

All cis [10] annulene
There are three isomeric [10] annulenes (cyclodecapentaenes), all of which are non-planar. All of them contain 10 π-electrons hence appear to be aromatics. All cis-annulene assumes non-planar geometry to relieve high angle strain (144° as against 120° required for sp² hybridisation) and the second annulene having two trans C=C (trans,cis,cis,trans,cis isomer) is non-planar because of high steric strain due to internal H atoms (transannular steric strain). The H atoms at C₁ and C₆ are so close that they are bound to remain on opposite sides, for which the molecule sacrifices its planarity. The third isomer which has only one trans C=C is most stable among them. All of them are therefore neither more stable like aromatics nor less stable like antiaromatics, in stead, as much stable as their open chain analogue. Note that if these two carbons (C₁ and C₆) in the 2nd [10] annulene are bridged by a sigma bond, that becomes naphthalene which becomes aromatic. Even a methylene bridge between them also makes the molecule aromatic.

You remember that the dianion formed from cyclooctatetraene having 10 π-electrons was aromatic, although being a large size ring. Since it is a dianion, the repulsion factor helps to retain planarity. [12] annulene which appears to be antiaromatic is non-planar and hence non-aromatic. Other examples of nonaromatic species:

All the above are nonaromatics are as they are all nonplanar. The first two have 6p electrons, could have been aromatic, but are nonaromatic, as they are not planar. The last one has 10p electrons, could have been aromatic, but it is nonaromatic as it lacks planarity which is lost to relieve strain.

The above two compounds are non-aromatic because they lack proper conjugation. The exocyclic C=C (lying outside the ring) will not conjugate totally with the C=C lying inside the ring, as one p-orbital will remain completely isolated. So, although they have 6p electrons, they will not have proper conjugation, as happens in benzene. Hence are nonaromatics.
Molecular Orbital Theory for Aromatics
(This theory will not be required for your purpose, I know. Still I feel tempted to discuss this. Please bear with me.)

Benzene:
The six p-atomic orbitals in benzene will undergo LCAO to form 6 MOs with increasing energy with increase in the number of nodes (nodal planes).

BMOs:
\( \pi_1 \) has six pairs of bonding interactions as all +ve lobes are above the plane and all the –ve lobes are below the plane. All the +ve lobes will combine to form an upper ring and all the lower lobes will combine to form a lower ring. This will be visualised as given below.

In \( \pi_2 \), three +ve lobes are above the plane and three –ve lobes are also above the plane. Hence there will be four pairs of bonding interaction (shown by dotted lines) and two pairs of antibonding interactions. So net effect is due to two pairs bonding interactions. There is one nodal plane passing in between the molecule as shown. Hence it is of higher energy than \( \pi_1 \) and it has net bonding characteristics.

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In $\pi_3$, four $+ve$ lobes are lying above the plane in the continuous manner and two negative lobes are lying above the plane also in a continuous manner. It is actually a complicated situation to understand how this MO is having same energy as $\pi_2$, i.e. it has also one node. Look to the two opposite orbitals which have been given cross(X) marks. Each of these orbitals carries no bonding capacity as, it suffers from one bonding interaction and one antibonding interaction on the two sides. Hence each of them turn out to be nonbonding orbital and hence the nodal plane passes through these carbon atoms carrying nonbonding orbitals, as these orbitals no longer are considered for bonding purpose. This MO has net bonding power due to two pairs of bonding interactions. $\pi_2$ and $\pi_3$ are degenerate MOs.

Note that $\pi_1$, $\pi_2$ and $\pi_3$ are bonding MOs (BMOs).

**ABMOs:**

$\pi_4$ and $\pi_5$ have two nodes each and have higher energy than than BMOs. Since, the net interaction is antibonding, they are ABMOs. Each of them has four pairs of antibonding interactions and two pairs of bonding interactions. Hence net effect is due to two antibonding interactions.

In $\pi_4$, two $+ve$ and two $-ve$ lobes lie above the plane in a continuous manner. Other two lobes are with opposite signs lie above (have a look). You can find that two orbitals on opposite sides shown with cross marks (X) turn out to be nonbonding and hence a node passes through these carbon atoms. The other node shown passes through the bonds as shown. Hence it has two nodal planes.

In $\pi_5$, four $+ve$ lobes lie above the plane facing front to front and two $-ve$ lobes lie on the two opposite sides in between them (have a look). So you can find two nodes pass in between the bonds.

$\pi_4$ and $\pi_5$ are also degenerate MOs.

In $\pi_6$, adjacent lobes carry $+ve$ and $-ve$ lobes above or below the plane. So all the six pairs give antibonding interactions (no bonding interaction) and hence there are 3 nodal planes present in the MO as shown.

$\pi_4$, $\pi_5$ and $\pi_6$ are ABMOs.

As you know, in MOT too, we have to follow aufbau principle, Pauli’s exclusion principle and Hund’s rule. So how the six $\pi$ electrons are arranged in these MOs?

$\pi^2$, $\pi^2$, $\pi^2$ is the configuration of $\pi$ electrons of benzene. ABMOs lie above the energy of a nonbonding $p$-orbitals while BMOs lie below. Since all the $\pi$ electrons occupy in the BMOs to form a ‘Closed Bonding Shell’, it acquires extra stability, which could not be explained by Resonance alone in VBT.
**MOT for ANTIAROMATICS:**

**Cyclobutadiene:**
There are 4p orbitals whose LCAO gives four MOs as follows.

- **π₁**: All the four lobes are lying above the plane. Hence, it has four pairs of bonding interactions and has no node.
- **π₂** and **π₃**: Each of them has two pairs and two pairs antibonding interactions and hence the net bonding power is ZERO. The energy of these MOs is same as an nonbonding p-orbital. Each MO has one nodal plane. Note that the assignment of nodes in this case is not truly correct, since none of the four p-orbitals carry any bonding power.
- **π₄**: Has four pairs of antibonding interactions. Hence in the true sense it is an ABMO.

If we distribute the 4π electrons in the four MOs, then **π₁** will contain an electron pair and the two degenerate **π₂** and **π₃** will contain one electron each (Hund’s rule). Thus butadiene is a diradical in the ground state and hence is extremely unstable. You know that radicals are unstable species and have high reactivity. In case of benzene, all the six electrons occupy the BMOs which lie below the nonbonding line. But in this case, two electron have energy of nonbonding orbital. So total energy of cyclobutadiene is much greater than benzene. As compared to butadiene (its acyclic analogue), the four electrons occupy the two BMOs in two pairs. No unpaired electron were there in it. Please look the MO diagram of butadiene in the chapter ‘General Organic
Chemistry-Part I’, if you have not seen before. It has also no non-bonding MO, as it is in
cyclobutadiene. Therefore cyclobutadiene is less stable and more reactive than butadiene.
N.B: All ‘4n’ π electrons planar annulenes show butadiene type of behaviour and hence are
unstable and more reactive. These are called antiaromatics. All (4n+2) planar annulenes shows
benzene type of behaviour and are called aromatics.

POLYGON RULE:
In general MO energy diagram can predicted for any annulene(aromatics or antiaromatics) by
drawing the relevant polygon shape on its apex(of energy levels) and drawing MOs at each
vertex.
You have seen a hexagon drawn in the MO energy profile for benzene(6 π electrons) and a
square drawn for butadiene(4 π electrons). The nonbonding line passes horizontally exactly
through the middle of the polygon. Then you have to fill the electrons following all the three
rules including Hund’s rule.
Cyclooctatetraene:

\[
\begin{align*}
&\text{nonbonding line} \\
&\text{e} \\
&\text{c} \\
&\text{b} \\
&\text{a} \\
&\text{f} \\
&\text{d} \\
&\text{g} \\
&\text{h}
\end{align*}
\]

Out of 8 MOs three are BMOs and 3 are ABMOs and two are nonbonding type. So
cyclooctatetraene should be unstable and antiaromatic. Fortunately, it stabilises by going away
from planarity(tub-shaped) and we cannot apply the LCAO to orbitals which are not parallel to
each other. When the molecule becomes puckered i.e 3D shaped, then the p-orbitals cannot
remain parallel to each other for overlapping.

Substituent Effects in Benzene Ring:

All the three permanent electronic effects (namely I- effect, M(R)- effect and H- effect) can be
experienced by benzene ring if it carries a suitable substituent. It is the substituent which will
produce these effects.

**+M Effect in Electrophilic Substitution:**

+M groups like –OH, –NH₂, –OR, –NR₂, –OCOR; –NHCOR, etc produce +M effect on
the benzene ring to selectively produce fractional negative charge(–δ) on the *ortho and para positions* with respect to the substitent. See this example.

\[
\begin{align*}
&\text{OH} \\
&\text{ipso position} \\
&\text{ortho(o)} \\
&\text{meta(m)} \\
&\text{para(p)}
\end{align*}
\]

C-1 to which the substituent is attached is called the ipso carbon or ipso position. C-2 and C-
6 are called ortho(o) positions, while C-3 and C-5 are called meta(m) positions and C-4 is called
para(p) position. Hence there are two equivalent ortho positions, two equivalent meta positions
and only one para position with respect to any substituent.

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Electrophilic Substitution Reaction of monosubstituted benzene ring

From the resonance hybrid, we see that there is $-\delta$ charge in both the ortho positions and one para position. Note that meta positions remain as such and have not enriched electron density like ortho and para positions. Due to this any electrophile $E^+$ will attack only to o/p positions (not meta) and bring about substitution there. Supposing you want to put a Cl$^-$ group in phenol and convert it from monosubstituted benzene to disubstituted benzene. We shall know little later that chlorine attacks as an electrophile Cl' (chloronium ion), and we get a mixture of ortho and para chloro phenols (not m-chlorophenol) This is called electrophilic substitution reaction. See this example.

When phenol will be chlorinated by using Cl$_2$/FeCl$_3$, the electrophile Cl$^+$ produced will substitute only at the ortho and para positions. Since only one Cl$^-$ group is to enter, ring, we always get a mixture of ortho and para isomeric products. Statistically, the ortho isomer should be the major product and para as the minor product in the ratio 2 : 1. as there are 2 ortho positions as against one para position. But we shall see later, that various other factors will complicate this issue, and the percentage of ortho and para will not be the same as predicted by statistical factor. But note that meta product won’t be formed in this reaction, as electrophile Cl$^+$ only attacks the nucleophilic centres ($-\delta$) created in the benzene ring due to the $+M$ effect of existing $-\delta$OH group.

In electrophilic substitution, commonly H$^+$ ion is the leaving group.

(NB: We have seen similar RSs before in case of PhO$^-$ before while explaining the acidic nature of phenol. Phenol is more acidic than alchohol because, phenoxide ion is stabilised by resonance. Did you remember ?)

So all the $+M$ groups are therefore called ortho-para directors for the incoming electrophile i.e for electrophilic substitution.

$-M$ effect in Electrophilic Substitution:

Electron withdrawing groups like $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{SO}_3\text{H}$ etc. are called $-M$ groups. Such groups will create $+\delta$ charge on the ortho/para positions.
Since, ortho and para positions acquire +δ charge, electrophile cannot attack to these positions. Instead, if it has to attack the benzene ring, it will attack the meta position, which is relatively less electron deficient. Note that both the meta positions are equivalent and E⁺ can attack any of these. So –M groups are called meta directors for electrophilic substitution. See below.

**Activation for Electrophilic substitution:** Note that +M group, not only directs the incoming electrophile to o/p positions, but also enhances the rate of reaction by increasing the electron density in the benzene ring. Such groups are, therefore, called ACTIVATORS which increases the rate of reaction compared to unsubstituted benzene. But –M group, though directs the incoming E⁺ to the meta position, the reaction rate becomes slower than the unsubstituted benzene. Since it has reduced the electron density from the ring (although from o/p positions), the overall attraction of the substrate to the electrophile (E⁺) is lowered. Therefore these groups are called DEACTIVATORS which reduce the rate of electrophilic substitution reaction compared to unsubstituted benzene.

**Effect of –Cl(halo) group on Orientation and Reactivity:**
-Cl(any halo group) is a o/p director but a deactivation. Note that halo group produces two opposing effects namely +R and –I and the net effect is –I. Hence presence of a halo group deactivates the ring and thus slows down an electrophilic substitution reaction. But ironically it is a o/p director. This is the only o/p director which does not activate the ring. We can explain the orientation by drawing the RSs of the intermediate arenonium carbocation and making comparison between o/p attack and m-attack of the electrophile. In case of o/p attack, there is one RS in which the +ve charge is adjacent to the –Cl group which is stabilised by π-π back bonding. We can call this R-effect also. No harm. But this is a localised R-effect in which the RS is stabilised, but the lone pair of Cl does not delocalise into benzene ring. In case of meta attack, no such stable RS is there.
The details of the steps in electrophilic substitution, we shall study a bit later.

N.B: (1) Do not be surprised if you find in some texts saying –I effect of –Cl group explains deactiation and +M effect explains the o/p orientation. I do not agree with the second part. –Cl group does not have any net +M effect onto the ring. Yes, its +M effect is restricted to stabilise the carbocation.

(2) Due to small size of F atom, the +R effect is more in Ph–F than Ph–Cl and others. This makes the net –I effect of -F group less than –Cl. So for many purposes in halobenzene, the the order of – I effect is as follows.

\[-Cl > –F > –Br > –I\]

(3) Benzene is famous for electrophilic substitution, as benzene ring itself is a nucleophile and has a strong affinity for electrophiles(E+) rather than nucleophiles(Nu–). We shall study this aspect in details later.

**Nucleophilic Substituion Reaction of monosubstitued benzene ring:**

Since benzene itself is a nucleophile, substitution of an existing group(to become the leaving group) on the ring by another nucleophile is not easy. However, it is possible if another –M group is present ortho or para w.r.t to the leaving group.

A nucleophile will preferably attack the o/p position w.r.t –M group as such positions becomes an electrophilic centre(+δ) provided the leaving group is located at that position. So –M groups are ortho/para directors for a nucleophilic substitution and also activators the reaction.

Here –Cl will leave as Cl– (leaving group), unlike a H+ which is the leaving group in most electrophilic substitution reactions. The presence of the –NO2 group produces +δ charge on the carbon bearing the leaving group(–Cl), so that the incoming nucleophile OH– attacks that carbon(an electrophilic centre) to expel out Cl– as the leaving group. Had there been no –Cl group, substitution would not have happened, as H+ ion is not a leaving group in most cases. Had there been no –NO2 group, then the nucleophilic substitution would have happened, but with much difficulty under drastic conditions. But the presence of a –M group has activated the reaction and happens more easily. We shall discuss this aspect in details later.

Dr. S. S. Tripathy
N.B: When nucleophilic substitution itself is not easy for benzene, the effect of +M group like –OH on the reaction sounds ridiculous. +M effect enhances the electron density of the ring (although ortho/para positions) and nucleophile will not be interested to attack the carbon bearing the leaving group, particularly when it is attached the ortho/para position w.r.t to the +M group. For now, we stop further discussion on this.

**Hyperconjugation in alkyl benzene:**
Alkyl group (R–) attached to benzene ring will produce +H effect while groups like –CCl₃ will produce reverse hyperconjugation effect (–H). See the following diagram.

An alkyl group having at least one α-H atom w.r.t benzene ring can give hyperconjugation structures as shown. We have shown only one α-H atom, similarly we can draw four more for each of the other two H atoms. Even though, H-effect is less pronounced that R-effect, due to this the ortho and para positions become electron rich compared to meta position. Hence in electrophilic substitution, E⁺ attacks o/p positions like for any other +M group discussed before. Hence alkyl group (R–) group having at least one α-H atom are ortho/para directors for electrophilic substitution reactions.

–CCl₃ group produces reverse hyperconjugation effect (–H effect) and produces +δ charge on the ortho and para positions. Hence an electrophile will preferably attack meta position which is less electron deficient than the ortho/para positions. Hence –CCl₃ group is a meta director in the electrophilic substitution reactions.

Note that without invoking H-effect, we cannot explain why R– group is o/p directors and –CCl₃ group is a meta director in electrophilic substitution reactions.

N.B: We have discussed these things a bit early only with an objective of telling you the effect of a +M and –M group can have on the benzene ring. Our primary interest now is to study the effect of different groups in benzene ring on the acid strengths of substituted phenols and benzoic acids and also base strengths in substituted anilines.

Dr. S. S. Tripathy
Relative Acid Strength in Substituted Phenols:

![Diagram showing relative acid strength of substituted phenols with pKa values]

We already know that –I and –M effect stabilise the conjugate base of the acid and increases the acid strength while electron releasing (+I, +H, +M) groups will destabilise the conjugate base and hence reduce the acid strength.

In p-nitrophenol, the –ve charge of the p-nitrophenoxide ion (conjugate base) will be delocalised into the –NO₂ group, if it occupies in the o/p position with respect to the relectron releasing group. The –M effect of both para and ortho isomers is shown below.

![Diagram showing delocalisation of charge in p-nitrophenol]

Only when a –M group occupies ortho/para position w.r.t a +M group, then M-effect operates. If the –M group occupies in the meta position w.r.t to +M group the negative charge of the phenoxide ion cannot enter into the –NO₂ group, it will be bypassed to other positions. Hence –M effect of the group will not be exhibited. In stead it will act as a –I group to polarise the sigma bond chain and no doubt stabilise the phenoxide ion, but not to the extent of para and ortho isomers where there is a M-effect. Just remember now, m-nitrophenol also is more acidic than phenol, but less acidic than both ortho and para nitrophenols.

In p-chlorophenol, the phenoxide ion is stabilised only by the –I effect of –Cl group, which is less pronounced than –M effect. So it is less acidic than p-nitrophenol. But both p-nitrophenol and p-chlorophenols are more acidic than phenol.

p-methyl phenol is less acidic than phenol because there a -δ charge at the o/p position w.r.t the CH₃– group due to hyperconjugation. The phenoxide ion will be destabilised by the presence of -δ charge on the carbon to which it is bonded(para w.r.t the CH₃– group). p-methoxy phenol is still less acidic because still more –δ charge lies on the carbon bearing the O– group, due to +M effect of –OCH₃ group. See the following.

Dr. S. S. Tripathy
If the +M group like –OR is located ortho/para to O– group, then -δ will be created o/p w.r.t the +M group i.e on the carbon bearing the O– group which will destablise the phenoxide ion. However, if the said group occupies the meta position, then -δ charge does not appear on the carbon bearing the –O (phenoxide ion), in stead it is bypassed. In such case, +M group shows –I effect. You know that all the +M groups having hetero atoms like O, N etc are intrinsically –I groups, but becomes +M when there is conjugation. So in case of m-methoxyphenol, –OCH3 group will act as a –I group to stabilise the phenoxide ion relative to phenoxide ion. So the m-methoxyphenol is more acidic than phenol. We shall see this thing a bit later.

But for now, we have convinced ourselves that due +M effect, p-methoxyphenol is less acidic than p-methylphenol(p-cresol) which destabilises the phenoxide ion by +H or +I effect, which is less pronounced than +M effect.

**Disubstituted Isomeric Phenols:**

**Nitrophenols:**

In both o/p isomers, there is –M effect of –NO2 group, hence they are convincingly more acidic than meta isomer in which there is –I effect of –NO2 group. Ortho isomer is bit less acidic because there is some resistance for ionisation due to intramolecular H-bonding present in it. All the three are more acidic than phenol due to electron withdrawing nature of –NO2 group. Note that 2,4,6-trinitrophenol popularly called picric acid is much stronger acid(pK_A = 0.71) as there –M effect of three –NO2 group at the favourable o/p positions and 2,4-dinitrophenol(pK_A=4.11) is also much stronger than phenol due to –M effect two –NO2 groups.
Chlorophenols:

\[
\begin{align*}
\text{OH} & \quad \text{Cl} \\
\text{OH} & \quad \text{Cl} \\
\text{OH} & \quad \\
\text{OH} & \\
\end{align*}
\]

\[pK_A \begin{array}{cccc}
8.48 & > & 9.02 & > \\
& > & 9.38 & > \\
& & 9.98(10) & \\
\end{array}\]

Chlorophenols are more acidic than than phenol (not as much as nitrophenols) due to the –I effect of –Cl group. Since I effect decreases with distance, ortho isomer is most acidic and para is the least acidic. There is no anomaly here.

Methoxyphenols:

\[
\begin{align*}
\text{OH} & \quad \text{OMe} \\
\text{OH} & \quad \text{OMe} \\
\text{OH} & \quad \text{OMe} \\
\text{OH} & \\
\end{align*}
\]

\[pK_A \begin{array}{cccc}
9.65 & > & 9.98(10) & > \\
& > & 9.98 & > \\
& & 10.21 & (+M) \\
\end{array}\]

Just before a minute, you knew that +M group like –OMe acts as –I group if occupied in the meta position w.r.t to an electron releasing group. So meta isomer is more acidic than phenol. In both ortho and para isomers, there is +M effect of –OMe group which destabilise the phenoxide ion. So they should be less acidic than phenol. But if you look at the pK\textsubscript{}\text{A} values, you will find that this is true for para isomer, as already explained before. But ortho isomer has same acid strength as phenol itself. This, to me, the effect of SIR(steric inhibition of resonance) which is trying to undo the effect of +M effect to the extent that the acid strength becomes equal.

(Caution: Let me, honestly confide with my readers that in many cases, the actual cause is not known. Sometimes, we feel like giving a vague explanation with our full knowledge, that we are not convinced and trying to impose on the young reader like you. But i shall refrain myself in doing so. I shall be equally happy to write in such cases, the cause is not known to me)

Fluorophenols:

\[
\begin{align*}
\text{OH} & \quad \text{F} \\
\text{OH} & \quad \text{F} \\
\text{OH} & \quad \text{F} \\
\text{OH} & \\
\end{align*}
\]

\[pK_A \begin{array}{cccc}
8.48 & > & 9.28 & > \\
& > & 9.95 & > \\
& & 9.98(10) & \\
\end{array}\]

Like chlorophenols, the order is the same. –I effect is reduced with distance therefore ortho isomer is most acidic and para least acidic. All of them are more acidic than phenol. But meta and para isomers are very near to phenol in strength.

Dr. S. S. Tripathy
IMP: Do you observe one thing? Fluorophehols are less acidic than respective chlorophenols, although –I effect of –F is greater than –Cl. This is because there is appreciable +M effect in flouro isomer due its small size. So the –I effect is appreciably nullified by the +M effect, though the net effect is a small –I. In chloro isomer, -Cl has a very little +M effect due to its large size. The resultant –I effect is greater in than that in fluoro isomer. That is why fluorophenols are less acidic than chlorophenols. But flouroacetic acid is stronger than chloroacetic acid, as there is no M- effect to compete with –I effect.

Cresols(methylphenols):

All methyl phenols are weaker than phenols due to electron releasing nature(+H and +I) nature of –CH3 group which will destabilise the methylphenoxide ions relative to phenoxide ion.

In meta isomer, hyperconjugation(like resonace) will not work, only +I works, for which it is more acidic than the o/p isomers, in which +H effect, in addition to +I. In ortho isomer, the +I effect is maximum due its proximity with the –OH group. Hence it will destabilise the phenoxide ion the most and hence is least acidic.

(Caution: We are using a few theories to explain the experimental data. To me, these explanations are more of speculative type than realistic. The small difference in pKA values and reproducibility literature data cannot make us confident to give a concrete explanation. We mostly do it just for the sake of explanation.)

What about dihydroxybenzenes?

If you look to the pKA data of diydroxy bezennes as compared to phenol, all the three isomers are more acidic than phenol. Does not match with the trend that we got for methoxyphenols. Like –OMe, –OH is also a +M group, and hence same explanation would make the order similar to methoxy phenols. While m-dihydroxybenzene is expected to be stronger than phenol due to –I effect of the other –OH group on stabilising the phenoxide ion, ortho and para isomers should be less acidic than phenol. In reality, they are also more acidic than phenol. So can we give here any convincing explanation? The answer from my side is NO.

Here, our hands are tight. If we open our mouth to show our proficiency, it will turn out to be our greatest foolishness. So i can dare write, that the cause of above trend is not known.
What about aminophenols?

\[
\begin{array}{cccc}
& \text{OH} & \text{NH}_2 & \text{OH} \\
\text{pK}_A & 9.71 & 9.87 & 9.98(10) \\
\text{NH}_2 & 10.21
\end{array}
\]

Like –OH group –NH\textsubscript{2} group is also +M. So p-aminophenol is less acidic than phenol. This is understandable. The meta isomer is more acidic than phenol is also understandable due –I effect of –NH\textsubscript{2} group at that position. But what about ortho isomer ? One can argue here that –I effect is working the most as +M is totally cancelled by SIR. But this is unacceptable as –NH\textsubscript{2} group is a small size group which will not produce any steric hindrance for SIR. Here, as many authors believe, so i have to, a unique ‘ortho effect’ is in force in aromatic amino compounds and carboxylic acids, which make the it to behave uniquely. Although, in this case cause of ‘ortho effect’ is not known, some other ‘ortho effects’ can be explained(see below).

**Substituted Benzoic acids:**

\[
\begin{array}{cccc}
& \text{COOH} & \text{COOH} & \text{COOH} & \text{COOH} \\
\text{NO}_2 & 2.17 & 3.98 & 4.17 & 4.37 & 4.47 \\
\text{Cl} & -(-M) & -(-I) & (+H/+I) & (+M)
\end{array}
\]

Like substituted phenols, more the stability of bezoate ion(conjgate base), more is the acid strength. In p-nitrobezoic acid, there is a +\(\delta\) charge on carbon atom carry the COO\textsuperscript{-}. This stabilises the carboxylate ion by its pronounced –I effect. Note that there is no resonance of COO\textsuperscript{-} with the benzene ring, as it is not a conjugate system(separated by two C–C). Benzene ring also cannot produce +M effect on COO\textsuperscript{-}, as the two units do not conjugate with each other. There is a resonance in COO\textsuperscript{-} within the three atoms like any aliphatic carboxylate ion. In benzene ring too, there is 6\(\pi\) electron delocalisation. So the two systems do not conjugate with each other. The other reason for this is that benzene ring does not lie in the same as COO\textsuperscript{-} due to repulsion effect. –COO\textsuperscript{-} is a strong +I group.

In p-chloro isomer, there is –I effect of Cl– group which stabilises the carboxylate ion, of course, to a lesser extent than p-nitro isomer.

p-methyl isomer destabilises the –COO\textsuperscript{-} due to +H/+I effect while p-methoxy by +M effect. This has been explained before in case of phenols)

(N.B: Note that there is resonance in benzoic acid, in which –COOH acts as a –M group and benzene ring as +M group and hence produces +\(\delta\) charge in o/p positions, like any other –M group lik –NO\textsubscript{2}, –CN, –CHO etc. But –COO\textsuperscript{-} does not act as –M group, in stead as +I group.)
Ortho effect:
In substituted benzoic acids and anilines (to be discussed later), a unique and uniform observation has been found that ortho isomer of each substituted benzoic acids is more acidic than the meta and para isomers. In most cases, it is even stronger than benzoic acid itself. Although, it is not always possible to give a convincing explanation for this behaviour, we can approximately believe, like many authors, that SIR is the main cause for +M or +H/+I substituents and the intramolecular H-bonding stabilisation for the –M substituent. For pure –I group like, as such the ortho isomer should be most acidic due to its proximity with the –COOH group.

Hydroxybenzoic acids:

\[
\text{COOH} \quad \text{COOH} \quad \text{COOH} \quad \text{COOH} \\
\text{OH} \quad \text{OH} \quad \text{OH} \\
\begin{array}{c}
\text{Salicylic acid} \\
pK_A = 2.98 \\
(\text{Ortho effect})
\end{array} \quad \\
\begin{array}{c}
\text{>}
\end{array} \\
\begin{array}{c}
\text{>}
\end{array} \\
\begin{array}{c}
\text{>}
\end{array} \\
\begin{array}{c}
\text{>}
\end{array} \\
\text{OH}
\]

+M effect of –OH should make the o/p-hydroxy benzoic acids less acidic than benzoic acid, as was found in case of phenols. In this case, while para isomer is less acidic than benzoic acid, ortho isomer is the strongest among all. The SIR plea can make the ortho isomer close or equal to benzoic acid, but not so strong acid (pK_A = 2.98). This can be explained by the stabilisation of the carboxylalate ion by intramolecular H-bonding. This is corroborated from the still greater acid strength of 2,6-dihydroxybenzoic acid in which there is stabilisation of carboxylate ion from both the side.

\[
\begin{array}{c}
\text{O} \quad \text{O} \quad \text{O} \\
\text{O} \quad \text{O} \quad \text{O} \\
\begin{array}{c}
\text{Intramolecular H-bondin}
\end{array} \\
(\text{salicylate ion})
\end{array}
\]

m-hydroxybenzoic acid is stronger than benzoic acid due to –I effect of –OH group acting at the meta position. This has been already explained before in case of phenols. In para isomer, +M effect produces a –δ charge on carbon adjacent to –COO (para to OH) which destabilise the carboxylate ion by pronounced +I effect. Hence it is weaker than benzoic acid.

Methylbenzoic acids:

\[
\begin{array}{c}
\text{COOH} \quad \text{COOH} \quad \text{COOH} \quad \text{COOH} \\
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\begin{array}{c}
pK_A = 3.91 \\
(\text{Ortho effect})
\end{array} \quad \\
\begin{array}{c}
4.17 \\
(+I)
\end{array} \\
\begin{array}{c}
4.27 \\
(+H)
\end{array} \\
\begin{array}{c}
4.37 \\
(+H)
\end{array}
\]

Dr. S. S. Tripathy
We expected that all methylbenzoic acids to be less acidic than benzoic acid due the electron releasing effect of –Me group. In reality, o-methylbenzoic acid stronger than benzoic acid due to ortho effect while m- and p- isomers are less acidic than benzoic acid, as expected. Para isomer is less acidic than meta isomer because, in para, there is hyperconjugation to produce -d charge adjacent to –COO– which destabilise it more than +I effect produced by –CH3 group in the meta isomer.

The ortho effect in ortho isomer needs special treatment. If SIR will totally eliminate hyperconjugation, then it would be as acidic as benzoic acid. But it is convincingly stronger than benzoic acid. Here the SIR is also increasing the ease of proton release(i.e dissociation of –COOH) analogous to Field effect(see before) something which is hard to believe. Note that there is no intramolecular H-bonding stabilisation, as was found in ortho-hydroxybenzoic acid. This peculiar and interesting behaviour has been further confirmed by further substituting the other ortho position or with bulkier group than –Me. See the following.

\[
\begin{align*}
&\text{COOH} & \text{COOH} & \text{COOH} \\
&\text{H}_3\text{C} & \text{CH}_3 & \text{tBu} & \text{CH}_3 \\
&p\text{K}_A & 3.21 & 3.46 & 3.91
\end{align*}
\]

2,6-dimethylbenzoic acid is the strongest among them, 2-tert-butylbenzoic acid is weaker than the former and stronger than 2-methylbenzoic acid. This surprisingly confirms the role of SIR in controlling the acid strength.

SIR being the cause of ‘ortho effect’ in alkyl, alkoxy and halo benzoic acids is further corroborated by the following results.

\[
\begin{align*}
&\text{COOH} & \text{COOH} \\
&\text{H}_3\text{C} & \text{CH}_3 \\
&p\text{K}_A & 3.21 & 4.33
\end{align*}
\]

\[
\text{OCH}_3
\]

Methoxybenzoic acids:

This is similar to hydroxybenzoic acid, of course, for ortho effect, we cannot bring in intramolecular H-bonding in this case. In stead we shall explain like o-methylbenzoic acid.

\[
\begin{align*}
&\text{COOH} & \text{COOH} & \text{COOH} & \text{COOH} \\
&\text{OCH}_3 & \text{OCH}_3 & \text{OCH}_3 & \\
&p\text{K}_A & 4.09 & 4.09 & 4.17 & 4.47
\end{align*}
\]

(Ortho effect) 
(-I) 
(+M)

Dr. S. S. Tripathy
Here m-methoxy isomer is more acidic due to –I effect of –OMe in the meta position. para isomer is less acidic because of +M effect of –OMe(already explained). Ortho isomer, coincidentally has the same acid strength as meta isomer. It is due to ortho effect. Here ortho effect is only due to SIR. But why o-methoxybenzoic acid is less acidic than o-methylbenzoic acid, because there is some +M effect in –OCH₃ which would tend to cancel some ortho effect(SIR) and net ortho effect is less. Note that these explanations, at many occasions, appear to be abstract and not fulling convincining. Let us accept this.

Nitrobenzoic acids:

\[
\begin{align*}
\text{COOH} & \quad \text{COOH} & \quad \text{COOH} & \quad \text{COOH} \\
\text{NO}_2 & > & \text{NO}_2 & > & \text{NO}_2 & >
\end{align*}
\]

- M

Ortho effect

\[
p_{\text{K}_A} 2.17 \ 3.43 \ 3.49 \ 4.17
\]

Like nitriphenols, all nitrobenzoic acids are stronger than benzoic acid due to –M/–I effect. The ortho and para isomers are expected to be stronger than meta, as the latter has –I effect the the formers have –M effect. But the much stronger acid strength of ortho isomer is due to ‘ortho effect’, which is in this case is the intramolecular H-bonding type of stabilisation of the carboxylate ion.

\[
\begin{align*}
\text{COO}^- & \quad \text{COO}^- \\
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O}
\end{align*}
\]

Even, one can think of a bond formation between COO⁻ and the nitro group as shown above to further stabilise it.

(If you ask me, why the meta and para isomers have nearly equal acid strength, then i am handicapped. At least i can raise apprehension on the credibility of the data for the para isomer, or if data is reproducible then i shall say that the actual cause is not known to me. After all these explanations are more of theoretical in nature than practical. We show our proficiency in GOC by somehow convincing the reader. Ha ha.....)

Like tinitrophenol, 2,4,6-trinitrobenzoic acid much strongly acidic having \(p_{\text{K}_A} = 0.65\).

Chlorobenzoic acids:

\[
\begin{align*}
\text{COOH} & \quad \text{COOH} & \quad \text{COOH} & \quad \text{COOH} \\
\text{Cl} & > & \text{Cl} & > & \text{Cl} & >
\end{align*}
\]

- M

Ortho effect

\[
p_{\text{K}_A} 2.94 \ 3.83 \ 3.98 \ 4.17
\]

Dr. S. S. Tripathy
As expected, as distance increases, –I effect decreases and the acid strength decreases. All chlorobenzoic acids are stronger than benzoic acid due to –I effect of –Cl. But the ortho isomer is unusually more acidic due to Ortho effect. Here we can take the plea of SIR to explain the ortho effect.

**Fluorobenzoic acids:**
Like flurophenols, fluorobenzoic acids are weaker than the respective chlorobenzoic acids, as there is some +M effect to nullify the –I effect due to its highest EN. So net result is reduced –I effect.

\[
o-\text{fluoro} \text{benzoic acid}(3.27) > m-\text{fluoro} \text{benzoic acid}(3.87) > p-\text{fluoro} \text{benzoic acid}(4.14)
\]

**Amiobenzoic acids:**
In this case, the literature gives conflicting data.

*Data for Organic chemistry by I.L Finar*

\[
o-\text{amino} \text{benzoic acid}(4.98) < p-\text{amino} \text{benzoic acid}(4.92) < m-\text{amnio} \text{benzoic acid}(4.79)
\]

If we rely on this data, we find that all aminobenzoic acids are weaker than benzoic acid. Though we can accept this for ortho and para isomer where +M effect of –NH₂ is responsible, but what about meta isomer? Here –I effect is not acting like –OR and –OH groups. Since the major effect of –NH₂ is +M, it cannot stabilise the benzoate ion even when present in the meta position. It will destabilise by its electron releasing nature. According to this data, ortho effect is not noticed in the ortho isomer as it is least acidic instead of most.

*Data from Wikipendia:*

\[
o-\text{amino} \text{benzoic acid}(2.14) < p-\text{amino} \text{benzoic acid}(2.38) < m-\text{amnio} \text{benzoic acid}(3.1)
\]

From this data, we find that all aminobenzoic acid is stronger acids than benzoic acid. This is something unacceptable to us at first sight.

Note that if we consider the pKₐ of aniline (its conjugate acid) being 4.58 and pKₐ of benzoic acid being 4.17, we believe that internal acid-base reaction is possible between –COOH and –NH₂ group to form a zwitterion. However, the values are too close to happen predominantly at pH=7. But due to appreciable tendency of –NH₂ group to accept a proton, the tendency to lose a proton by –COOH group might be enhanced due to this reason. That is why, we can accept that all aminobenzoic acids are stronger than benzoic acid. The ortho isomer called anthranilic acid, has an additional possibility of stabilising the carboxylate ion by intramolecular H-bonding. Hence it is most acidic and here ortho effect is valid.

I am stopping further discussion on aminobenzoic acids in this edition.

**Basicity of substituted anilines:**

![Chemical structures and pKₐ values]

We already know that the popular way of comparing base strength is to compare the pKₐ values of the conjugate acids of these bases. Greater the pKₐ greater is the base strength.
In p-methoxyaniline, the +M effect of \(-\text{OMe}\) group produces a \(-\delta\) charge on the carbon bearing the \(-\text{NH}_2\) group. Hence p-methoxyphenyl group acts as a strong +I group to reduce the extent of delocalisation of lone pair on nitrogen atom into benzene ring. Hence it is most basic. Alternatively we can say, the +M of both \(-\text{NH}_2\) and \(-\text{OMe}\) in opposite directions reduces the extent of delocalisation of lone pair on N atom, which makes the molecule more basic. Note that the basicity is due to the lone pair on N-atom, not due to lone pair of O-atom. In p-methyl, same thing happens but with a lesser magnitude due to hyperconjugation of \(-\text{CH}_3\) group.

So both p-methoxy and p-methylanilines are stronger bases than aniline.

In p-chloroaniline, the \(-\text{I}\) effect of \(-\text{Cl}\) group increases the extent of delocalisation of the lone pair and hence is less available on N-atom. Hence it is less basic than aniline.

In p-nitroaniline, the lone pair is further delocalised into the \(-\text{NO}_2\) group as it produces \(-\text{M}\) effect being located para to \(-\text{NH}_2\) group. Like we did for p-nitrophenol, we can show the RSs where the \(-\text{NO}_2\) is involved in resonance. Hence, the lone pair is least available and it is least basic.

**Substituted isomeric anilines:**

Like substituted benzoic acids, in this case too, there is a ‘ortho effect’ for which the ortho isomer in each case has unexpectedly lower base strength. In benzoic acid, the ortho isomer was most acidic, there it is the opposite. In some cases, it is the least, in others, it is less than expected. The ortho effect here is better explained by intramolecular H-bonding or the lack of stability of conjugate acid(anilium ion) by hydration due to steric hindrance. Steric factor is involved though not SIR.

**Methoxyanilines:**

\[
\begin{array}{ccc}
\text{NH}_2 & \text{OMe} & \text{NH}_2 \\
5.29 & 4.58 & 4.49 \\
(+M) & (Ortho effect) & (-I)
\end{array}
\]

p-methoxyaniline: We have already discussed how it is more basic than aniline due +M effect of \(-\text{OMe}\).

The ortho isomer also should be more basic than aniline due to the same reason as for para isomer. But it is less basic than aniline. It is also referred to as “ortho effect”. The steric crowding in ortho isomer localises the lone pair to some extent. Alternatively, the conjugate acid anilium ion cannot be stabilised by by hydration effectively due to steric hindrance. The meta isomer is expected to be less basic due to \(-\text{I}\) effect of OMe at the meta position which delocalises the lone pair on N atom more.

**Methylanilines:**

\[
\begin{array}{ccc}
\text{NH}_2 & \text{CH}_3 & \text{NH}_2 \\
5.12 & 4.69 & 4.58 \\
(+H) & (+I) & \\
\end{array}
\]

4.39 Ortho effect

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All methylanilines (toluidines) are expected to be more basic than aniline due to the electron releasing property of –CH₃ group. Actually the para and meta isomers are more basic than aniline while the ortho isomer is less basic than aniline. This is due the ‘ortho effect’. In this case, this effect is due to a kind of intramolecular H-bonding between the lone pair on N atom and the C–H hydrogen atom, which is very unique.

![Methylaniline Structure]

Although the –CH₃ group at the ortho position is constantly rotating about the single bond and the H-bonding interaction occurs for a short time period and is a fleeting type, even then, this interaction is thought to be responsible to localise the lone pair and reduce the base strength. Alternatively, lack of proper hydration of the conjugate acid (anilinium ion) due to steric hindrance makes it least stable and hence the ortho isomer least basic.

**Chloroanilines:**
Since only –I effect operates here, the distance factor matters. All the chloroanilines are less basic than anilines, therefore.

![Chloroaniline Structures]

The ortho isomer is expected to be the least as –I effect is maximum at the least separation. But it is less basic than expected of this. You look to its pKₐ value. Definitely some ‘ortho effect’ is involved here too. But we cannot explain this by intramolecular H-bonding as Cl is itself carries the –ve pole and cannot interact with the –ve pole of nitrogen atom. So we are left with the reason of lack of stability by hydration of the conjugate acid (anilinium ion) due to steric hindrance.

**Nitroanilines:**
Nitro group produces stronger –I as well as –M effect and hence are still less acidic than chloroanilines.

![Nitroaniline Structures]

The ortho and para isomers have –M effect of –NO₂ for which the lone pair of –NH₂ is further delocalised, so they are less basic than meta isomer, in which delocalisation takes place by the –I effect of –NO₂ group at meta position. But ortho isomer is unexpectedly less basic due to ortho effect. This can be also explained by instability of conjugate acid by poor hydration due to steric hindrance.

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