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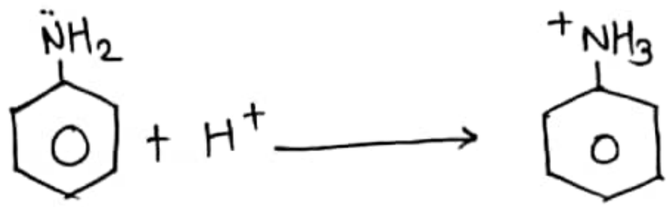
Effects of substituents on Basicity of Aromatic Amines:

- As we know that non-bonding e⁻ pair at Nitrogen atom in aromatic amine accepts proton thus they are Basic in Nature.



Aniline Anilinium Ion.

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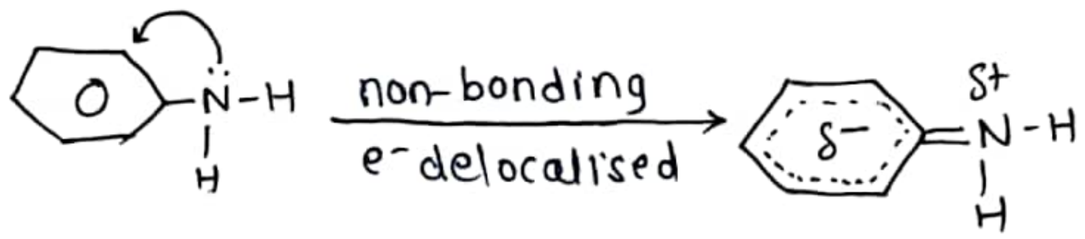
In aromatic Amine the Non-bonding e⁻ is delocalized into Benzene ring by resonance so they are less available for protonation.



- The basicity of Aromatic amine is greatly influences by the Nature of substituent as well as their positions on aromatic ring.

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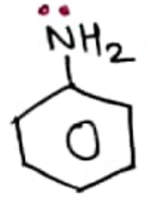
① Electron Releasing Groups:

Such as $-CH_3$, $-OCH_3$, $-OH$, $-NH_2$, ↑↑ basicity of Aromatic Amines.



- This is due to these groups ↑↑ e⁻ density on the amino group thus the Lone pair e⁻ on N is more available.

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- At the same time, also stabilized the Substituted Aniline ion by resonance effect.
- So e⁻ releasing groups ↑↑ the basicity of aromatic Amines.
- If we consider the position of these groups on Benzene the para substituted Amines are more stronger basic than ①

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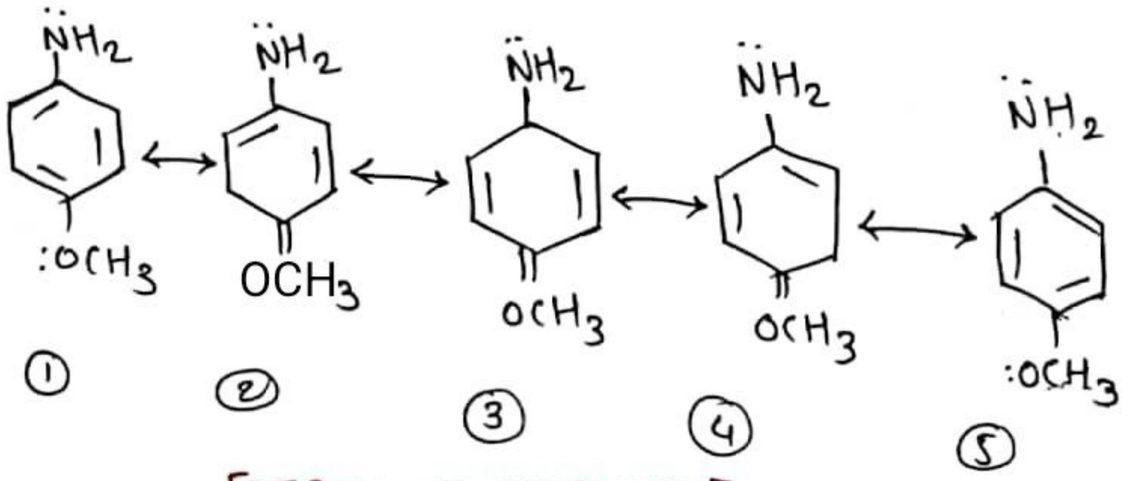
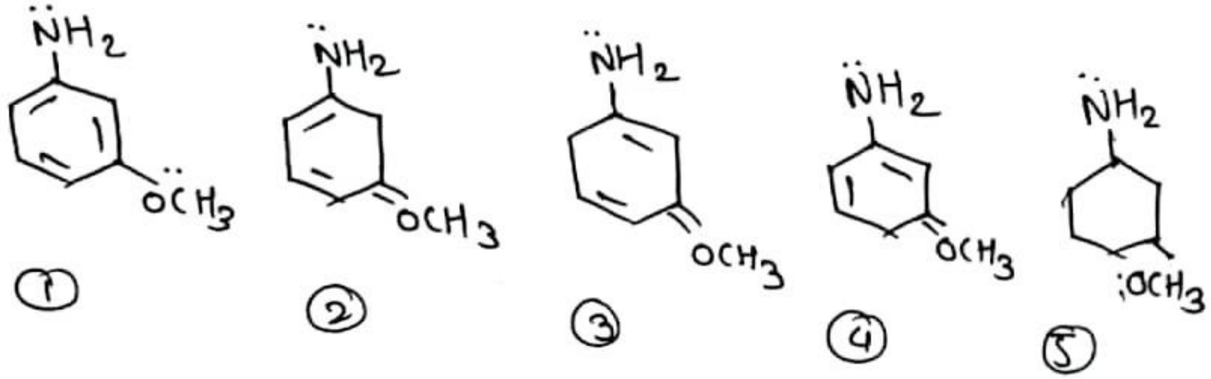
★ Meta Substituted Amines →



★ Resonance in p-Methoxy Aniline.

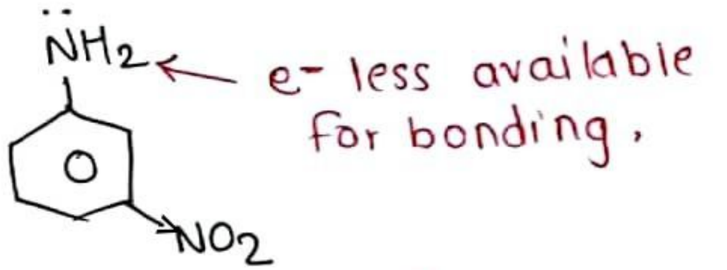


Resonance in Meta Methoxy Aniline,

In structure (3) in p-methoxyaniline there is a -ve charge on carbon with N, will make more difficult to lone pair of e⁻ of Nitrogen to get dispersed in Benzene so more available on Nitrogen so more basic.

- ortho substituted Anilines always less basic - ortho effect & the cause of ortho effect is not well known.

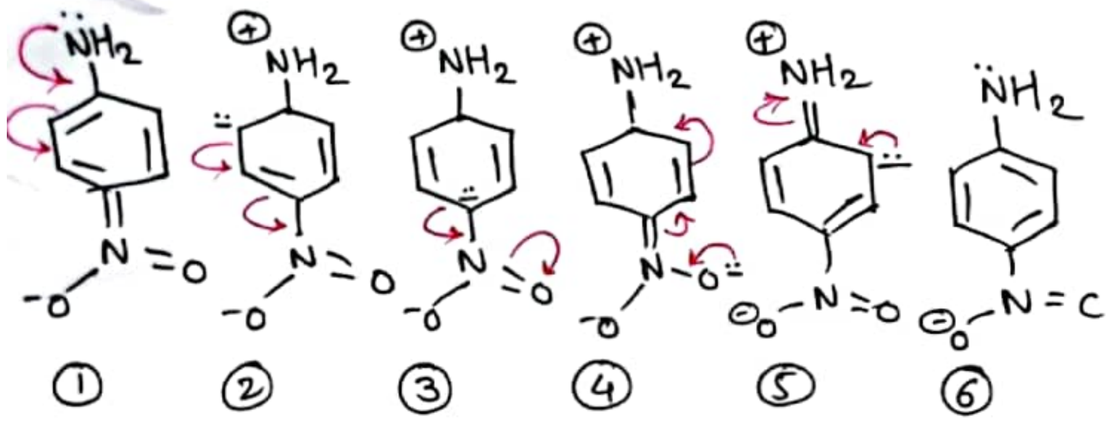
② Electron withdrawing Group effects:
- Such as $-NO_2$, $-CN$, $-CHO$, on benzene ring decreases the basic strength.



These groups decreases the e⁻ density on Amino group & thus lone pair e⁻ become less available for sharing with an acid.

- Para substituted amines are less basic than meta substituted amines.

eg: p-Nitroaniline is less basic than m-Nitroaniline & Aniline.



★ Resonance of p-NitroAniline:

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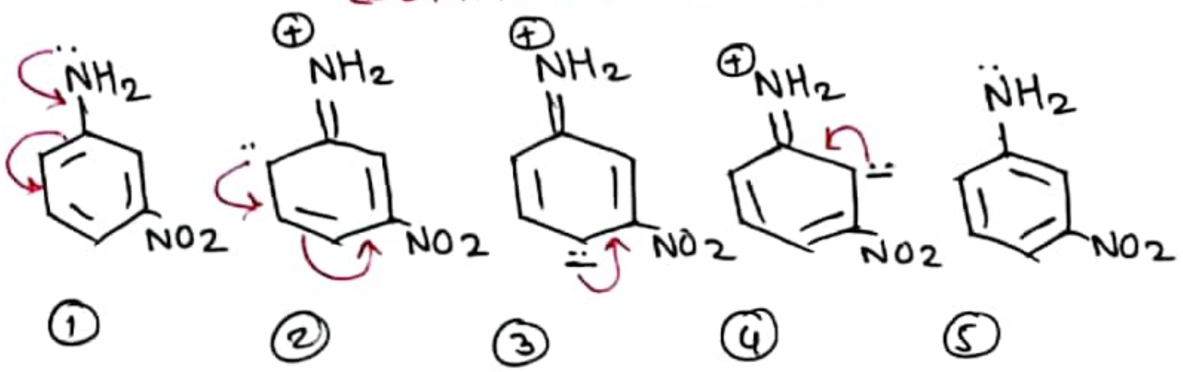

Resonance In m-NitroAniline.

- Clearly seen that p-Nitroaniline delocalise non-bonding e⁻ of Nitrogen (amino group) more than meta Nitro-aniline.
- So, p-Nitroaniline is less basic than m-Nitroaniline.

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- Some ortho effect is in case of e⁻ with-drawing groups.

- ortho substituted anilines are least basic in Nature which is not yet well known this case also.

- The chloro & Bromo substituted aniline show little different effects.

- The meta-substituted chloro (or) Bromo anilines are the least basic than p-substituted (or) unsubstituted anilines.

- This is due to at p-position these groups shows resonance and Induc-tive effect both.

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