



Saturday, February 9, 2019

Steric inhibition of resonance and its influence of on acidity and basicity.

What is steric inhibition of resonance ?

Resonance can occur only when all the atom involved in resonance lie in the same plane or nearly in the same plane.

Any change in structure which **prevent planarity** will diminish or inhibit resonance, this phenomenon is known as **steric inhibition** of resonance.

Few example of **steric inhibition of resonance** with explanation are as follows,



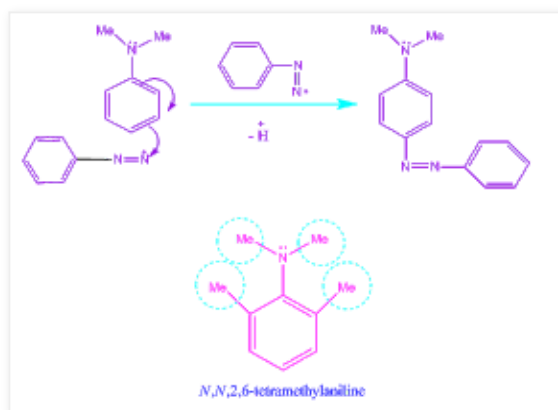
Why N,N dimethyl aniline couple with diazonium salt but N,N,2,6 tetramethyl does not ?

N,N-dimethyl aniline and its **2,6-dialkyl derivatives** the NMe₂ group in **N,N- dimethyl aniline** and the ring is coplanar. So p-electron on N atom and pi orbitals are remain in the same plane.

For this the p-electron on N-atom can delocalized via pi orbital in the benzene ring and its result the electron availability in para position is high. So **N,N dimethyl aniline** couple with diazonium cation **PhN₂⁺** to form **diazonium salt**.

On the other hand , in case of **N,N,2,6 tetramethyl aniline** having two bulky methyl group in ortho position of the benzene ring , the NMe₂ group can not remain in the same plane.

That is why the p-electron on N-atom can not delocalized through pi orbital in para position . Thus **2,6 dimethyl derivative** does not couple with **diazonium cation** under these condition that is due to **steric inhibition of resonance**.

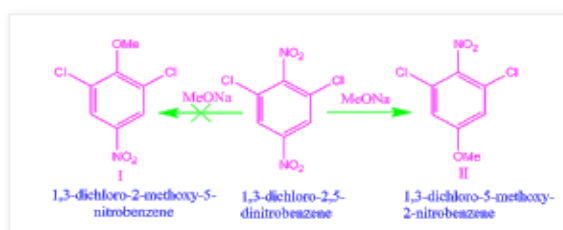


An interesting example of **steric inhibition of resonance** in activated **nucleophilic substitution** of **1,3 dichloro 2,5 dinitro benzene**.

When this is warmed with **methanolic sodium methoxide**, only one product **1,3 dichloro 5 methoxy 2 nitro benzene** is formed.

The two nitro group can not stabilize the carbanion leading to (I), since it is prevented from entering into resonance with the benzene ring because of the **steric effect** of the o-chloro atoms.

On the other hand this steric inhibition of resonance is absent in the carbanion leading to (II). Hence the carbanion leading to (II) has a lower energy of activation energy than that leading to (I) and so only (II) is produced.



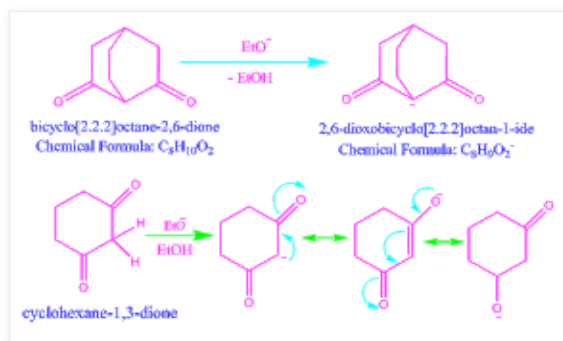
How **steric inhibition of resonance** affect the acidity and basicity of a organic compounds ?

Steric inhibition of resonance has a great **effect on acidity** and **basicity** of organic compounds as like **steric hindrance**. The influence of **steric inhibition of resonance** on acidity and basicity are discussed below.

Why cyclohexane-1,3-dione is much more acidic than bicyclo[2,2,2] oct-2,6-dione ?

Cyclohexane-1,3-dione is much more acidic than **bicyclo[2,2,2] oct-2,6-dione**, because the enolate ion of the cyclo hexadione stabilizes through resonance, whereas **bicycle[2,2,2] oct-2,6-dione** does not due to the **steric inhibition of resonance**.

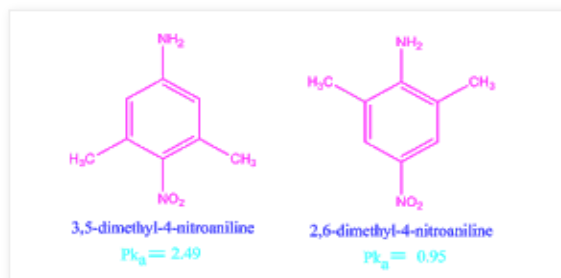
Besides, the filled p-orbital of the enolate ion of the later compound being out of plane of the C = O groups, it can not overlap with the pi electrons of the carbonyl group.



Why 3,5 dimethyl 4-nitro aniline is a stronger base than 2,6 dimethyl 4-nitro aniline ?

3,5 dimethyl 4-nitro aniline is a stronger base than 2,6 dimethyl 4-nitro aniline, because in 3,5 dimethyl 4-nitro aniline, amino group can not enter into resonance with the nitro group due to the steric inhibition of resonance, whereas it can in 2,6-dimethyl isomer.

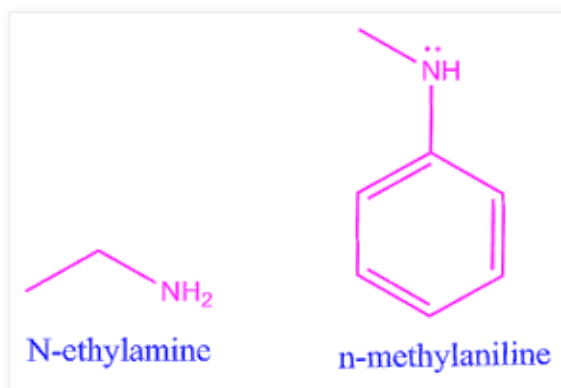
Thus in the former, the lone pair on the N-atom is more available for **protonation** and consequently, the former is more basic than the later.



Why N-ethyl amine is stronger base than N-methyl aniline ?

Since the ethyl group is larger than the methyl group. So **the steric effect** is greater for the former and hence there is greater **steric inhibition of resonance** in the former.

Thus, in the former the lone pair on N-atom is more available for protonation and consequently the **basicity of N-ethyl amine** is greater than that of **N-methyl aniline**.



Summary:

What is steric inhibition of resonance ?

Why N,N dimethyl aniline couple with diazonium salt but N,N,2,6 tetramethyl does not ?

Why 3,5 dimethyl 4-nitro aniline is a stronger base than 2,6 dimethyl 4-nitro aniline ?

Why N-ethyl amine is stronger base than N-methyl aniline ?

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Unknown February 10, 2020 at 5:52 PM

Great explanation good job 👍

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BY P GHOSH May 14, 2020 at 4:16 PM

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