AROMATICITY

CSIR CHEMISTRY BRIEF NOTES

CONDITIONS FOR AROMATICITY

- The molecule should be cyclic
- It should have alternating single and double bonds, or it should have conjugation.
- It should be planar
- It should obey Huckel's rule, that is, it should have 4n+2 π electrons where n= 0,1,2,3 etc.

CONDITIONS FOR ANTI-AROMATICITY

- The molecule should be cyclic
- It should be conjugated
- It should be planar
- It however has $4n\pi$ electrons where n=0,1,2,3 etc.

NON-AROMATICITY

- The molecule is usually non-planar, example, tub-shaped cyclooctatetraene which has 8 pi electrons (4n pi electrons) but is not anti-aromatic as expected. It is non-aromatic.
- Usually in the case of non-aromatic molecules, they disobey at least one of the conditions for aromaticity or anti-aromaticity.

HOMOAROMATICITY

- Usually a positively-charged sp3 carbon is present in between 2 sp2 carbons…eg. Homotropylium cation.

ANNULENES

- [10]-annulene is non-aromatic even though we expect it to be aromatic as it obey Huckel's rule. This is because of steric hindrance between the inner 1, 6- hydrogens which causes it to lose planarity. However, if the inner hydrogens are bridged, or connected as in 1,6-methanocyclodecapentene, aromaticity is restored. Also aromaticity in [10]-annulene can be achieved by removing hydrogens to form naphthalene.
- [12]-annulene is supposed to be anti-aromatic, but it is non-planar, so it's non-aromatic. If reacted with 2 equivalents of K+ to form dianion, becomes planar and aromatic.

ANNULENES

- [14]-annulene is aromatic because it is larger and steric hindrance between inner hydrogens is less…however it is not a very stable system so if we introduce triple bond or we remove hydrogens we get a more stable system.
- [16]-annulene is anti-aromatic if planar.
- [18]-annulene is planar and aromatic, also it is more aromatic and more stable if it exists as a fused ring system by removing the inner hydrogens.

STABILITY

- Stability of molecules follows the order: Aromatic > Non-aromatic > Anti-aromatic
- Also, aromaticity in fused ring systems increases, or stability increases, with increase in the number of rings. Eg. Anthracene > Napthalene
- Phenathrene and other systems that are not straight are more stable than those that are staright. Hence phenanthrene is more stable than anthracene.
- Benzene is an exception, it’s more stable than naphthalene.

AZULENE

- Azulene is an aromatic, intense blue compound which has a dipole moment due to presence of two rings, one which behaves as negatively charged cyclopentadienyl anion and the other as positively charged cycloheptatrienyl cation.

FULVALENES

- Fulvalenes are bicyclic systems where the two rings are connected by a single double bond. If the two rings are same, as in pentafulvalene, there is no charge separation, and no dipole moment.
- If one ring is positively charged, the other negative, there is charge separation and dipole moment. Eg. Fulavalene containing cyclopentadiene (-ve) and cycloprene (+ve) rings.
- If both rings are different have the same charge, there is no charge separation and hence there is no dipole moment. Eg. Fulavelene containing cycloheptatriene and cycloprepene rings.

REFERENCES

- Upkar’s CSIR-UGC/NET?JRF/SET - Dr. Hemant Kulshreshtha & Prof. Ajay Taneja
- Organic Chemistry – Jonathan Clayden, Nick Greeves and Stuart Warren