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I Aromaticity

Hucke I Rule: The compounds with odd number of pairs of electrons, (which is mathematically written as 4n+2 (n = 0,1,2,3 etc), show aromaticty .Molecules which do not obey these rules partially fall in the category of anti-aromatic and non aromatic compounds. The p orbital array (A) and delocalization (B) in benzene can be pictorially represented as show n below.



Fig:1

Molecular orbital description of a maticity and antiaromaticity

According to molecular orbital theory, the six p orbitals combine to form six molecular orbitals, three of w hich are bonding and three are anti-bonding. Six π electrons occupy the bonding orbitals, w hich are lower in energy compared to the un-hybridized p orbitals (atomic orbitals). The relative energies of atomic orbitals and molecular orbitals are show n in Figure.





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The relative energies of p molecular orbitals in planar cyclic conjugated systems can be determined by a simplified approach developed by Frost. This involves the following steps:

1) First of all we draw a circle,

2) Then place the ring (polygon representing the compound of interest) in the circle with one of its vertices pointing down. Each point where the polygon touches the circle represents an energy fixel.

3) Then place the correct number of electrons in the orbitals, starting with the lowest energy orbital tirst, in appordance with Hund's rule.

I the polygon touches the circle at a horizontal diameter, that point would represent a nonbonding orbital. Energy levels below this line indicate bonding MOs and those above are anti-bonding.



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Fig:4

Points to remember while making predictions on aromaticity using Frost's circle

Aromatic compounds will have all occupied molecular orbitals completely filled where as antiaromatic compounds would have incompletely filled orbitals.



• **I** an antiaromatic system (4n electrons) has the freedom to undergo conformational change and become nonaromatic that would do so. Remember that antiaromatic state is less stable than aromatic and nonaromatic forms. A comparison of molecular orbitals in aromatic and antiaromatic systems is presented in figure 5.





The criteria for aromaticity that we discussed earlier can be applied to higher annulenes as well. How ever, achieving planarity is a hurdle for many larger rings due to potential steric clashes or angle strains. If the ring (with $4n+2\pi$ electrons) is sufficiently large such that planarity does not cause steric or angle strains, the system would adopt that conformation, get stabilization through electron delocalization and becomes aromatic. Larger annulenes with 4n



 π electrons are not antiaromatic because they are flexible enough to become non-planar and become non-aromatic.

h [10]-annulene, there is considerable steric interaction between hydrogens at 1 and 6 positions. Further, a planar form (regular decagon) requires an angle of 144° between carbon atoms which is too large to accommodate in a sp² framework. The system prefers a nonplanar conformation and is not aromatic (the fact that angle strain need NOT always be a problem in achieving planarity is evident from examples such as cyclooctatetraenyl damine. Which is stable and aromatic). Bridging C1 and C6 in [10]-annulene leads to the compound V II (Figure) which is reasonably planar with all the bond distances in the range of 37-1.42 Å and show aromaticity (In NMR, outer protons are found at 6.9-7.3 ä and the bridgehead methylene at - 5.0 ä).



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[14]-annulene

Bond lengths in [14]-annulene range from 1.35-1.41 Å but do not show the alternating pattern of localized polyenes. It is aromatic (except for the isomers that are not planar). NMR shows that it is in conformational equilibrium as shown below Figure. The steric interactions associated with internal hydrogens can be minimized if C3, C6, C10 and C13, positions are boked using suitable bridging units. Thus trans-15,16-dimethyldihydropyrene and its diethyl and dipropyl homologs are aromatic with C-C bond distances between 1.39-1.40 Å. Conformational flexibility in [14]-annulene can be restricted by inserting triple bond in place of one of the more double bonds. Here, the triple bond contributes on two electrons for delocalization leaving the other two localized.

Homoaromaticity

f a stabilized cyclic conjugated system $(4n+2e^{-s})$ can be formed by bypassing one saturated atom, that lead to homoaromaticity. Compared to true aromatic systems, the net stabilization here may be low due to poorer overlap of orbitals. Cyclonetatriènyl cation (homotropyliumion) formed when cyclooctatetraene is dissolved in concentrated sulfuric acid is the best example to demonstrate homoaromaticity. Here, six electrons are spread over seven carbon atoms as in Tropylium cation.

II Coordination complexes

CFT : APPLICATIONS

(1) Colour of transition metal complexes

CFT provides an explanation for the observed colours of transition metal complexes. When the light falls on a complex, the follow ing observations may occur :

- (i) The complex may absorb the whole of white light. In this case complex appears black.
- (ii) The complex may reflect (or transmit) the whole light. In this case it appears white.
- (iii) The absorption of light by the coloured complexes takes place in the visible region of the spectrum which extends from 4000 to 7000 in wavelength. The colour of the absorbed light is different from that of the transmitted light

EXAMPLES :

(i) Hydrated cupric sulphate containing $[Cu(H_2O)_4]^{2+}$ ions is blue (colour of the transmitted light) because it absorbs yellow light.







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According to crystal field theory of complex compounds, since the number of unpaired electrons in the central metal ion with d^4 to d^7 configuration in high spin and low spin octahedral complexes is different their magnetic moments are also different

(3) Distortion of octahedral complexes and Jahn Teller Effect

The six-coordinated complexes in which all the six distances between the ligand electron clouds and central metal ion are the same are said to be regular (i.e., symmetrical) octahedral complexes. On the other hand the six - coordinated complexes in which the distances are not equal are said to be distorted octahedral complexes, since their shape is changed (i.e distorted). The change in shape is called distortion. Distorted octahedral complexes may be of the following three types.

- (i) Diagonally distorted octahedral complexes which are obtained when the distortion of a regular octahedron takes place along a two -fold axis
- (ii) Trigonally distorted octahedral complexes in which the distortion takes place along a threefold axis.
- (iii) Tetragonally distorted octahedral complexes which are also known as tetragonal complexes. These are obtained when the distortion of a regular octahedron takes place along a four-fold axis.
- **eg.(i)** Most of the square planar complexes of Cu^{2+} ion are distorted octahedral (i.e. tetra-gonal), e.g. the tetrammine Cu(+2) complex, $[Cu(NH_3)_4]^{2+}$ in aquous solution is actually $[Cu(NH_3)_4$ $(H_2O)_2]^{2+}$ in which two water molecules are a larger distance from the central Cu^{2+} ion than the four coplanar NH₃ molecules and consequently the complex has a tetragonal shape rather than square planar:
- (ii) Low-spin octanedral complexes of N^{2+} , Pd^{2+} and Pt^{2+} (all d^8 ion) undergo strong distortion and assume square planar geometry in which the two ligands along the z-axis are at larger distance and tour ligands in the xy-plane are at shorter distance from M^{2+} ion. M^{II} (diars)₂I₂ is an example of such complex.
- (iii) h CuCl₂ crystal each Qu²⁺ ion is surrounded by six Cl⁻ ions; four are at a distance of 2.30 Å and the other two are 2.95 Å away.



The phase rule was derived from thermodynamics considerations and is an important tool concerning heterogeneous equilibria. Phase rule gives the relationship between the conditions which must be specified to describe the state

relationship between the conditions which must be specified to describe the state of a system at equilibrium. This rule is important for both chemical and physical heterogeneous equilibria.





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PHASERULE

The rule is stated in terms of the number of phases (P), the number of components (C) and the degrees of freedom (F) of a heterogeneous system.

Phase rule states that in a heterogeneous system at equilibrium the number of degrees of freedom plus the number of phases are equal to the number of components plus 2.

Mathematically it is expressed as

F = C - P + 2

Explanation of the terms used in Phase Rule

Phase - The homogeneous, physically distinct and mechanical separable parts of the heterogeneous system in equilibrium are called phases.

...(i)

$$CaCO_3(s) \leftarrow CaO(s) + CO_2(g)$$

There are three phases in equilibrium state) we solids and one is gas (CO_2) , water system can be expressed as

$$H_2O(s) \longrightarrow H_2O(l) \longrightarrow H_2O(g)$$

Ice water vapours

In this system there are three phases viz solid, liquid and vapours.

Component-

In a heterogeneous system, in equilibrium the minimum number of variables which are necessary to explain the chemical composition of a phase, by a chemical equation, is called component. The meaning of component can be understood by taking following examples:

🔍 👝) Ice – Water – Vapours system

$$H_2O(s) \xrightarrow{} H_2O(l) \xrightarrow{} H_2O(g)$$

This system has three phases i.e. solid (ice), liquid (water) and gas (vapour). Chemical composition of each phase can be expressed by H_2O in the form of chemical equation:





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Phase Component $H_2O(S) = H_2O$ $H_2O(I) = H_2O$ $H_2O(g) = H_2O$

Thus water system is a one component system.

(b) When solid NH₄ CI heated in a closed vessel, following equilibrium establishes:

 $\mathsf{NH}_4\mathsf{C}\ell(\mathsf{s}) \; \xleftarrow{} \; \mathsf{NH}_4\mathsf{C}\ell(\mathsf{g}) \; \xleftarrow{} \; \mathsf{NH}_3(\mathsf{g}) \; + \; \mathsf{HC}\ell(\mathsf{g})$

This system has two phases i.e. solid $^{NH_4C\ell}$ and mixture of gases NH_3 and HCI. Here, although system has three components, but chemical composition of both phases can be expressed by a single component i.e. $^{NH_4C\ell}$. Since NH_3 and $^{HC\ell}$ are in equimolar ratio

Component

NH₂Cl

NH₂Cℓ

Phase

NH ₄CI(s)

 $NH_3(g) + HCl(g)$

Thus, this system is also a one component system. If some additional amount of either $NH_3(g)$ or HCl(g) is added in this system at equilibrium then each phase can not be expressed by NH_4Cl , then one more component with be required and number of components with be two in the system.

(c) When solid CaCO₃ is heated in a closed vessel, following heterogeneous requilibrium establishes:

 $CaCO_3(s) \xrightarrow{} CaO(s) = CO_2(g)$

This system consists of three phases i.e. solid $CaCO_3$, solid CaO and gaseous CO_2 . Although system has three components but they are not independent of each other. Any of these two can be independently variable. Thus out of three,



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