Bonding in Metallocenes (Cyclopentadienyl Complexes)

The bonding in ferrocene and other metallocenes containing cyclic polyenes is best explained by molecular orbital theory which is based on linear combination of atomic orbitals (LCAO–MO) approximation. C_5H_5 group is a regular pentagon and each carbon of C_5H_5 group is sp^2-hybridized. Each carbon atom uses these sp^2-hybrid orbitals in forming σ-bonds to hydrogen and neighbouring carbons. So each carbon atom has a p_z or $p\pi$ orbital perpendicular to the plane giving $5p_z$ orbitals (Fig.6.9).

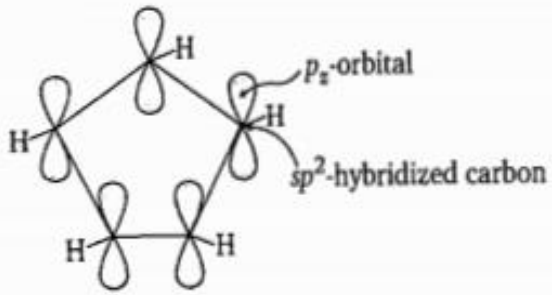


Fig. 6.9

The C—C σ-bonds are formed by overlapping of sp^2–sp^2 orbitals and C—H bond is formed by overlapping of sp^2-1s orbitals.

The p_z or $p\pi$-orbitals on each carbon of the planar C_5H_5 group are combined linearly to form five π-molecular orbitals. These π-MOs have the following symmetries:

One molecular orbital with no nodal plane–a symmetry. This orbital is strongly bonding. This orbital has unbroken i.e., doughnut electron density above and below the plane of ring. Two doubly degenerate molecular orbitals with one nodal planes perpendicular to the plane of the ring–e_1 symmetry. These two orbitals are weakly bonding. Two doubly degenerate MOs with two nodal planes–e_2 symmetry. These two orbitals are markedly anti-bonding.

The energy of π-molecular orbitals increase with increase in number of nodal planes. Thus, order of energy of π-orbitals of different symmetries is :

$$a < e_1 < e_2$$

This pattern continues with doubly degenerate π-MOs of increasing number of nodal planes and increasing energy until the number of π-MOs becomes equal to the number of $p\pi$ or p_z orbitals in the ring. If the number of MOs is odd, the highest energy anti-bonding molecular orbital is doubly degenerate and if the number is even, the highest energy anti-bonding molecular orbital is non-degenerate.

The five π-MOs of one C_5H_5 group (or ring) having same symmetry linearly combined (i.e., added or subtracted) with five MOs of the other ring to give ten ligand group orbital (LGOs) of gerade (g) or ungerade (u) symmetries, which in turn can be combined with atomic orbitals of matching symmetry on the metal to form MOs. The metal atomic orbitals have a_{1g}, a_{2u}, e_{1u}, e_{1g} and e_{2u} symmetries. The subscript g and u refers to the parity of the orbitals: g (German gerade, even)

indicates that the orbital is symmetric with respect to inversion, whereas the subscript u (ungerade, odd) indicates that the orbital is anti-symmetric with respect to inversion.

The LGOs for a pair of C_5H_5 rings are formed, when the π-MOs of same energy and same number of nodal planes are combined linearly. For example, consider the lowest energy π-MO with no nodal plane of the ring. If the wave functions for this orbital on the two rings are added, a gerade (g) LGO of the same symmetry (a_{1g}) as an s or d_{z^2} orbital is produced. On the other hand, if the two wave functions are substracted, an ungerade LGO of the same symmetry as an p orbital (a_{2u}) is obtained. Similarly, other LGOs can be constructed by either adding or subtracting the molecular orbitals of higher energies of the two rings.

The $+z$ direction of the upper ring is taken to be pointing downward while the $+z$ direction of the lower ring is taken to be pointing upward. It means that the $+z$ direction of both rings point towards the centre of the ring system (Fig. 6.10).

The ten LGOs of two C_5H_5 rings combine with nine orbitals (the five $3d$, one $4s$ and the three $4p$ orbitals) of similar symmetries giving a total nineteen molecular orbitals. If both rings have the positive lobes of lowest energy π MOs towards the metal, the s and d_{z^2} orbitals have correct symmetry. If one ring has the positive lobe towards the metal and the other the negative lobe towards the metal, the p_z orbital has the correct symmetry. There are some LGOs which remain non-bonding, there is no suitable metal orbital available to overlap them. It is not only necessary to use correct symmetry orbitals for appreciable bonding interaction but also the same energies.

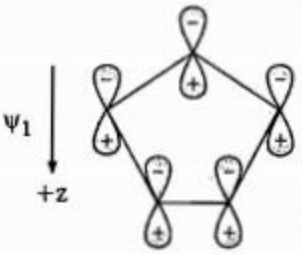
The metal orbitals which interact with the appropriate LGOs are shown in Table 6.1 :

Table 6.1

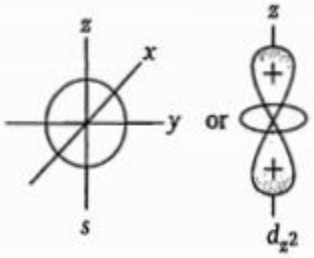
LGOs	Metal Orbitals
a_{1g}	s and d_{z^2}
$2e_{1g}$	d_{xz} and d_{yz}
$2e_{1u}$	p_x and p_y
$2e_{2g}$	d_{xy} and $d_{x^2-y^2}$
$2e_{2u}$	No suitable orbital on metal
a_{2u}	p_z

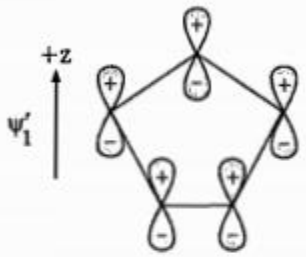
The symmetries of LGOs along with the metal orbitals with which they can overlap, are shown in figure 6.10.

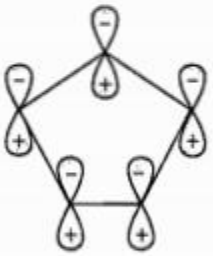
The interaction of LGOs with metal orbitals of appropriate symmetries produces bonding, non-bonding and anti-bonding molecular orbitals. The formation of bonding and anti-bonding molecular orbitals by the interaction, for example, between the d_{yz} orbital of metal and its appropriate group orbital (one of the one nodal plane group orbital) is shown in figure 6.11.

(1) 

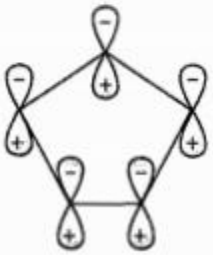
$$\psi_{a_{1g}} = \frac{1}{\sqrt{2}}(\psi_1 + \psi_1')$$



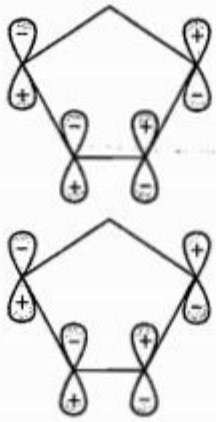


(2) 

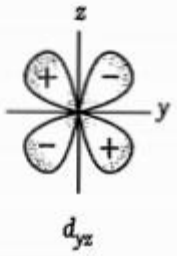
$$\psi_{a_{2u}} = \frac{1}{\sqrt{2}}(\psi_1 - \psi_1')$$



(3)

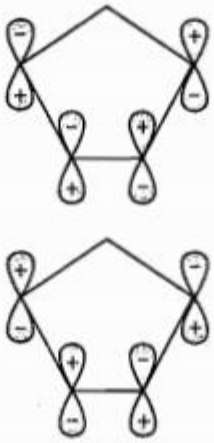


$$\psi_{e_{1g}} = \frac{1}{\sqrt{2}}(\psi_1 + \psi_1')$$



d_{yz}

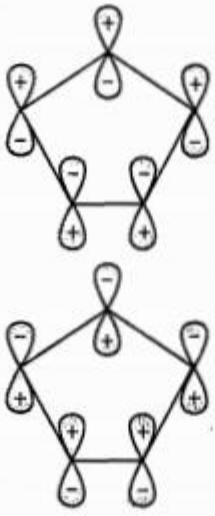
(4)



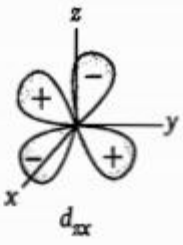
$$\psi_{e_{1u}} = \frac{1}{\sqrt{2}}(\psi_1 - \psi_1')$$

p_x

(5)

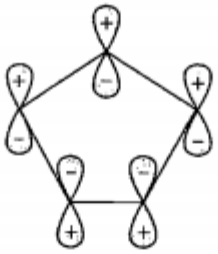


$$\psi_{e_{1g}} = \frac{1}{\sqrt{2}}(\psi_3 + \psi_3')$$

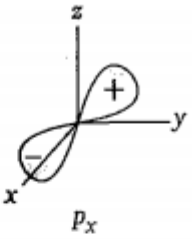


d_{zx}

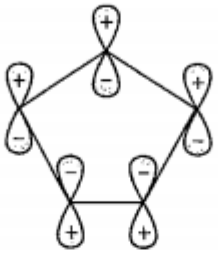
(6)



$$\Psi_{e_{1u}} = \frac{1}{\sqrt{2}}(\psi_3 - \psi_3')$$



p_x



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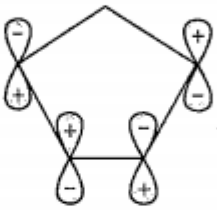
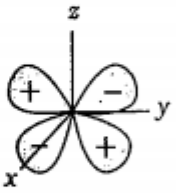
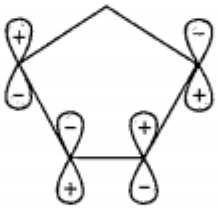


$$\Psi_{e_{2g}} = \frac{1}{\sqrt{2}}(\psi_4 + \psi_4')$$



d_{xy}



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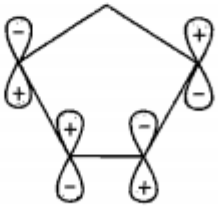
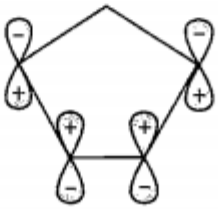


$$\Psi_{e_{2u}} = \frac{1}{\sqrt{2}}(\psi_4 - \psi_4')$$

No suitable orbital on metal



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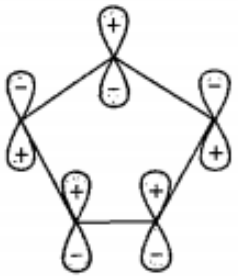
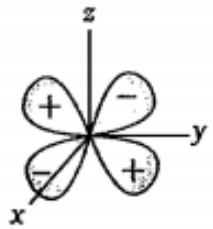
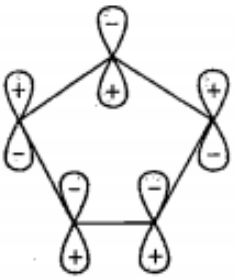
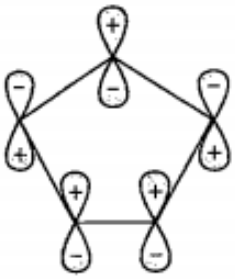


$$\Psi_{e_{2g}} = \frac{1}{\sqrt{2}}(\psi_5 + \psi_5')$$



$d_{x^2-y^2}$





(10)

$$\Psi_{e_{2u}} = \frac{1}{\sqrt{2}}(\psi_5 - \psi_5')$$

No suitable orbital on metal

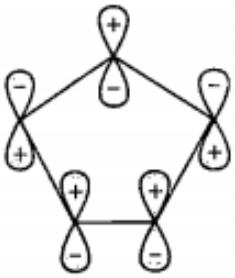


Fig. 6.10