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SEM-II

Physical Chemistry

Unit-IV

Huckel Molecular Orbital Theory

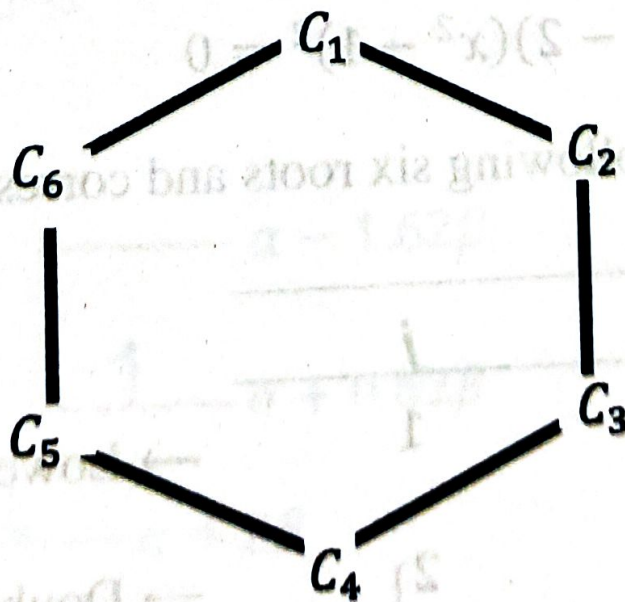
**Applications Of HMO Theory To
Benzene System**

Benzene

The HMO wave function for benzene is

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 + c_5\phi_5 + c_6\phi_6 \quad \dots(9.105)$$

and the secular equations in terms of x are,



$$\left. \begin{aligned} c_1x + c_2 + c_6 &= 0 \\ c_1 + c_2x + c_3 &= 0 \\ c_2 + c_3x + c_4 &= 0 \\ c_3 + c_4x + c_5 &= 0 \\ c_4 + c_5x + c_6 &= 0 \\ c_1 + c_5 + c_6x &= 0 \end{aligned} \right\} \dots(9.106)$$

The corresponding determinant is,

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \quad \dots(9.107)$$

The determinant can be expanded into the polynomial,

$$x^6 - 6x^4 + 9x^2 - 4 = 0 \quad \dots(9.108)$$

which can be factorised as

$$(x + 2)(x - 2)(x^2 - 1)^2 = 0 \quad \dots(9.109)$$

The equation leads to the following six roots and correspondingly six energy levels:

x_j	E_j	j	
$x_1 = -2$	$E_1 = \alpha + 2\beta$	1	→ Lowest bonding HMO
$x_2 = -1$	$E_2 = \alpha + \beta$	2}	→ Doubly degenerate bonding HMO's
$x_3 = -1$	$E_3 = \alpha + \beta$	3}	
$x_4 = +1$	$E_4 = \alpha - \beta$	4}	→ Doubly degenerate antibonding HMO's
$x_5 = +1$	$E_5 = \alpha - \beta$	5}	
$x_6 = +2$	$E_6 = \alpha - 2\beta$	6	→ Highest antibonding HMO.

Of these E_1 , E_2 and E_3 levels correspond to bonding MO's. Each of these bonding MO's can hold two π -electrons with antiparallel spins. The six π -electrons of benzene occupy these three bonding orbitals of low energy (Fig. 9.7). On the other hand, E_4 , E_5 and E_6 levels correspond to antibonding MO's. However, two of the bonding energy levels (E_2 and E_3) and two of the antibonding levels (E_4 and E_5) are degenerate.

Total π -electron energy,

$$E_{\pi} = 2(\alpha + 2\beta) + 2(\alpha + \beta) + 2(\alpha + \beta) = 6\alpha + 8\beta \quad \dots(9.110)$$

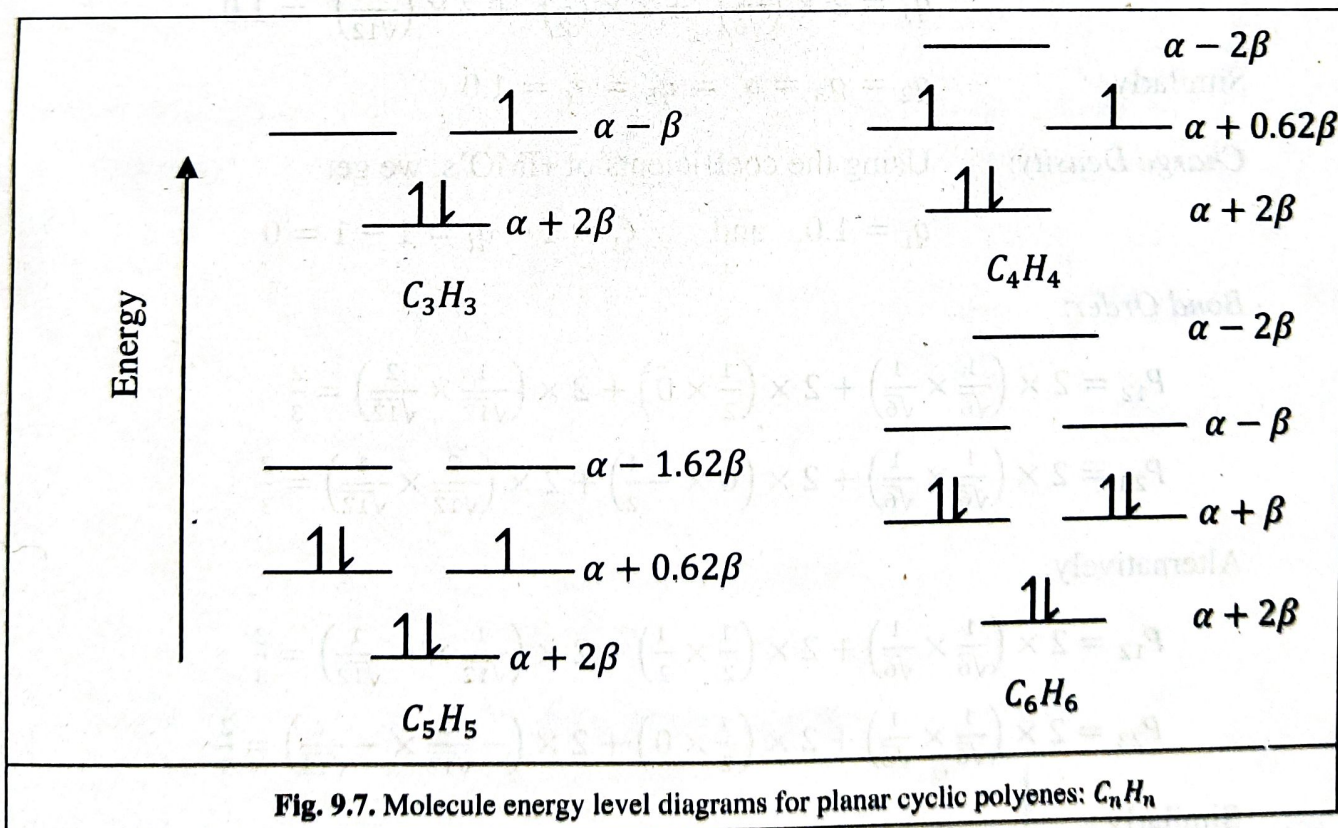
$$\pi\text{-bond energy} = 6\alpha + 8\beta - 6\alpha = 8\beta$$

If we assume that benzene consists of three localised single bonds and three localised double bonds, the energy of the molecule should be the sum of the energies of three π -bonds. The energy of the three ethene units is

$$3(2\alpha + 2\beta) = 6\alpha + 6\beta.$$

$$\text{Delocalisation energy} = 6\alpha + 8\beta - 3(2\alpha + 2\beta) = 2\beta$$

Therefore, Benzene is more stable than three ethylene molecules by an energy of 2β .



The molecular orbitals with bonding energies E_1 , E_2 and E_3 are ψ_1 , ψ_2 and ψ_3 respectively. Therefore the ground state electronic configuration of the molecule is $\psi_1^2 \cdot \psi_2^2 \cdot \psi_3^2$.

The HMO Functions:

$$\psi_1 = \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$\psi_2 = \frac{1}{2}(\phi_1 - \phi_3 - \phi_4 + \phi_6)$$

or

$$\psi_2 = \frac{1}{2}(\phi_1 + \phi_2 - \phi_4 - \phi_5)$$

$$\psi_3 = \frac{1}{\sqrt{12}}(\phi_1 + 2\phi_2 + \phi_3 - \phi_4 - 2\phi_5 - \phi_6)$$

or

$$\psi_3 = \frac{1}{\sqrt{12}}(\phi_1 - \phi_2 - 2\phi_3 - \phi_4 + \phi_5 + 2\phi_6)$$

$$\psi_4 = \frac{1}{2}(\phi_1 - \phi_3 + \phi_4 - \phi_6)$$

or

$$\psi_4 = \frac{1}{2}(\phi_1 - \phi_2 + \phi_4 - \phi_5)$$

$$\psi_5 = \frac{1}{\sqrt{12}}(\phi_1 - 2\phi_2 + \phi_3 + \phi_4 - 2\phi_5 + \phi_6)$$

or

$$\psi_5 = \frac{1}{\sqrt{12}}(\phi_1 + \phi_2 - 2\phi_3 + \phi_4 + \phi_5 - 2\phi_6)$$

$$\psi_6 = \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

Electron Density:

$$q_1 = 2 \times \left(\frac{1}{\sqrt{6}}\right)^2 + 2 \times \left(\frac{1}{2}\right)^2 + 2 \times \left(\frac{1}{\sqrt{12}}\right)^2 = 1.0$$

Similarly,

$$q_2 = q_3 = q_4 = q_5 = q_6 = 1.0$$

Charge Density:

Using the coefficients of HMO's, we get

$$q_i = 1.0, \text{ and } \xi_i = 1 - q_i = 1 - 1 = 0$$

Bond Order:

$$P_{12} = 2 \times \left(\frac{1}{\sqrt{6}} \times \frac{1}{\sqrt{6}}\right) + 2 \times \left(\frac{1}{2} \times 0\right) + 2 \times \left(\frac{1}{\sqrt{12}} \times \frac{2}{\sqrt{12}}\right) = \frac{2}{3}$$

$$P_{23} = 2 \times \left(\frac{1}{\sqrt{6}} \times \frac{1}{\sqrt{6}}\right) + 2 \times \left(0 \times -\frac{1}{2}\right) + 2 \times \left(\frac{2}{\sqrt{12}} \times \frac{1}{\sqrt{12}}\right) = \frac{2}{3}$$

Alternatively,

$$P_{12} = 2 \times \left(\frac{1}{\sqrt{6}} \times \frac{1}{\sqrt{6}}\right) + 2 \times \left(\frac{1}{2} \times \frac{1}{2}\right) + 2 \times \left(\frac{1}{\sqrt{12}} \times -\frac{1}{\sqrt{12}}\right) = \frac{2}{3}$$

$$P_{23} = 2 \times \left(\frac{1}{\sqrt{6}} \times \frac{1}{\sqrt{6}}\right) + 2 \times \left(\frac{1}{2} \times 0\right) + 2 \times \left(-\frac{1}{\sqrt{12}} \times -\frac{2}{\sqrt{12}}\right) = \frac{2}{3}$$

Similarly,

$$P_{34} = P_{45} = P_{56} = P_{61} = \frac{2}{3}$$

This shows that (i) all the six C - C bonds in benzene are equivalent, and (ii) the bonds are not true double bonds. The conclusions are supported by experimentally

observed bond length (1.39 \AA) in benzene which is intermediate between that of a single (1.54 \AA) and a double (1.33 \AA) bond.

Free Valence:

$$F_1 = 1.732 - (P_{12} + P_{61}) = 1.732 - \left(\frac{2}{3} + \frac{2}{3}\right) = 0.40$$

$$F_2 = 1.732 - (P_{12} + P_{23}) = 1.732 - \left(\frac{2}{3} + \frac{2}{3}\right) = 0.40$$

It can be easily verified that

$$F_1 = F_2 = F_3 = F_4 = F_5 = F_6 = 0.40$$