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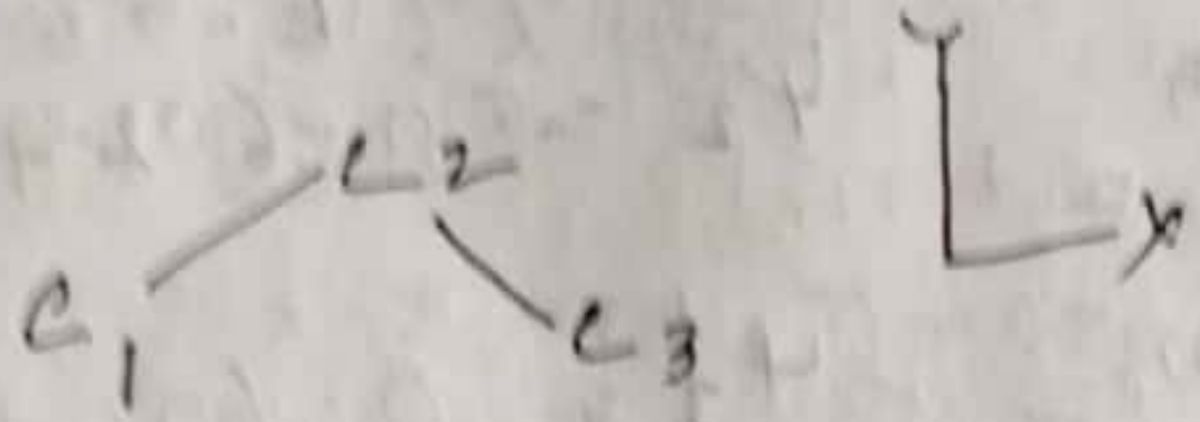
Application of HMO Theory - Allyl Group

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Application of Hückel molecular orbital theory to allyl group:

The allyl group:



$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3$$

Variation treatment leads to secular equations as follows

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) + c_3(H_{13} - ES_{13}) = 0$$

$$c_1(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) + c_3(H_{23} - ES_{23}) = 0$$

$$c_1(H_{31} - ES_{31}) + c_2(H_{32} - ES_{32}) + c_3(H_{33} - ES_{33}) = 0$$

The Hückel approximation simplifies

then to

$$c_1(2 - E) + c_2\beta = 0$$

$$c_1\beta + c_2(2 - E) + c_3\beta = 0$$

$$c_2\beta + c_3(2 - E) = 0$$

The corresponding secular determinant

equation is

$$\begin{vmatrix} 2-E & \beta & 0 \\ \beta & 2-E & \beta \\ 0 & \beta & 2-E \end{vmatrix} = 0$$

Putting $\frac{2-E}{\beta} = x$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 0 \\ 0 & 1 & x \end{vmatrix} = 0$$

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or $x^3 - 2x = 0$, or $x(x^2 - 2) = 0$, the roots

are $x_1 = -\sqrt{2}$, $x_2 = 0$ and $x_3 = +\sqrt{2}$

The required energy eigenvalues are

$$E_1 = \alpha + \sqrt{2}\beta, \quad E_2 = \alpha \quad \text{and} \quad E_3 = \alpha - \sqrt{2}\beta$$

Both α and β are negative quantities; α is negative as it represents the Coulombic energy of attraction in the $2p_z$ atomic orbital of e while β is negative because it represents additional energy lowering due to electron delocalization over further (neighbouring) $2p_z$ atomic orbital.

Therefore $E_1 < E_2 < E_3$, E_1 being less than α is the bonding level and $E_3 > \alpha$ the antibonding level.

To obtain the corresponding eigenfunctions (HMO's) we substitute roots x_1, x_2 and x_3 in the original secular equations.

$$\text{For } x_1 = -\sqrt{2} = -\sqrt{2}c_1 + c_2 = 0$$

$$\text{or } c_2 = \sqrt{2}c_1$$

$$c_1 - \sqrt{2}c_2 + c_3 = 0 \quad \text{and} \quad c_2 - \sqrt{2}c_3 = 0$$

$$\text{and } c_2 = \sqrt{2}c_3 \quad \therefore c_1 = c_3$$

By normalization,

$$c_1^2 + c_2^2 + c_3^2 = c_1^2 + (\sqrt{2}c_1)^2 + c_1^2 = 1$$

$$\text{or } 4c_1^2 = 1 \quad \text{or } c_1 = c_3 = \frac{1}{2}; \quad c_2 = \frac{\sqrt{2}}{2}$$

$$\psi_1 = \frac{1}{2}\phi_1 + \frac{\sqrt{2}}{2}\phi_2 + \frac{1}{2}\phi_3.$$

Similarly, $\psi_2 = \frac{1}{\sqrt{2}} (\phi_1 - \phi_3)$ (by substituting $x_2 = 0$)

$$\psi_3 = \frac{1}{2} \phi_1 - \frac{\sqrt{2}}{2} \phi_2 + \frac{1}{2} \phi_3 \quad (\text{by substituting } x_3 = +\sqrt{2})$$

Thus we have the following HMO levels in allyl carbanion. (allyl anion)

$$E_3 \text{ --- } 2 - \sqrt{2}\beta \quad \psi_3 = \frac{1}{2} \phi_1 - \sqrt{2} \phi_2 + \frac{1}{2} \phi_3$$

$$E_2 \text{ --- } 1\beta \text{ --- } 2 \quad \psi_2 = \frac{1}{\sqrt{2}} (\phi_1 - \phi_3)$$

$$E_1 \text{ --- } 1\beta \text{ --- } 2 + \sqrt{2}\beta \quad \psi_1 = \frac{1}{2} (\phi_1 + \sqrt{2} \phi_2 + \phi_3)$$

Electron density (q_i) at any carbon centre i is given as

$$q_i = \sum_j n_j c_{ji}^2$$

Where c_{ji} is the linear combination of Atomic orbital (LEAO) coefficient of the atomic orbital ϕ_i in the j th MO, and n_j is the number of electrons in the j th MO.

In allyl carbanion,

$$q_1 = 2 \times \left(\frac{1}{2}\right)^2 + 2 \times \left(\frac{1}{\sqrt{2}}\right)^2 + 0 = 1.5$$

$$q_2 = 2 \times \left(\frac{\sqrt{2}}{2}\right)^2 + 0 + 0 = 1.0$$

$$q_3 = 2 \times \left(\frac{1}{2}\right)^2 + 2 \times \left(\frac{1}{\sqrt{2}}\right)^2 = 1.5$$

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Bond order (P_{ik}) of a bond $c_i - c_k$ is defined as

$$P_{ij} = \sum_j n_j a_{ji} a_{jk}$$

In allyl carbocation

$$P_{12} = 2 \times \frac{1}{2} \times \frac{\sqrt{2}}{2} + 2 \times \frac{1}{\sqrt{2}} \times 0 = 0.707$$

$$P_{23} = 2 \times \frac{\sqrt{2}}{2} \times \frac{1}{2} + 2 \times 0 + \frac{1}{\sqrt{2}} = 0.707$$

This shows that the two bonds are equivalent

In case of benzene; BENZENE
Electron density

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

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

Charge density Using the coefficients of

Huckel molecular orbitals, we get-

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

Bond order

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

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

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

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

Similarly

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

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

Huckel approximation in brief

(i) The HMO theory is meant for carbon π system only

(ii) As an approximation, the σ - π electron interaction in the molecule is ignored.

(iii) The HMO's are then expressed as

$$\psi = c_1 \phi_1 + c_2 \phi_2 = \sum c_i \phi_i$$

where ϕ_i is the $2p_z$ atomic orbital of the i th carbon, the molecular plane being the xy plane

(iv) The basis orbitals (ϕ_i) are orthogonal $\langle \phi_i | \phi_j \rangle = \delta_{ij} = 1$ for $i=j$ and $= 0$ for $i \neq j$

(v) To simplify the secular equation, it is assumed that all Coulombic integrals of the type $H_{ii} = \langle \phi_i | \hat{H} | \phi_i \rangle = \alpha$. Similarly, all resonance integrals of the type $H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle = \beta$ if the centres i and j are bonded and $= 0$ if i and j are not bonded.

(vi) The Schrödinger equation is not solved: the eigen values are obtained directly from the secular equation in terms of α and β whose values are obtained by experiment