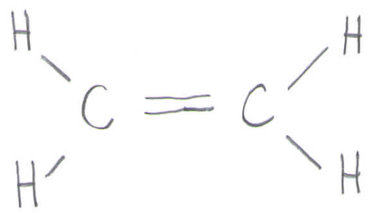
Hücklova teorija mol. orbital

Razlaga aromatičnosti spojin.



– osredotočimo se na π vezi

$$\psi = \overbrace{c_1\phi_1 + c_2\phi_2}^{2p_z} \qquad E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = f(c_1, c_2)$$

$$\frac{\partial E}{\partial c_1} = 0 \ \wedge \ \frac{\partial E}{\partial c_2} = 0$$

$$\begin{vmatrix} H_{11} - S_{11}E & H_{12} - S_{12}E \\ H_{21} - S_{21}E & H_{22} - S_{22}E \end{vmatrix} = 0 \qquad \begin{aligned} S_{ij} &= \langle \phi_i | \phi_j \rangle \\ H_{ij} &= \langle \phi_i | \hat{H} | \phi_j \rangle \end{aligned}$$

$$S_{ij} = \begin{cases} 1; & i = j \\ 0; & i \neq j \end{cases} \qquad H_{ij} = \begin{cases} \alpha; & i = j \\ \beta; & i, j \text{ soseda} \\ 0; & \text{drugo} \end{cases}$$

α = −IONIZACIJSKI POTENCIAL

$\beta = \frac{1}{2}\left(E(C{=}C) - E(C{-}C)\right)$

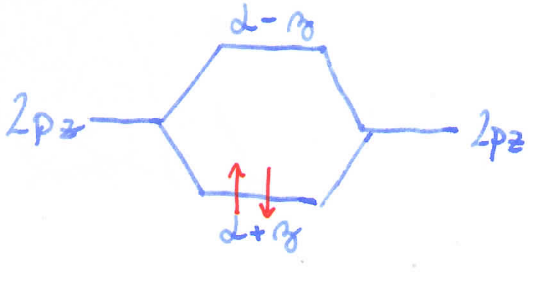
$$\begin{vmatrix} \alpha - 1E & \beta - 0 \cdot E \\ \beta - 0 \cdot E & \alpha - 1 \cdot E \end{vmatrix} = \begin{vmatrix} \alpha - 1E & \beta \\ \beta & \alpha - 1E \end{vmatrix} =$$

$$= (\alpha - E)^2 - \beta^2 = 0 \Rightarrow$$

$$(\alpha - E - \beta)(\alpha - E + \beta) = 0$$

$E_1 = \alpha - \beta$

$E_2 = \alpha + \beta$



$$E = 2(\alpha + \beta) = 2\alpha + 2\beta$$

$\underline{\underline{E_{VEZ} = 2\beta}}$, saj $\dot{C}$ α $\dot{C}$ α

$$\boxed{E = \alpha + m\beta}$$

$m > 0$ - vezne
$m = 0$ - nevezne
$m < 0$ - razvezne

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

$$E = \alpha + \beta$$

$$\begin{bmatrix} \alpha-(\alpha+\beta) & \beta \\ \beta & \alpha-(\alpha+\beta) \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

$$\begin{bmatrix} -\beta & \beta \\ \beta & -\beta \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \quad \Rightarrow \quad -\beta c_1 + \beta c_2 = 0 \quad /:\beta$$

$$-c_1 + c_2 = 0$$

$$\boxed{c_1 = c_2}$$

$$\psi = c_1\phi_1 + c_1\phi_2 = c_1(\phi_1 + \phi_2)$$

$$\langle \psi | \psi \rangle = 1$$

$$c_1^2 \langle \phi_1 + \phi_2 | \phi_1 + \phi_2 \rangle = 1$$

$$c_1^2 \big(\underbrace{\langle \phi_1 | \phi_1 \rangle}_{1 = S_{11}} + \underbrace{\langle \phi_1 | \phi_2 \rangle}_{0 = S_{12}} + \underbrace{\langle \phi_2 | \phi_1 \rangle}_{0 = S_{21}} + \underbrace{\langle \phi_2 | \phi_2 \rangle}_{1 = S_{22}} \big) = 1$$

$$c_1^2 \, 2 = 1$$

$$c_1 = \frac{\sqrt{2}}{2}$$

$$\psi = \frac{\sqrt{2}}{2}\phi_1 + \frac{\sqrt{2}}{2}\phi_2 \quad \text{za} \quad E = \alpha + \beta \ \text{(vezna)}$$

$$\psi = \frac{\sqrt{2}}{2}\phi_1 - \frac{\sqrt{2}}{2}\phi_2 \quad \text{za} \quad E = \alpha - \beta \ \text{(razvezna)}$$

SPLOŠNO:

E_n, ψ_n

$\psi_n = \sum_i c_{in}\phi_i$

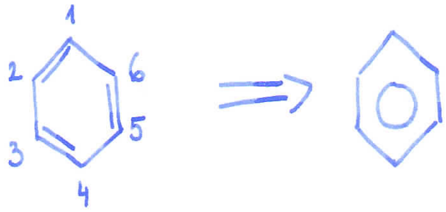
red vezi med atomoma r in s

$$\boxed{P_r = \sum_j n_j c_{rj} c_{sj}}$$

n_j - zasedenost (vrednosti 0, 1, 2)

$\dot{Q}_R = P_{rr} = \sum n_j c_{rj}^2$ naboj na posameznem atomu

Primer BENZENA:



Imamo 6 p_z orbital (če imamo 3 dvojne vezi):

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \dots \\ H_{21}-ES_{21} & & \\ H_{31}-ES_{31} & & \\ \vdots & & \end{vmatrix}$$

$H_{11} = \alpha$

$S_{ii} = 1$

$S_{ij} = 0\ ;\ i \neq j$

$H_{ij} \Rightarrow$ $H_{12} = \beta$, $H_{23} = 0$, $H_{34} = \beta$, $H_{45} = 0$, $H_{56} = \beta$

cikloheksatrien

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

$$= \left((\alpha-E)^2 - \beta^2\right)^3 = (\alpha-E-\beta)^3 (\alpha-E+\beta)^3$$

$E_{1,2,3} = \alpha+\beta$

$E_{4,5,6} = \alpha-\beta$

— — — $\alpha-\beta$

↑↓ ↑↓ ↑↓ $\alpha+\beta$

$E = 6(\alpha+\beta) = 6\alpha + 6\beta$ CIKLOHEKSATRIEN

benzen

$H_{12} = \beta$

$H_{23} = \beta$

$H_{34} = \beta$

$H_{45} = \beta$

$H_{56} = \beta$

$H_{61} = \beta$

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-E \end{vmatrix} \Rightarrow \text{rešitve}$$

$E_1 = \alpha + 2\beta$

$E_{2,3} = \alpha + \beta$

$E_{4,5} = \alpha - \beta$

$E_6 = \alpha - 2\beta$

— $\alpha - 2\beta$

— — $\alpha - \beta$

↑↓ ↑↓ $\alpha + \beta$

↑↓ $\alpha + 2\beta$

$E = 2(\alpha+2\beta) + 4(\alpha+\beta) =$

$= 6\alpha + 8\beta$ BENZEN

E(BENZEN) < E(CIKLOHEKSATRIEN)