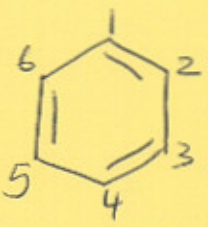
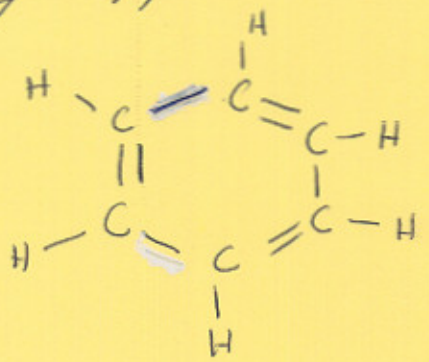
Hückel theory applied to benzene





Secular determinant

$$
\begin{vmatrix}
H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} & H_{15}-ES_{15} & H_{16}-ES_{16} \\
H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} & H_{25}-ES_{25} & H_{26}-ES_{26} \\
H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} & H_{35}-ES_{35} & H_{36}-ES_{36} \\
H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} & H_{45}-ES_{45} & H_{46}-ES_{46} \\
H_{51}-ES_{51} & H_{52}-ES_{52} & H_{53}-ES_{53} & H_{54}-ES_{54} & H_{55}-ES_{55} & H_{56}-ES_{56} \\
H_{61}-ES_{61} & H_{62}-ES_{62} & H_{63}-ES_{63} & H_{64}-ES_{64} & H_{65}-ES_{65} & H_{66}-ES_{66}
\end{vmatrix} = 0
$$

Using Hückel approximations:

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

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Expanding the determinant and solving the equation gives the following solutions

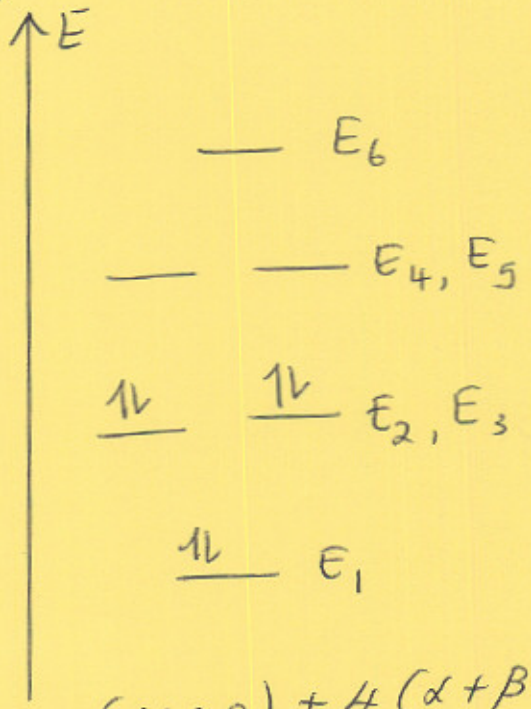
$E_1 = \alpha + 2\beta$

$E_2 = E_3 = \alpha + \beta$

$E_4 = E_5 = \alpha - \beta$

$E_6 = \alpha - 2\beta$

[Remember $\beta < 0$]



π electron energy of benzene $= 2(\alpha + 2\beta) + 4(\alpha + \beta)$

$= \underline{\underline{6\alpha + 8\beta}}$

$\psi_1 = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 + c_5\phi_5 + c_6\phi_6$

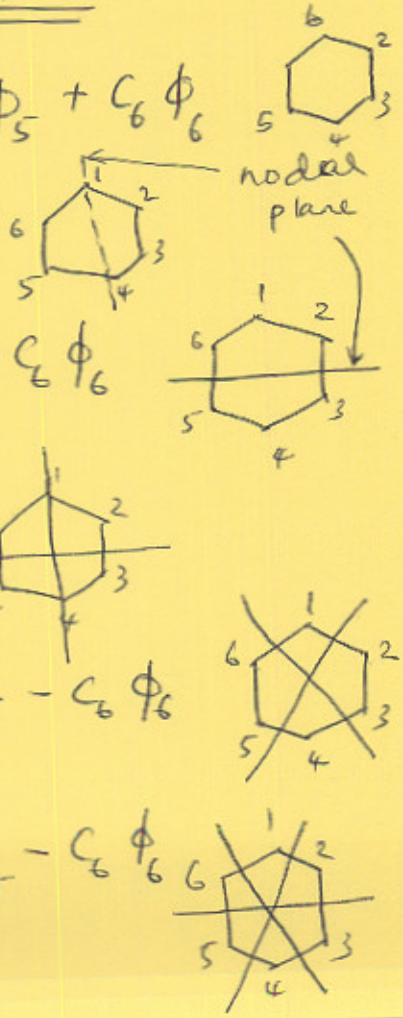
$\psi_2 = c_2\phi_2 + c_3\phi_3 - c_5\phi_5 - c_6\phi_6$

$\psi_3 = c_1\phi_1 + c_2\phi_2 - c_3\phi_3 - c_4\phi_4 - c_5\phi_5 + c_6\phi_6$

$\psi_4 = c_2\phi_2 - c_3\phi_3 + c_5\phi_5 - c_6\phi_6$

$\psi_5 = c_1\phi_1 - c_2\phi_2 - c_3\phi_3 + c_4\phi_4 - c_5\phi_5 - c_6\phi_6$

$\psi_6 = c_1\phi_1 - c_2\phi_2 + c_3\phi_3 - c_4\phi_4 + c_5\phi_5 - c_6\phi_6$



The π electron system of C_2H_2 has energy $= 2\alpha + 2\beta$

$\therefore$ 3 (C_2H_2 molecules) $= 3(2\alpha + 2\beta) = 6\alpha + 6\beta$.

energy of benzene $<$ energy of $3(C_2H_2)$

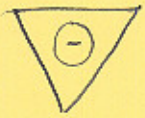
This means that benzene does not have 3 double bonds. The difference is energy is due to conjugation and is called conjugation energy.

conjugation energy $= (6\alpha + 8\beta) - (6\alpha + 6\beta)$

$= 2\beta < 0$

$\therefore$ benzene is more stable (by 2β) than 3 C_2H_2 molecules.

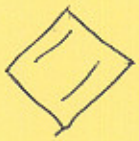
π electronic energy of cyclic polyenes



$C_3H_3^-$

$\alpha - 2\beta$ (2e)

$\alpha + 2\beta$

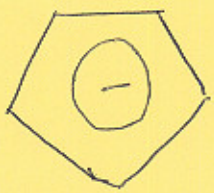


C_4H_4

$\alpha - 2\beta$ (2e)

α (2e)

$\alpha + 2\beta$

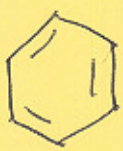


$C_5H_5^-$

$\alpha - 0.618\beta$ (2e)

$\alpha + 0.618\beta$ (2e)

$\alpha + \beta$



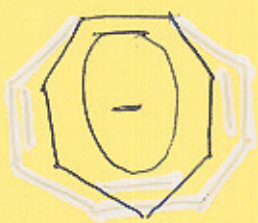
C_6H_6

$\alpha - 2\beta$ (2e)

$\alpha - \beta$ (2e)

$\alpha + \beta$ (2e)

$\alpha + 2\beta$



$C_7H_7^-$

$\alpha - 1.802\beta$ (2e)

$\alpha - 0.445\beta$ (2e)

$\alpha + 1.247\beta$ (2e)

$\alpha + 2\beta$