ATOMS, MOLECULES & RESEARCH

QUANTUM MECHANICS - SPRING - WEEK 5

Chapter 11

(17) 1,3 butadiene $H_2C=\overset{H}{\underset{|}{C}}-\overset{H}{\underset{|}{C}}=CH_2$

We evaluated the π electronic energy $= 4\alpha + 4.472\beta$

# of ethylene molecules in butadiene $= 2$

energy of two ethylene molecules $= 2[2\alpha + 2\beta]$

$= 4\alpha + 4\beta$

$\therefore$ delocalization energy $= (4\alpha + 4.472\beta) - (4\alpha + 4\beta)$

$= \underline{0.472\beta}$

For benzene

π electronic energy $= 6\alpha + 8\beta$

# of ethylene molecules in benzene $= 3$

energy of three ethylenes $= 3(2\alpha + 2\beta) = 6\alpha + 6\beta$

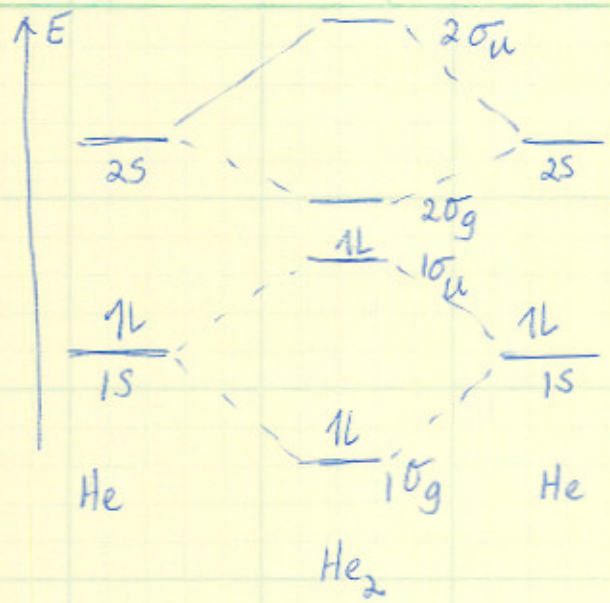
$\therefore$ delocalization energy $= (6\alpha + 8\beta) - (6\alpha + 6\beta)$

$= \underline{2\beta}$

$\beta < 0$

$\therefore$ π electrons are more delocalized in benzene than in 1,3-buladiene.

(25)



first excited state electron configuration

$= 1\sigma_g^2\ 1\sigma_u^1\ 2\sigma_g^1$

$M_S = \sum m_s = m_{s_1} + m_{s_2}$

$= \left(\pm \tfrac{1}{2}\right) + \left(\pm \tfrac{1}{2}\right)$

$M_S = \pm 1, 0, 0$

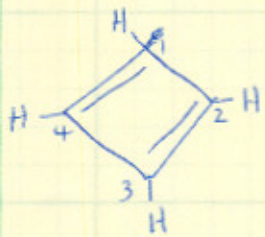
$S = 1, \overset{+}{0}, \overset{-}{0}$

∴ Possible spin states are singlets and triplets

bond order $= \frac{1}{2}(3-1) = 1$

The electronic states will be $^1\Pi$

(27)



$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} \end{vmatrix} = 0$$

∴ using Hückel approximations;

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

Divide through by β and let $\frac{\alpha-E}{\beta} = x$

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

$$x \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 1 & 1 & x \end{vmatrix} + 0 \begin{vmatrix} 1 & x & 0 \\ 0 & 1 & 1 \\ 1 & 0 & x \end{vmatrix}$$

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

$$x\left[x(x^2-1) - 1(x-0)\right] - 1\left[1(x^2-1) - 1(0-1)\right]$$

$$- 1\left[1(1-0) - x(0-x) + 1(0-1)\right] = 0$$

$$x\left[x^3 - x - x\right] - \left[x^2 - x + x\right] - \left[x + x^2 - x\right] = 0$$

$$x^4 - 2x^2 - x^2 - x^2 = 0$$

$$x^4 - 4x^2 = 0$$

$$x^2(x^2 - 4) = 0$$

$\Rightarrow x^2 = 0$ OR $x^2 - 4 = 0$

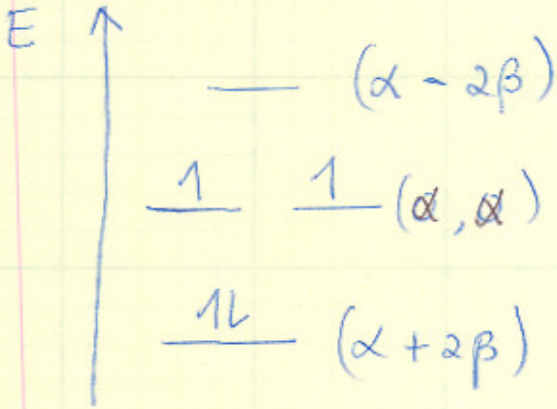
$\Rightarrow x = 0, 0$ OR $(x-2)(x+2) = 0$

$\Rightarrow x = \pm 2$

$\therefore$ solutions are $x = +2, 0, 0, -2$

$x = \frac{\alpha - E}{\beta} \Rightarrow E = \alpha - x\beta$ $\quad x = 2, 0, 0, -2$

$E = \alpha - 2\beta, \alpha, \alpha, \alpha + 2\beta$ $\quad \beta < 0$



π electronic energy $= 2(\alpha + 2\beta) + 2(\alpha)$

$= 4\alpha + 4\beta$

C_4H_4 has two ethylene groups.

energy of two ethylenes $= 2[2\alpha + 2\beta)]$

$= 4\alpha + 4\beta$

~~π electronic energy of C_4H_4 > energy of two ethylene~~

~~$(\alpha < 0)$~~

energy difference $= (4\alpha + 4\beta) - (4\alpha + 4\beta)$

$= 0$

There is no extra stabilization.

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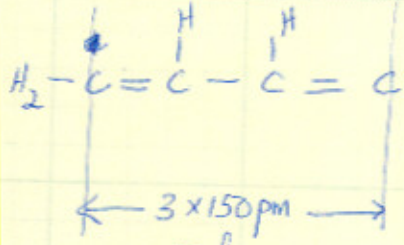
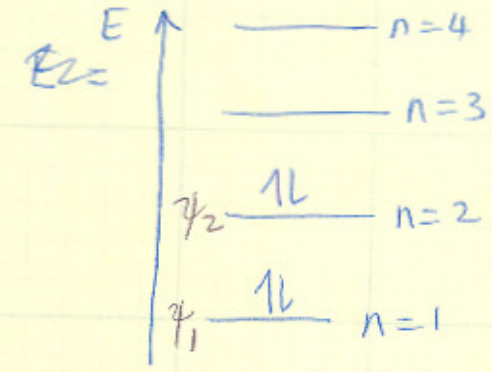


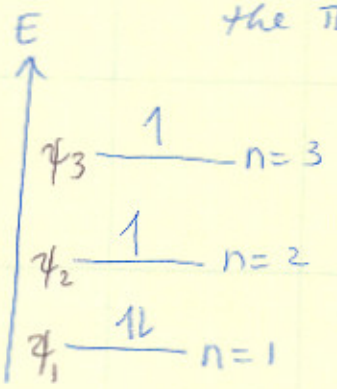
Since we can treat this system as a particle in a box;

$$E_n = \frac{n^2 h^2}{8 m l^2}$$ where l = length of box

for butadiene $l = 3 \times 150$ p.m

~~$E_2 = 2H_2$~~ Since there are 4 electrons in the π system





electron config = $\psi_1^2 \psi_2^2$

first excited state = $\psi_1^2 \psi_2^1 \psi_3^1$

$$\text{Excitation energy} = \frac{3^2 h^2}{8 m l^2} - \frac{2^2 h^2}{8 m l^2}$$

$$= \frac{h^2}{8 m l^2}(9-4) = \frac{5\left(6.626 \times 10^{-34}\ \text{JS}\right)^2}{8\left(9.109 \times 10^{-31}\ \text{kg}\right)\left(3 \times 150 \times 10^{-12}\ \text{m}\right)^2}$$

$$= \underline{1.488 \times 10^{-18}\ \text{J}}$$

$$\frac{\text{J}^2\text{S}^2}{\text{kg m}^2} = \frac{(\text{kg m}^2\text{S}^{-2})^2 \text{S}^2}{\text{kg m}^2}$$

$$= \text{kg m}^2 \text{S}^{-2}$$

$$= \text{J}$$

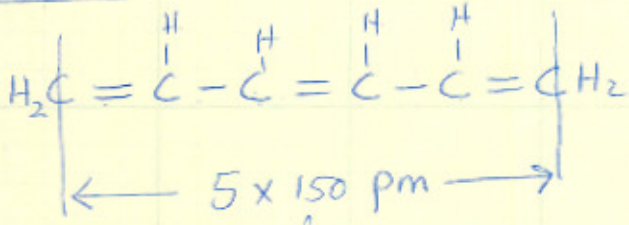
$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E} = \frac{\left(6.626 \times 10^{-34}\ \text{JS}\right)\left(2.99 \times 10^{8}\ \text{ms}^{-1}\right)}{\left(1.488 \times 10^{-18}\ \text{J}\right)}$$

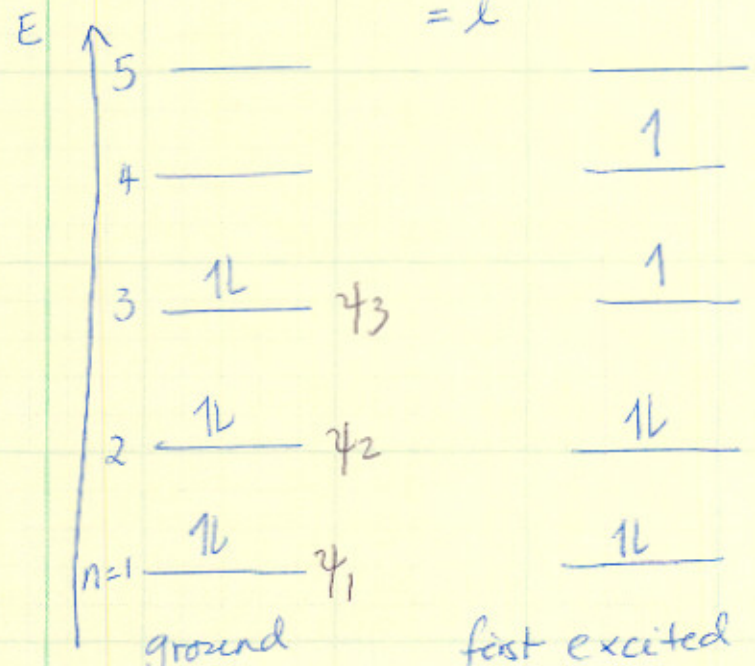
$$\lambda = 1.3317 \times 10^{-7}\ \text{m}$$

$$= \underline{133\ \text{nm}}$$

hexatriene



There are 6 π electrons



ground state $= \psi_1^2 \psi_2^2 \psi_3^2$

first excited state $= \psi_1^2 \psi_2^2 \psi_3^1 \psi_4^1$

Excitation energy $= \frac{4^2 h^2}{8ml^2} - \frac{3^2 h^2}{8ml^2}$

$= \frac{h^2}{8ml^2}(16-9) = \frac{7(6.626 \times 10^{-34}\ Js)^2}{8(9.109 \times 10^{-31}\ kg)(5 \times 150 \times 10^{-12}\ m)^2}$

$= 7.498 \times 10^{-19}\ J$

$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\ Js)(2.99 \times 10^{8}\ ms^{-1})}{(7.498 \times 10^{-19}\ J)}$

$\lambda = 264.2 \times 10^{-9}\ m = 264\ nm$

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Li_2^+ $\quad 1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^1$

bond order $= \left(\frac{3-2}{2}\right) = 0.5$

Be_2^+ $\quad 1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^1$

bond order $= \frac{1}{2}(4-3) = 0.5$

B_2^+ $\quad 1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^1$

bond order $= \frac{1}{2}(5-4) = 0.5$

N_2^+ $\quad 1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 1\pi_u^3$

bond order $= \frac{1}{2}(9-4) = 2.5$