

1. 請利用Huckel Theory 計算1,3-cyclobutadiene 的 π 電子能量
及 delocalization energy, 並與 乙炔及 1,3-butadiene 比較。

50%

Ans:  by Huckel theory, $\alpha > 0$
 $\beta < 0$

$$\begin{vmatrix} \alpha - E_{\pi} & \beta & 0 & \beta \\ \beta & \alpha - E_{\pi} & \beta & 0 \\ 0 & \beta & \alpha - E_{\pi} & \beta \\ \beta & 0 & \beta & \alpha - E_{\pi} \end{vmatrix} = 0 \xrightarrow{\text{簡化同除}\beta} \begin{vmatrix} \frac{\alpha - E_{\pi}}{\beta} & 1 & 0 & 1 \\ 1 & \frac{\alpha - E_{\pi}}{\beta} & 1 & 0 \\ 0 & 1 & \frac{\alpha - E_{\pi}}{\beta} & 1 \\ 1 & 0 & 1 & \frac{\alpha - E_{\pi}}{\beta} \end{vmatrix}$$

$$\frac{\alpha - E_{\pi}}{\beta} = x \Rightarrow \begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0 \xrightarrow{\text{降階}} x \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 1 & 1 & x \end{vmatrix} - \begin{vmatrix} 1 & x & 1 \\ 0 & 1 & x \\ 1 & 0 & 1 \end{vmatrix} = 0$$

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

$$x^2 = 0$$

$$x = \underline{0, 0} \pm 2$$

重根

$$\frac{\alpha - E_{\pi}}{\beta} = 0, E_{\pi} = \alpha, \alpha$$

$$\frac{\alpha - E_{\pi}}{\beta} = 2, E_{\pi} = \alpha - 2\beta$$

$$\alpha - E_{\pi} = -2, E_{\pi} = \alpha + 2\beta$$

orbital energy

$$\begin{array}{c} \alpha - 2\beta \\ \alpha \\ \alpha + 2\beta \end{array}$$

$$E_{\pi} (\text{cyclobutadiene}) = 4\alpha + 4\beta$$

$$E_{\pi} (\text{ethene}) = 2\alpha + 2\beta$$

\Rightarrow delocalization Energy =

$$\text{Energy} = (4\alpha + 4\beta) - 2(2\alpha + 2\beta) = 0$$

$$E_{\pi} (\text{ethene}) = 2\alpha + 2\beta$$

$$E_{\pi} (1,3\text{-butadiene}) = 4\alpha + 4.48\beta$$

$$E_{\pi} (\text{cyclobutadiene}) = 4\alpha + 4\beta$$

2. HF/6-311+G(d,p)

acetic acid

50%

(a) How many basis functions are used?

(b) How many occupied MOs? unoccupied MOs?

(a)

CH₃COOH

4H, 2C, 2O

H:

1s: 3x1

p: 3

6

C, O 1s = 1x1

2s = 1x3+1

2p = 3x3+3

d 5

22

$$(6 \times 4) + (22 \times 4) = 112 \text{ (basis functions)}$$

(b)

H: $\rightarrow 17e^-$

C: $\rightarrow 67e^-$

O: $\rightarrow 87e^-$

$$\text{總 } e^- = 4 \times 1 + 2 \times 6 + 2 \times 8 = 32e^- = 16 \uparrow \text{ 或 } 16 \downarrow e^- \text{ (16 } \uparrow \text{ occupied)}$$

$$112 - 16 = 96 \text{ (unoccupied)}$$