

### ❖ Antiaromaticity

The phenomenon of antiaromaticity in organic chemistry may simply be defined as a property of planar conjugated cyclic structures by which it becomes less stable than its acyclic conjugate.

In order to find whether the compound is antiaromatic or not, it is a necessary pre-condition to confirm that its delocalization energy is less than its acyclic conjugate. After studying a lot of conjugated molecules, it was found that in almost all antiaromatic compounds, the total number of the  $\pi$ -electrons can be fitted by the formula  $4n$  delocalized ( $\pi$  or lone pair) electrons in it. Unlike aromatic systems, which are governed by Hückel's rule ( $4n+2$   $\pi$ -electrons) and are very stable compounds, these antiaromatic systems are extremely unstable and very reactive. In order to evade this instability due to antiaromaticity, the compound may transform its shape, becoming a non-planar, and therefore, removing some of the  $\pi$ -interactions. In contrast to the diamagnetic ring current of aromatic systems, antiaromatic molecules have a paramagnetic type ring current, which can be detected by the NMR spectroscopic methods. Common examples of antiaromatic systems are. Pentalene, biphenylene, cyclopentadienyl cation. The archetypal case of antiaromaticity, cyclobutadiene molecule, is widely debated with some scientists saying that antiaromaticity is not the primary factor to its large destabilization.

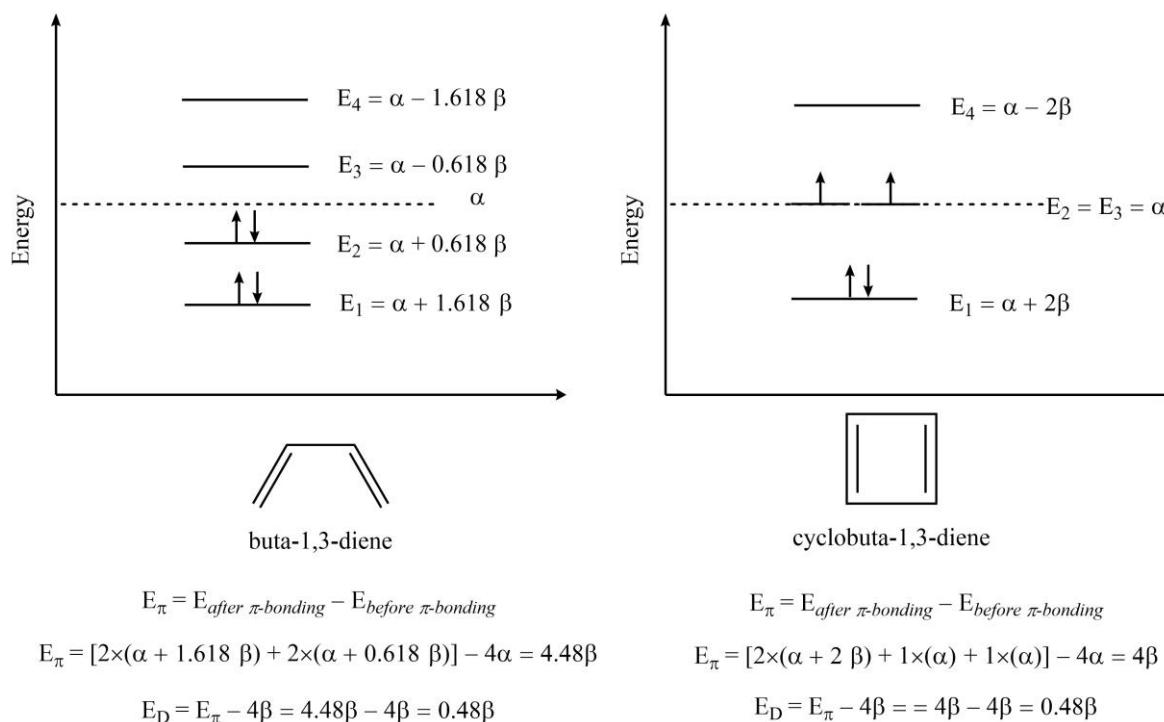
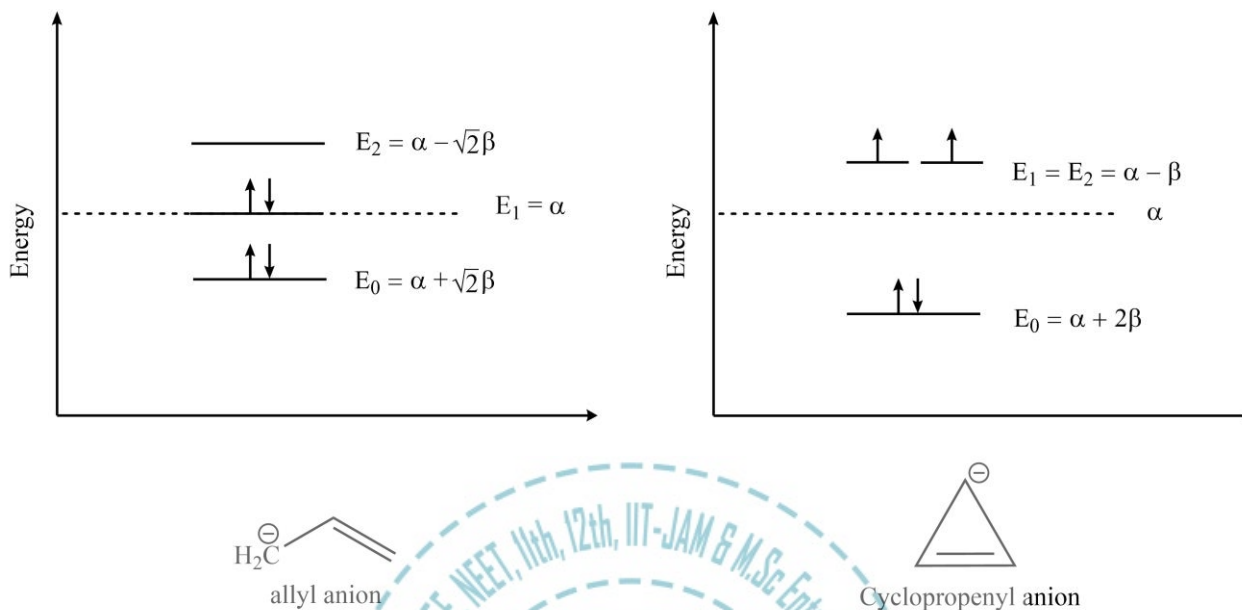


Figure 19. The  $\pi$ -molecular orbital energy level diagram of cyclobutadiene.

It is obvious that the delocalization energy ( $E_D$ ) of cyclobutadiene is less than its acyclic conjugate, and therefore, it is antiaromatic in nature.

Similarly, we can prove the antiaromaticity of cyclopropenyl anion as given below.



$$E_{\pi} = E_{\text{after } \pi\text{-bonding}} - E_{\text{before } \pi\text{-bonding}} \quad E_{\pi} = E_{\text{after } \pi\text{-bonding}} - E_{\text{before } \pi\text{-bonding}}$$

$$E_{\pi} = [2 \times (\alpha + \sqrt{2}\beta) + 2 \times (\alpha)] - 4\alpha = 2\sqrt{2}\beta \quad E_{\pi} = [2 \times (\alpha + 2\beta) + 1 \times (\alpha - \beta) + 1 \times (\alpha - \beta)] - 4\alpha = 2\beta$$

$$E_D = E_{\pi} - 4\beta = 2\sqrt{2}\beta - 2\beta = 0.83\beta \quad E_D = E_{\pi} - 2\beta = 2\beta - 2\beta = 0\beta$$

Figure 20. The  $\pi$ -molecular orbital energy level diagram of cyclobutadiene.

Cyclooctatetraene is the most popular case of a molecule becoming a non-planar geometry to avoid antiaromatic destabilization. Had it been planar, it would have a single  $8\pi$ -electron system around the cycle, nonetheless, it becomes a boat-like shape with four separate  $\pi$  bonds.



Cyclooctatetraene

Cyclooctatetraene  
(Tub conformation)

Since antiaromatic systems are usually short-lived and difficult to detect experimentally, the antiaromatic destabilization energy is frequently modeled by computer simulation rather than by actual experiment.

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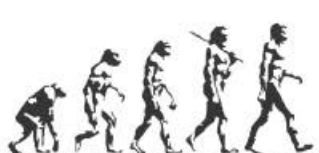
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# A TEXTBOOK OF ORGANIC CHEMISTRY

**Volume I**

**MANDEEP DALAL**



*First Edition*

**DALAL INSTITUTE**

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*Mandeep Dalal*

*(M.Sc, Ph.D, CSIR UGC – NET JRF, IIT-GATE)*

*Founder & Educator, Dalal Institute*

*E-Mail: [dr.mandeep.dalal@gmail.com](mailto:dr.mandeep.dalal@gmail.com)*

*[www.mandeepdalal.com](http://www.mandeepdalal.com)*

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder of "Dalal Institute" (India's best coaching centre for academic and competitive chemistry exams), the organization that is committed to revolutionize the field of school-level and higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK), and Springer (Netherlands).

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