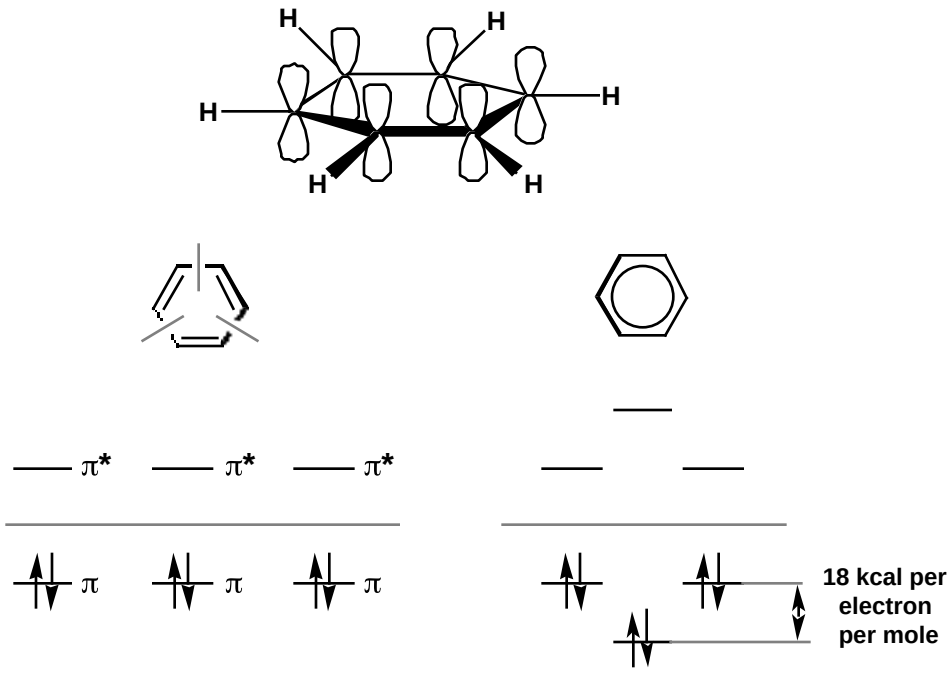
Text Related to Segment 8.03 ©2002 Claude E. Wintner

An extraordinary case that must be considered in any discussion of polyene bonding is that of the planar cyclic molecule benzene, C_6H_6. The six carbon atoms all have sp^2 hybridization, and formally they present a continuous cyclic array of six parallel p orbitals in which reside six electrons. Were we to imagine benzene as a cyclohexatriene with three entirely localized π bonds, as diagrammed on the left side of the following figure, our previous analysis would lead us to expect that we would be overestimating the predicted energy. However, the observed *magnitude* of the error — as obtained, for example, from appropriate hydrogenation experiments — is far out of the bounds of our previous experience: the localized model stands fully some 36 kcal/mole above real benzene in energy. The proper molecular orbitals of benzene, as outlined on the right side of the figure, will be discussed further below.

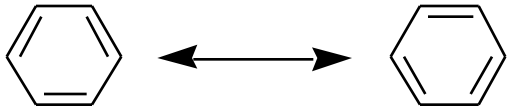


benzene is more stable than a hypothetical localized cyclohexatriene by 36 kcal/mole

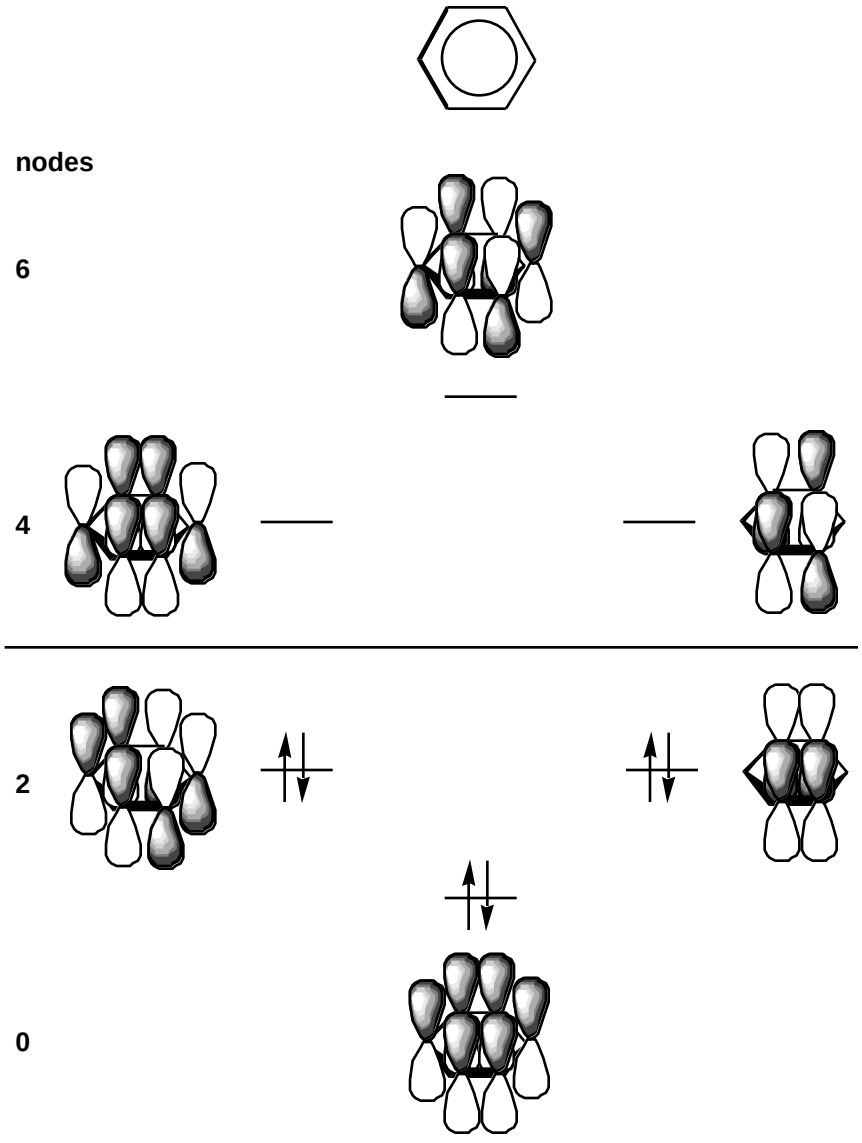
The unusual stability of continuous planar cyclic π electron systems containing 4n+2 electrons (where n is an integer) is well known, and often is phrased in terms of "Hückel's Rule." *Continuous planar cyclic π electron systems containing 4n+2 electrons, where n is an integer, and with orbitals having zero or even numbers of nodes, possess unusual stability (termed "aromatic stability"). Conversely, continuous planar cyclic π electron systems containing 4n electrons, and with orbitals having zero or even numbers of nodes, are destabilized (termed "anti-aromatic").* Thus, benzene (aromatic) is unusually stable, while cyclobutadiene (anti-aromatic) is unusually unstable.

cyclobutane ("antiaromatic") is observed to be extremely unstable

Pictorial renderings of the delocalized orbitals of benzene are given below. For many purposes the molecule is quite well represented by the simple formula in which a circle inscribed within the hexagon is understood to stand for the entire delocalized cyclic array. Another common usage for describing the bonding situation in benzene is the so-called "resonance" notation, depicted at the top of the figure, in which the delocalization is represented as a combination of two localized versions linked by a double-headed arrow. When this notation is used, as often conveniently is the case, then it is of the utmost importance to keep in mind that neither localized formula is in itself "correct," and that the double-headed arrow signifies "delocalization of the electrons" — *not* an equilibrium between the two formulae. The 36 kcal/mole of stabilization energy due to delocalization of the electrons in benzene frequently is referred to as its "resonance energy."



"resonance" notation used to describe delocalization in benzene



delocalized molecular orbitals of benzene