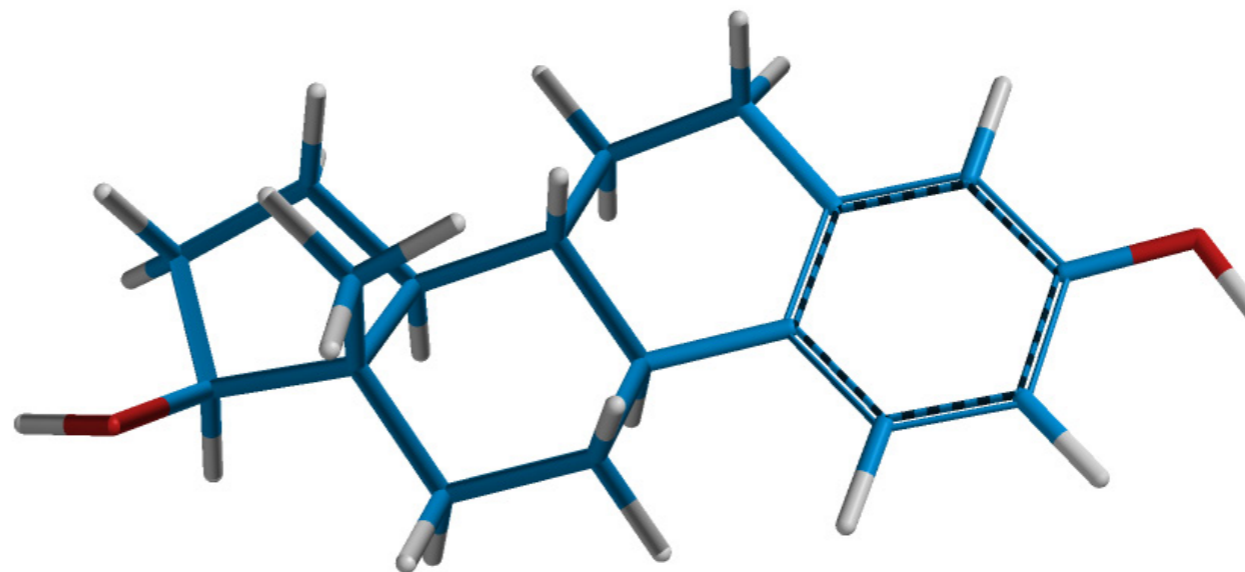


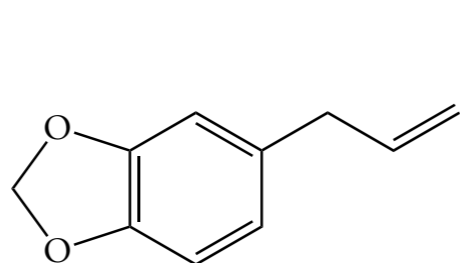
12

ARENES AND AROMATICITY

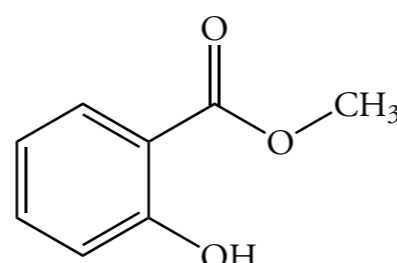


ESTRADIOL

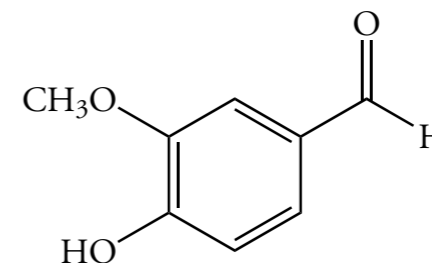
12.1 AROMATIC COMPOUNDS



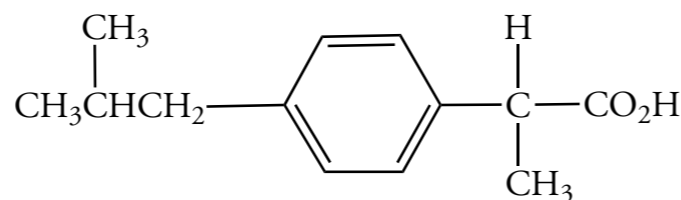
safrole
(oil of sassafras)



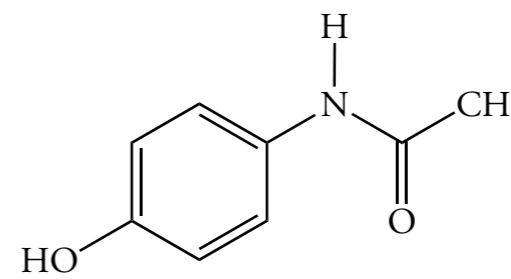
methyl salicylate
(oil of wintergreen)



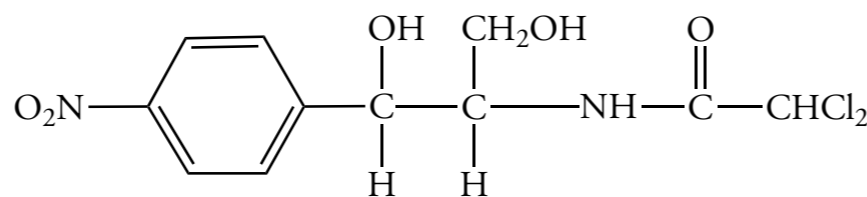
vanillin
(vanilla)



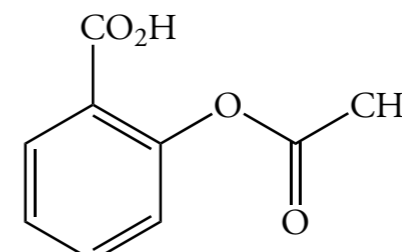
ibuprofen



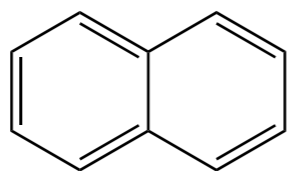
acetaminophen



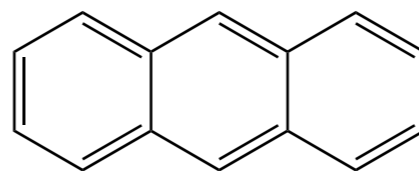
chloramphenicol



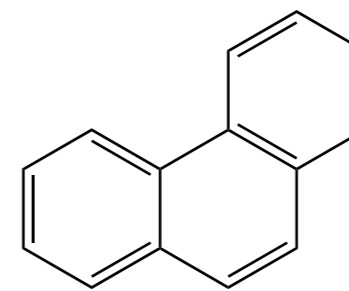
aspirin



naphthalene

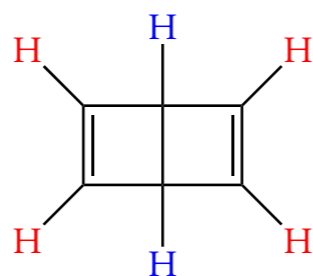
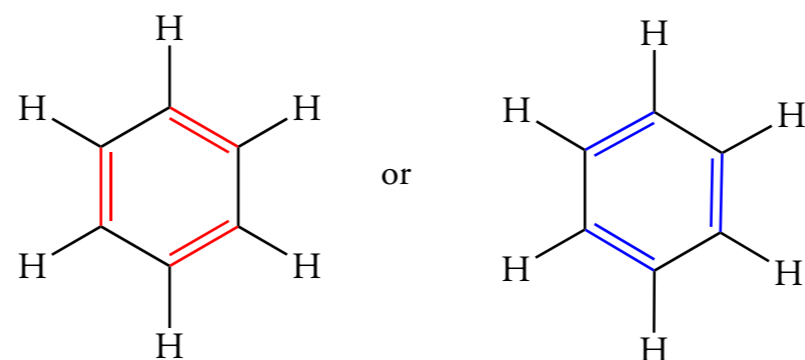


anthracene

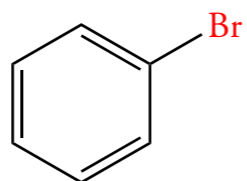
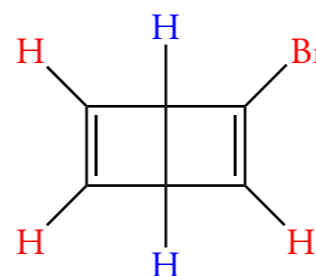
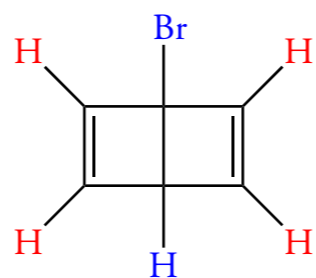


phenanthrene

12.2 THE COVALENT STRUCTURE OF BENZENE

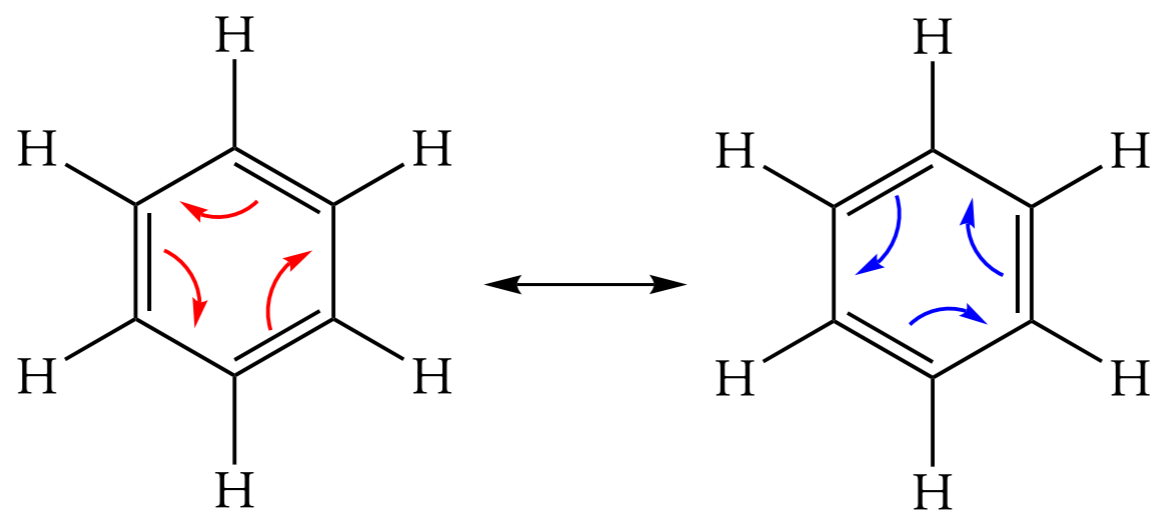


Hypothetical bicyclic benzene structure with nonequivalent secondary and tertiary hydrogen atoms.



Only one bromobenzene isomer exists. Therefore, all six hydrogen atoms in benzene must be equivalent.

Resonance Theory and Benzene



equivalent contributing structures for the resonance hybrid of benzene

Resonance Energy

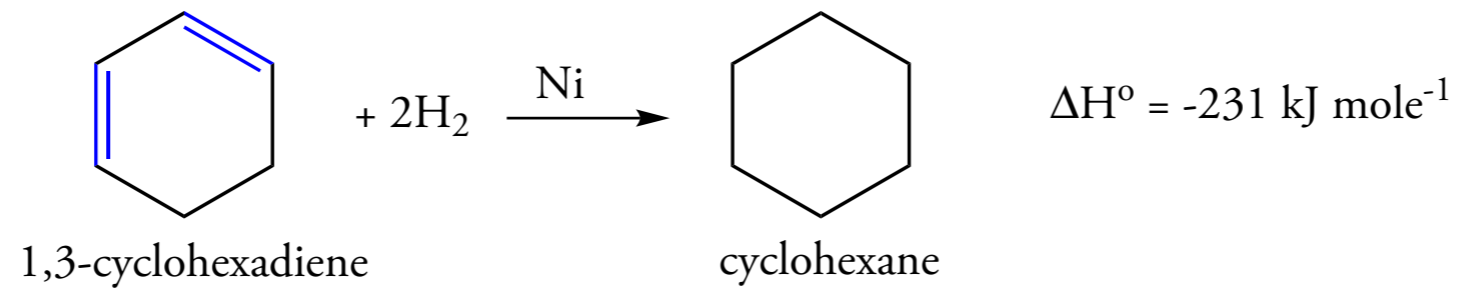
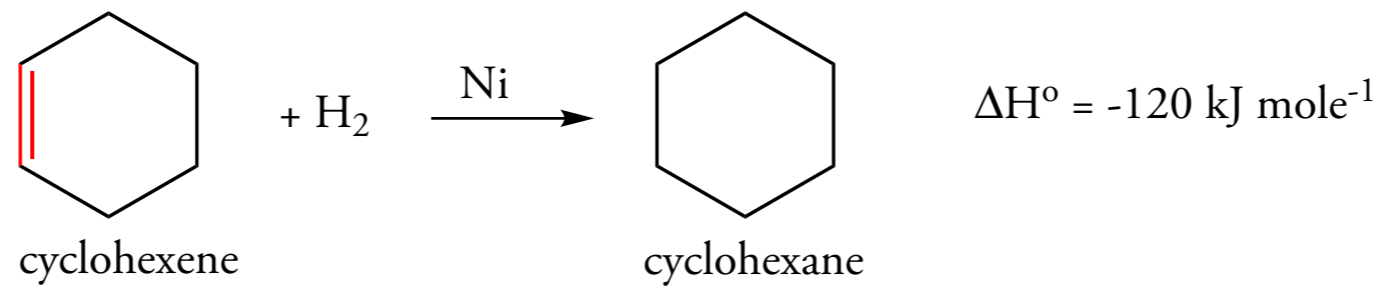
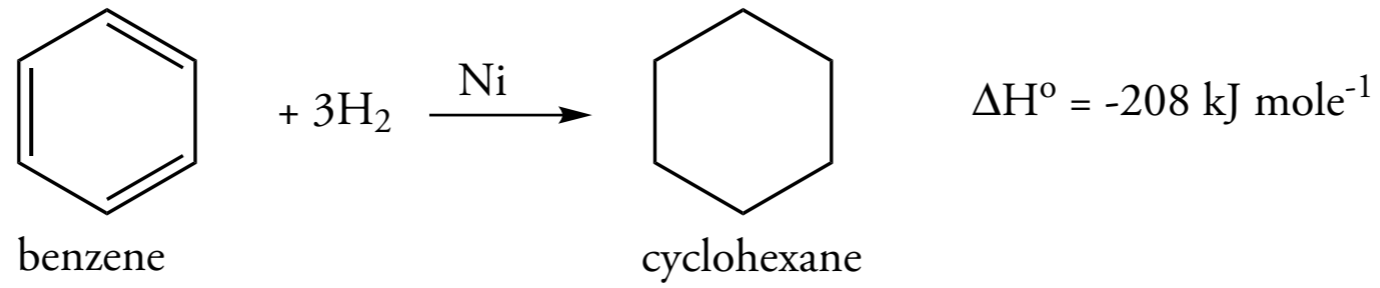
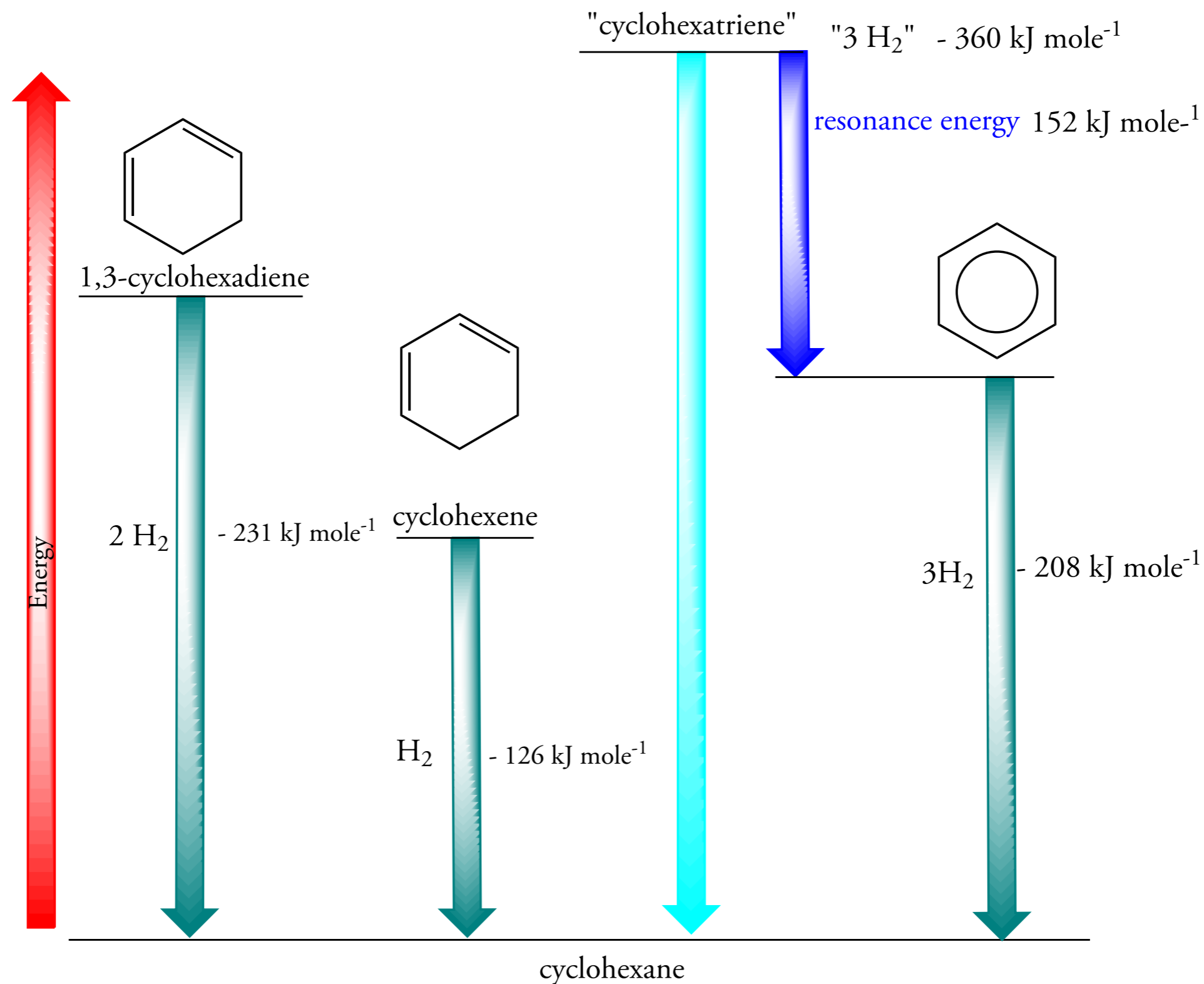


Figure 12.1 Heats of Hydrogenation and the Resonance Stabilization of Benzene

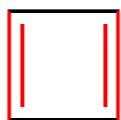
The relative energies of cyclohexene, 1,3-cyclohexadiene, "1,3,5-cyclohexatriene," and benzene and their heats of hydrogenation to form cyclohexane in kJ mole^{-1} .



12.3 THE HÜCKEL RULE

1. To be aromatic, a molecule must be *cyclic*.
2. The molecule must be *planar*.
3. The ring must contain only sp^2 -hybridized atoms that can form a delocalized system of π molecular orbitals.
4. *The number of π electrons in the delocalized π system must equal $4n + 2$, where n is an integer.*

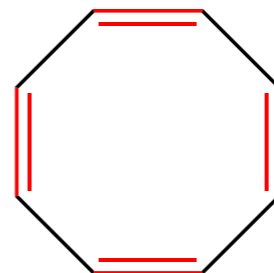
Nonaromatic and Antiaromatic Cyclic Polyenes



cyclobutadiene

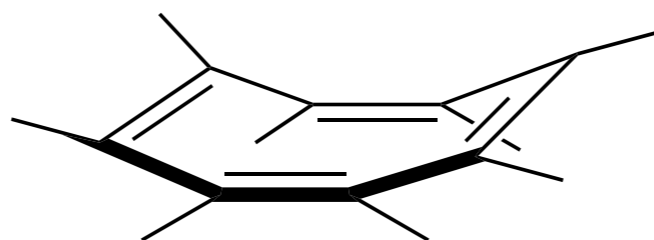
antiaromatic

$4n \pi$ electrons



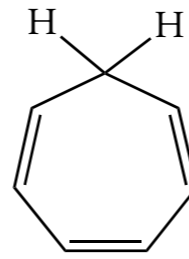
cyclooctatetraene

nonaromatic

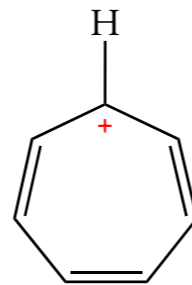


tub conformation of
cyclooctatetraene

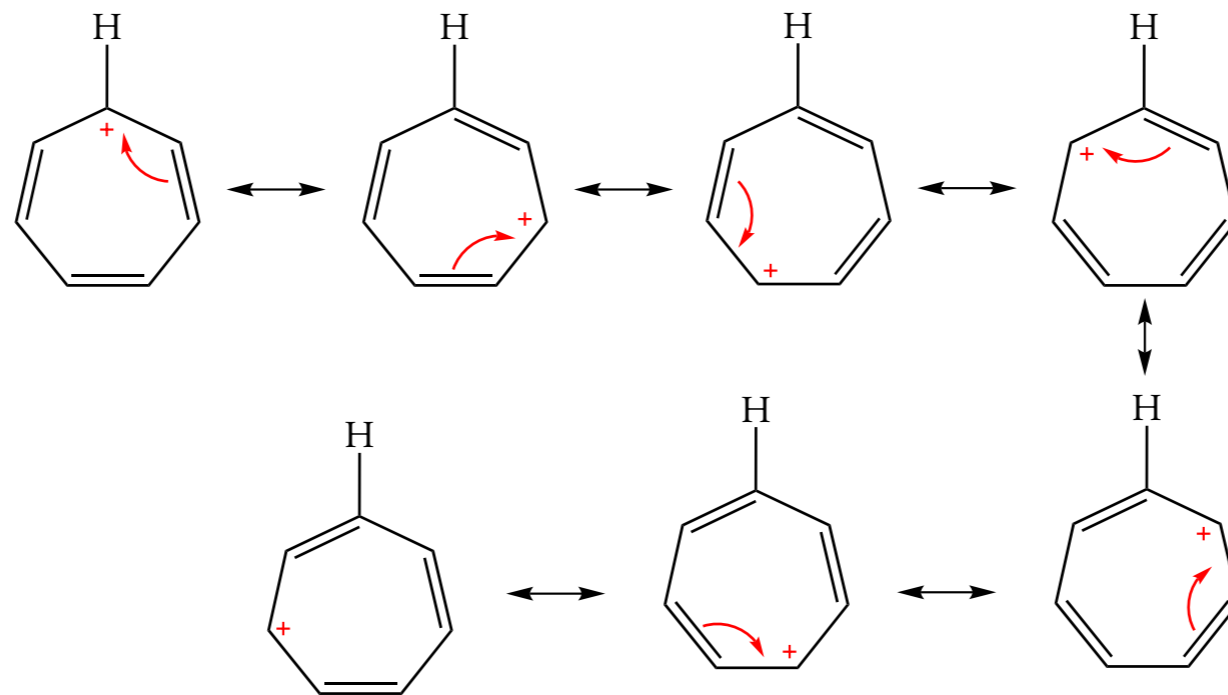
Aromatic Ions, I



1,3,5-cycloheptatriene

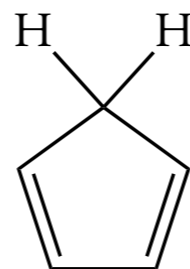


cycloheptatrienyl cation

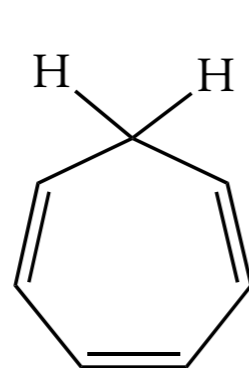
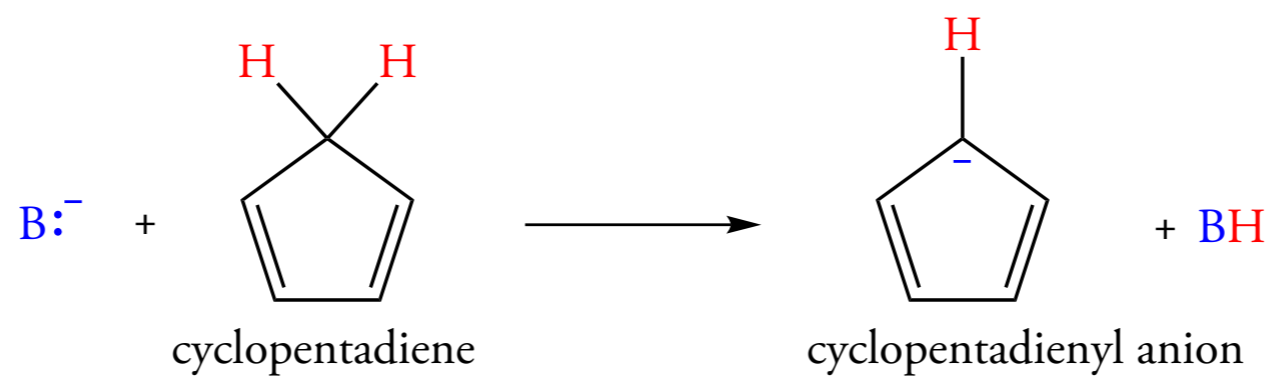


resonance structures of cycloheptatrienyl cation

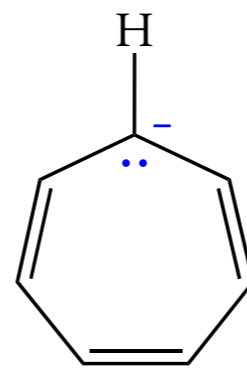
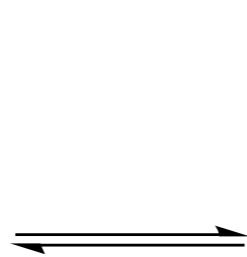
Aromatic Ions, II



cyclopentadiene



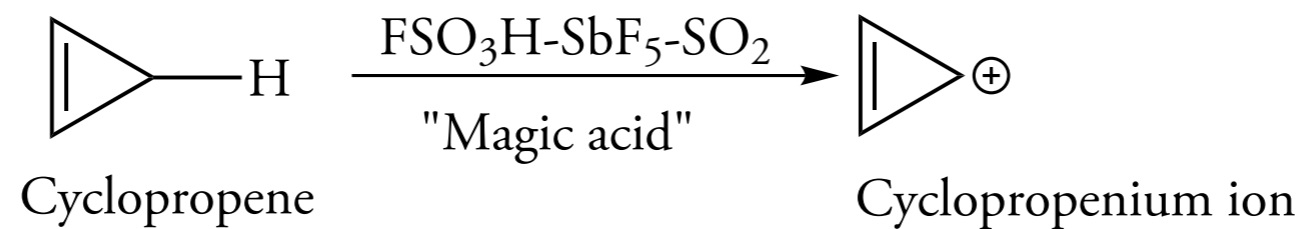
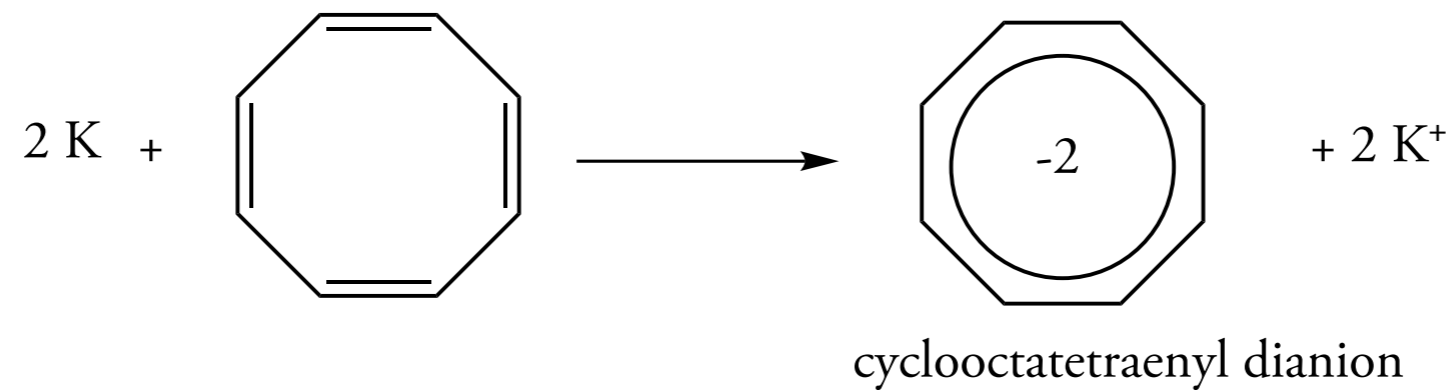
1,3,5-cycloheptatriene



1,3,5-cycloheptatrienyl anion



Aromatic Ions, III



12.4 MOLECULAR ORBITALS OF AROMATIC AND ANTIAROMATIC COMPOUNDS

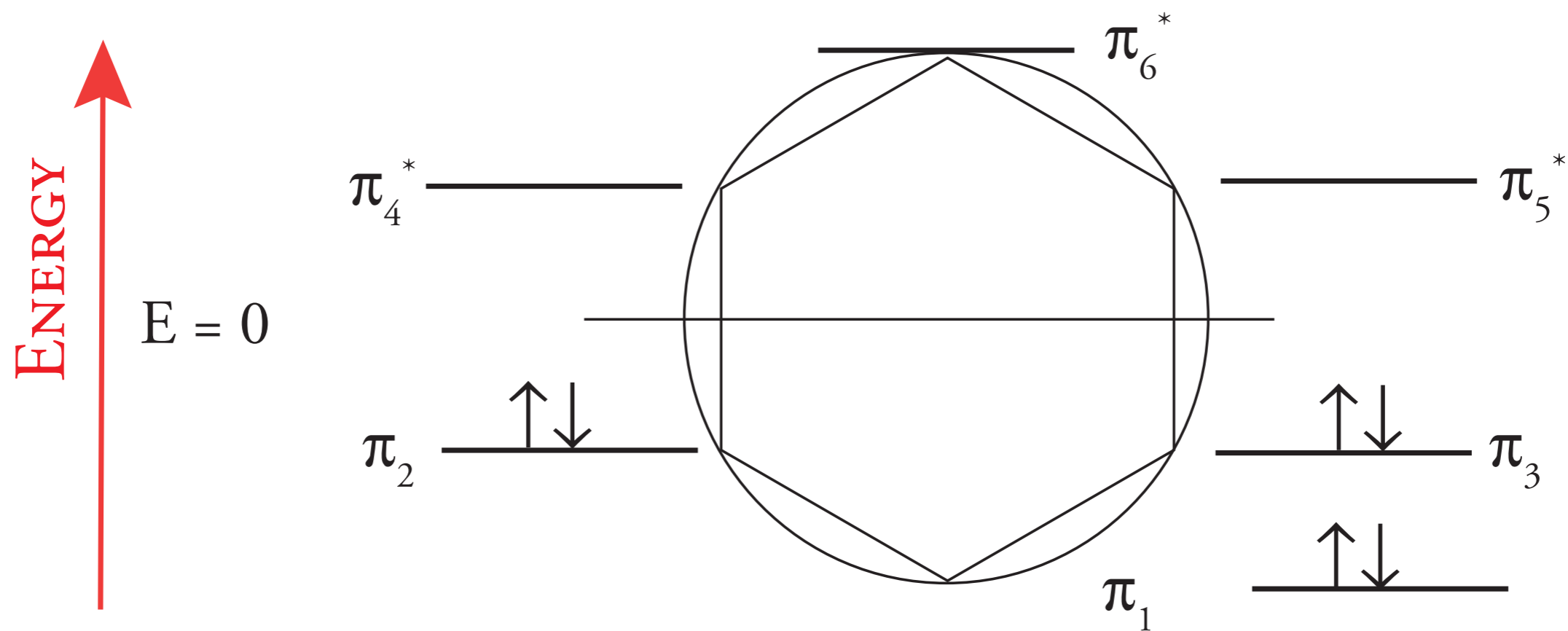


Figure 12.2 Relative energies of benzene's MOs and their occupancy.

Figure 12.3 Molecular Orbitals in Benzene and Their Relative Energies

Relative energies of benzene's MOs and their occupancy. The lowest energy MO, π_1 is symmetric, and has no nodal planes. Orbitals π_2 and π_3 , have the same energy. They are antisymmetric, and have one nodal plane. Each of the bonding MOs has two electrons. MOs π_4 , π_5 and π_6 have energy greater than zero. They are antibonding, and contain no electrons.

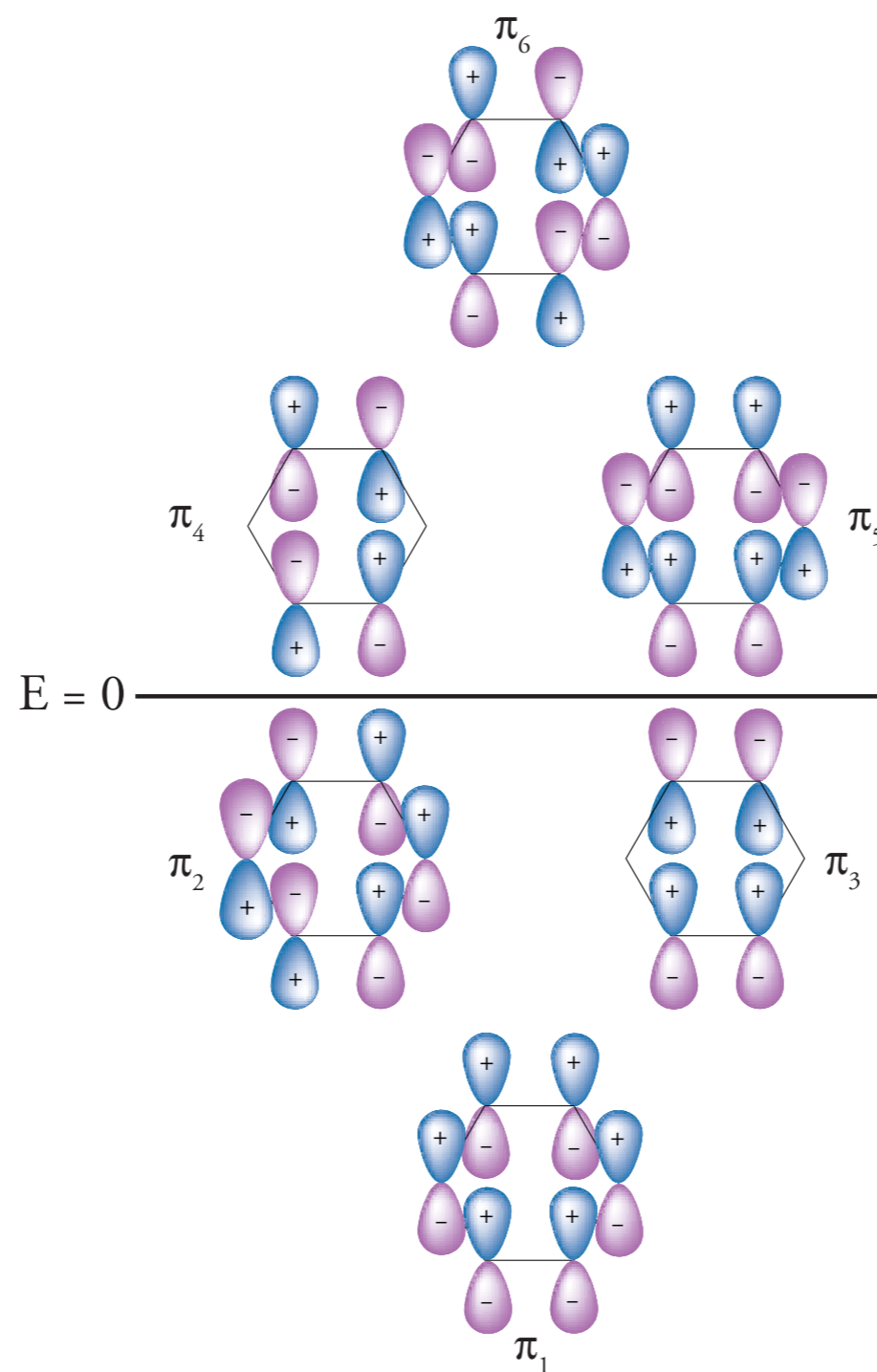


Figure 12.4 Energy Levels and Occupancies of the Molecular Orbitals of Cycloheptatrienyl Cation

The cycloheptatrienyl cation contains $4n + 2 = 6$ π electrons. Therefore, it is aromatic. All three bonding π MOs are fully occupied, and the antibonding orbitals are empty.

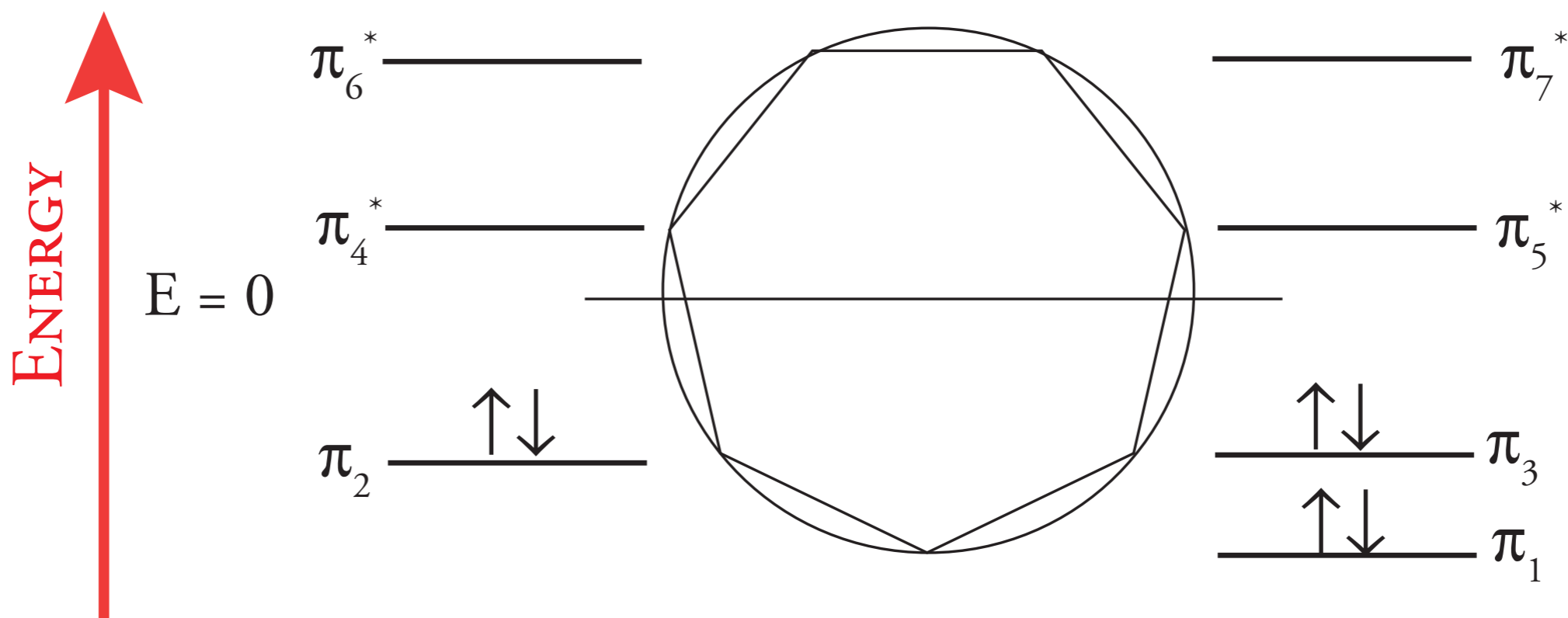


Figure 12.5 Energy Levels and Occupancies of the Molecular Orbitals of Cyclopentadienyl Anion

The cyclopentadienyl anion contains $4n + 2 = 6$ π electrons. Therefore, it is aromatic. All three bonding π MOs are fully occupied, and the antibonding orbitals are empty.

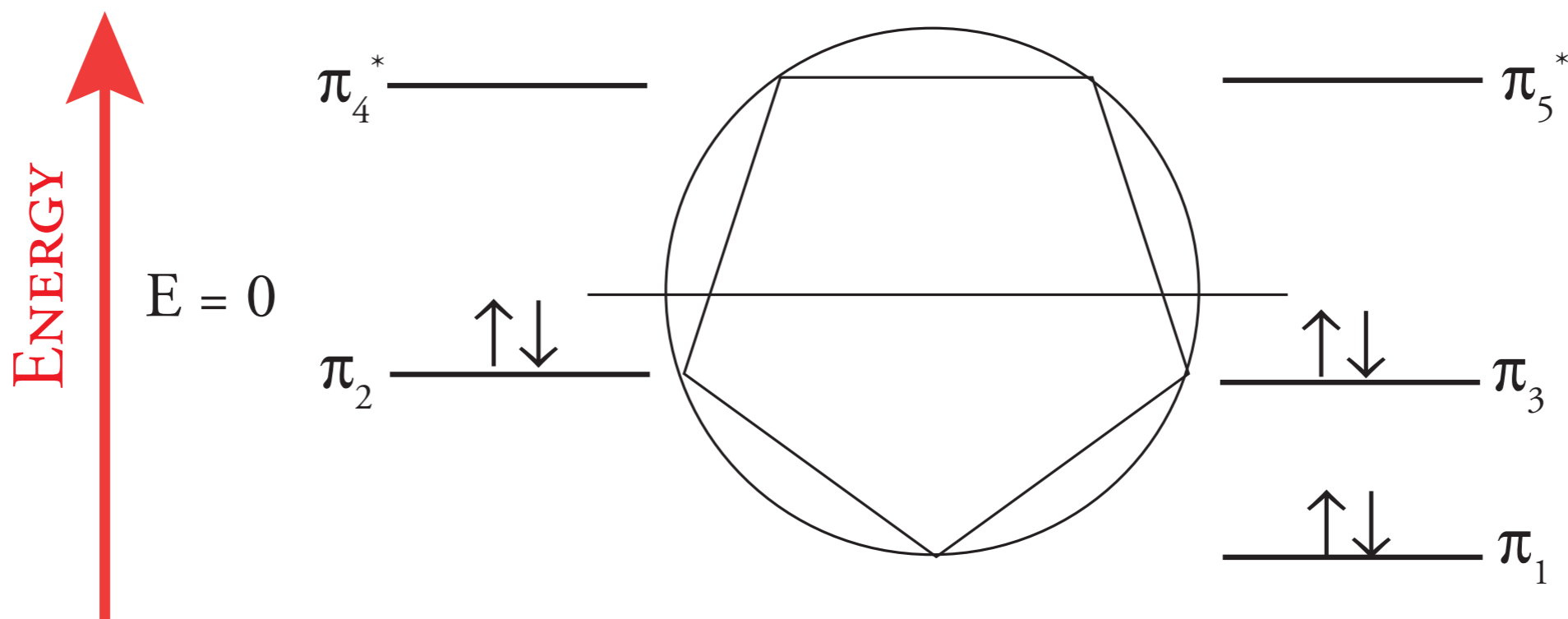
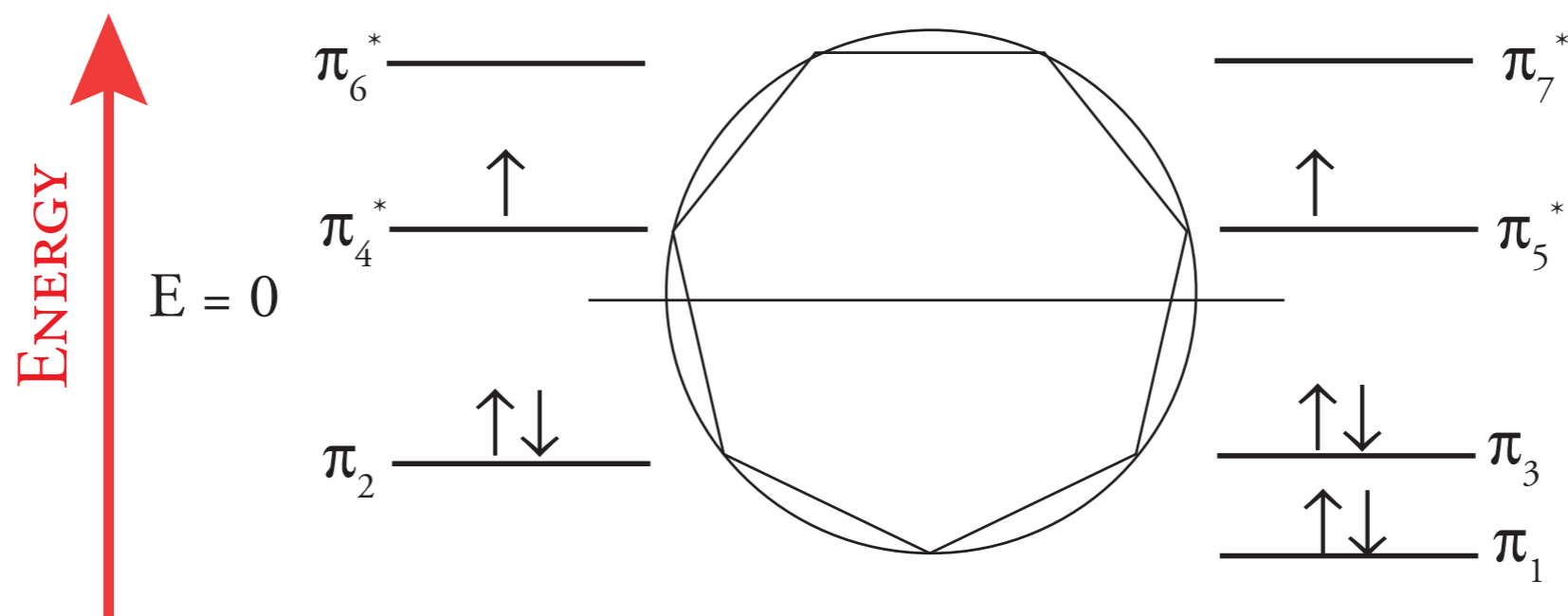
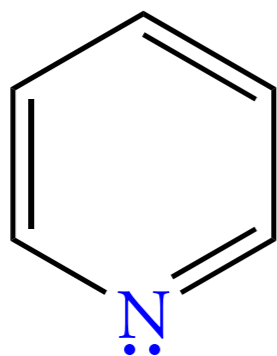


Figure 12.6 Energy Levels and Occupancies of the Molecular Orbitals of Cycloheptatrienyl Anion

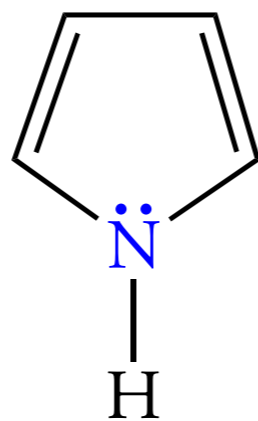
The cycloheptatrienyl anion contains $4n = 8 \pi$ electrons, where $n = 2$. Therefore, it is an unstable antiaromatic species. All three bonding π MOs are fully occupied, but the antibonding π_4^* , π_5^* orbitals each have one electron.



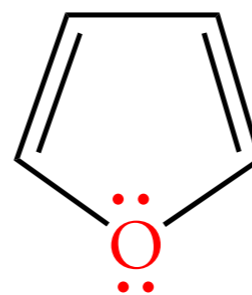
12.5 HETEROCYCLIC AROMATIC COMPOUNDS



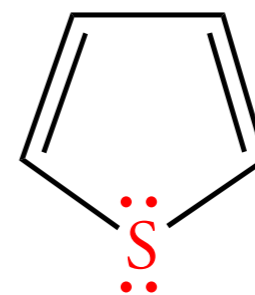
pyridine



pyrrole

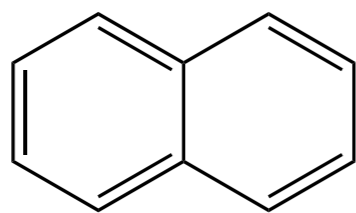


furan

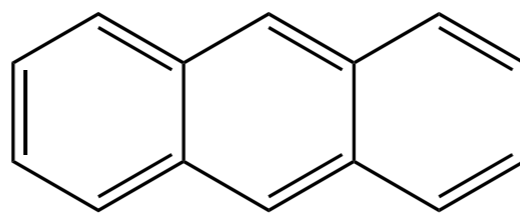


thiophene

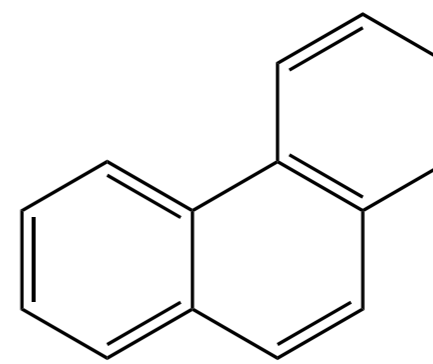
12.7 POLYCYCLIC AROMATIC COMPOUNDS



naphthalene



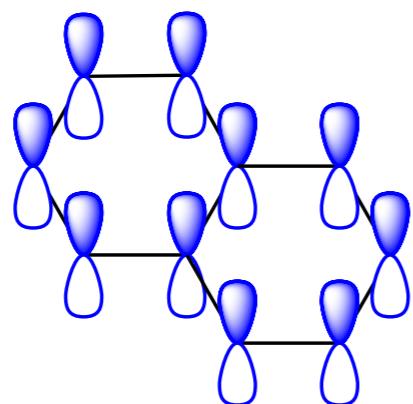
anthracene



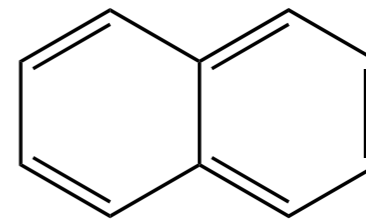
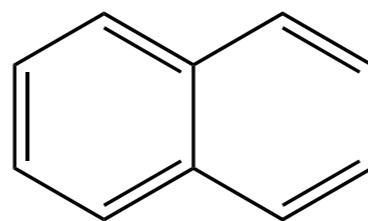
phenanthrene

Figure 12.8 Resonance Structures of Naphthalene

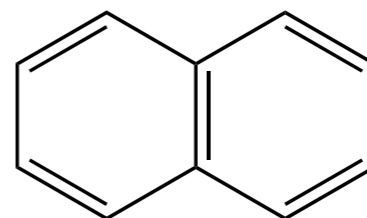
The ten π electrons of naphthalene are delocalized over both rings. Three resonance forms can be written using localized double bonds.



2p orbitals in naphthalene

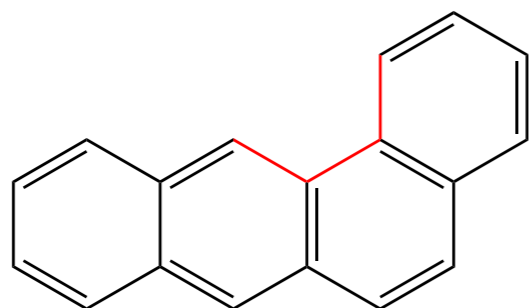


Less stable resonance form

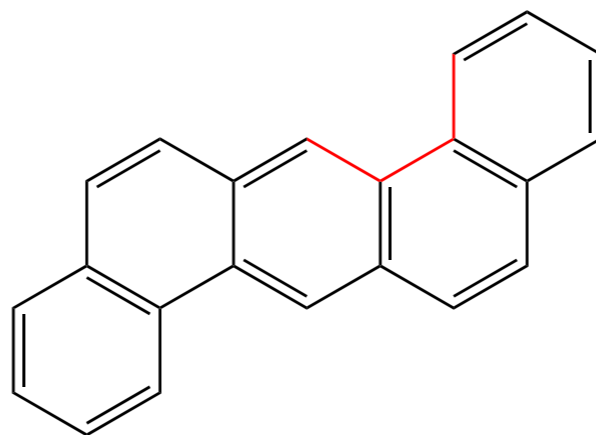


Most stable resonance form

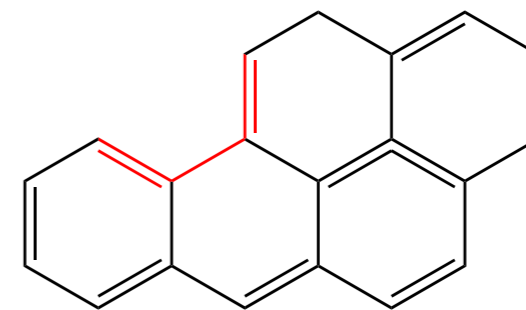
Carcinogenic Aromatic Compounds



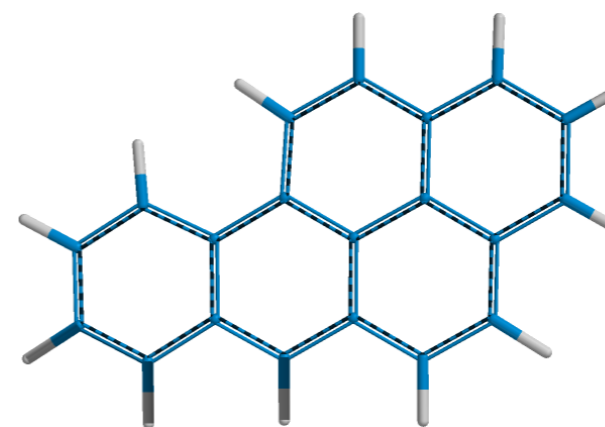
1,2-benzanthracene



1,2,5,6-dibenzanthracene



3,4-benzpyrene



3,4-benzpyrene

Figure 12.7 Relative Energy Levels of the Cyclopropenium Ion

The cyclopropenium cation contains $4n + 2 = 2$ π electrons for $n = 0$. Therefore, it is aromatic. Its two bonding π electrons occupy π_1 , and the antibonding π_2^* , π_3^* orbitals are empty.

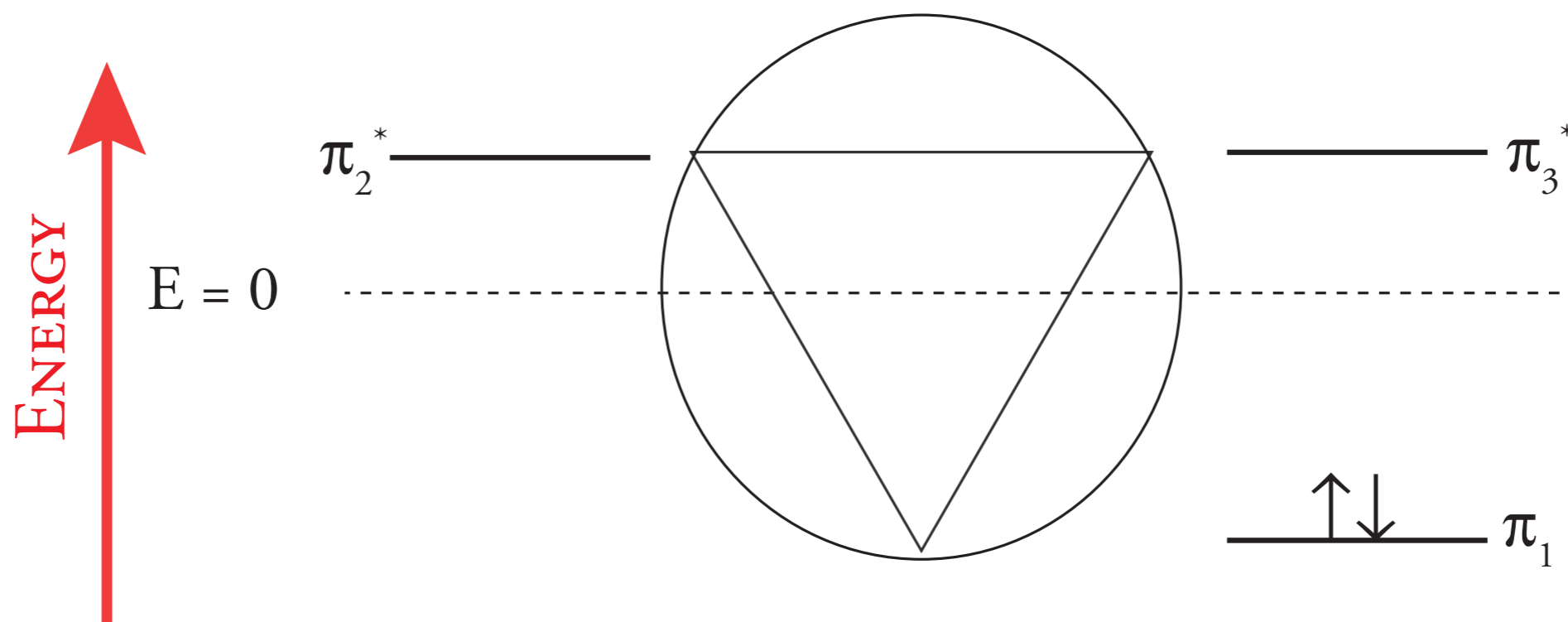


Figure 12.8 Relative Energy Levels of Cyclobutadiene

Cyclobutadiene is a $4n$ π antiaromatic molecule, for $n = 1$. It has two bonding electrons in π_1 , and one electron in each of the nonbonding π_2^* , π_3^* orbitals. It is a very unstable diradical.

