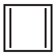
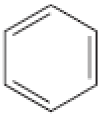
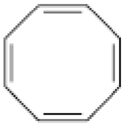
Aromaticity

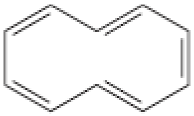
Annulenes:

Annulenes are compounds with alternating double and single bonds. The number in brackets tells us how many carbon atoms there are in the ring.


cyclobutadiene
[4]annulene


benzene
[6]annulene


cyclooctatetraene
[8]annulene

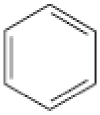

cyclodecapentaene
[10]annulene

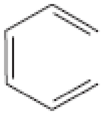
Aromatic, Antiaromatic and Nonaromatic compounds

Aromatic compounds are those that meet the following criteria:
1. The structure must be cyclic, containing some number of conjugated pi bonds.
2. Each atom in the ring must have an unhybridized *p* orbital. (The ring atoms are usually sp^2 hybridized or occasionally *sp* hybridized.)
3. The unhybridized *p* orbitals must overlap to form a continuous ring of parallel orbitals. In most cases, the structure must be planar (or nearly planar) for effective overlap to occur.
4. Delocalization of the pi electrons over the ring must *lower* the electronic energy.

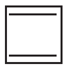
An **antiaromatic compound** is one that meets the first three criteria, but delocalization of the pi electrons over the ring *increases* the electronic energy.

Aromatic structures are more stable than their open-chain counterparts. For example, benzene is more stable than hexa-1,3,5-triene.


more stable (aromatic)

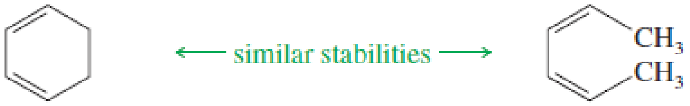

less stable

Cyclobutadiene meets the first three criteria for a continuous ring of overlapping *p* orbitals, but delocalization of the pi electrons *increases* the electronic energy. Cyclobutadiene is less stable than its open-chain counterpart (buta-1,3-diene), and it is antiaromatic.


less stable (antiaromatic)


more stable

A cyclic compound that does not have a continuous, overlapping ring of *p* orbitals cannot be aromatic or antiaromatic. It is said to be **nonaromatic,** or aliphatic. Its electronic energy is similar to that of its open-chain counterpart. For example, cyclohexa- 1,3-diene is about as stable as *cis*,*cis*-hexa-2,4-diene.



(nonaromatic)

<u>Huckel's rule:</u>

Erich Hückel developed a shortcut for predicting which of the annulenes and related compounds are aromatic and which are antiaromatic. In using Hückel's rule, we must be certain that the compound under consideration meets the criteria for an aromatic or antiaromatic system.

To qualify as aromatic or antiaromatic, a cyclic compound must have a continuous ring of overlapping *p* orbitals, usually in a planar conformation. Once these criteria are met, **Hückel's rule** applies.

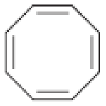
Hückel's Rule: If the number of pi electrons in the cyclic system is:
(4N+2), the system is aromatic.
(4*N*) the system is antiaromatic.
N is an integer, commonly 0, 1, 2, or 3.

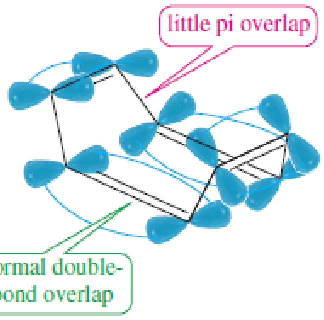
Benzene is [6] annulene, cyclic, with a continuous ring of overlapping *p* orbitals. There are six pi electrons in benzene (three double bonds in the classical structure), so it is a (4N+2) system, with N=1. Hückel's rule predicts benzene to be aromatic.

Like benzene, cyclobutadiene ([4]annulene) has a continuous ring of overlapping *p* orbitals. But it has four pi electrons (two double bonds in the classical structure), which is a (4*N*) system with N=1. Hückel's rule predicts cyclobutadiene to be antiaromatic.

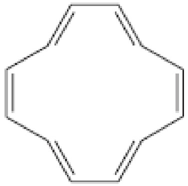
Cyclooctatetraene would be antiaromatic if Hückel's rule applied, so the conjugation of its double bonds is energetically unfavorable. Remember that Hückel's rule applies to a compound *only* if there is a continuous ring of overlapping *p* orbitals, usually in a planar system.

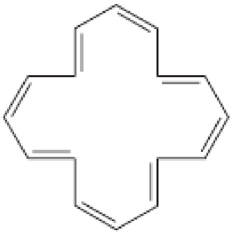
Cyclooctatetraene is more flexible than cyclobutadiene, and it assumes a nonplanar “tub” conformation that avoids most of the overlap between adjacent pi bonds. Hückel’s rule simply does not apply.

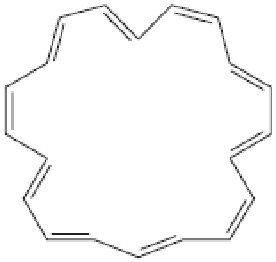

eight pi electrons



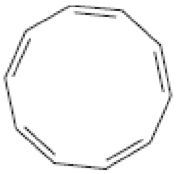
Large-Ring Annulenes like cyclooctatetraene, larger annulenes with (4*N*) systems do not show antiaromaticity because they have the flexibility to adopt nonplanar conformations. Even though [12]annulene, [16]annulene, and [20]annulene are (4*N*) systems (with N = 3, 4, and 5, respectively), they all react as partially conjugated polyenes.

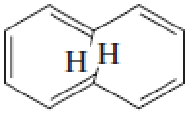

[12]annulene


[16]annulene

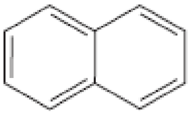

[20]annulene

Aromaticity in the larger (4N+2)annulenes depends on whether the molecule can adopt the necessary planar conformation. In the all-cis [10]annulene, the planar conformation requires an excessive amount of angle strain. The [10]annulene isomer with two trans double bonds cannot adopt a planar conformation either, because two hydrogen atoms interfere with each other. Neither of these [10]annulene isomers is aromatic, even though each has (4N+2) pi electrons, with N=2. If the interfering hydrogen atoms in the partially trans isomer are removed, the molecule can be planar. When these hydrogen atoms are replaced with a bond, the aromatic compound naphthalene results.

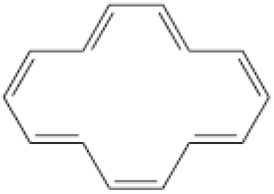

all-cis
nonaromatic



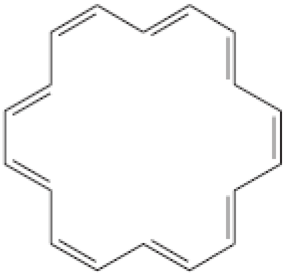
two trans
nonaromatic


naphthalene
aromatic

Some of the larger annulenes with (4N+2) pi electrons can achieve planar conformations. For example, the following [14]annulene and [18]annulene have aromatic properties.



[14]annulene (aromatic)



[18]annulene (aromatic)