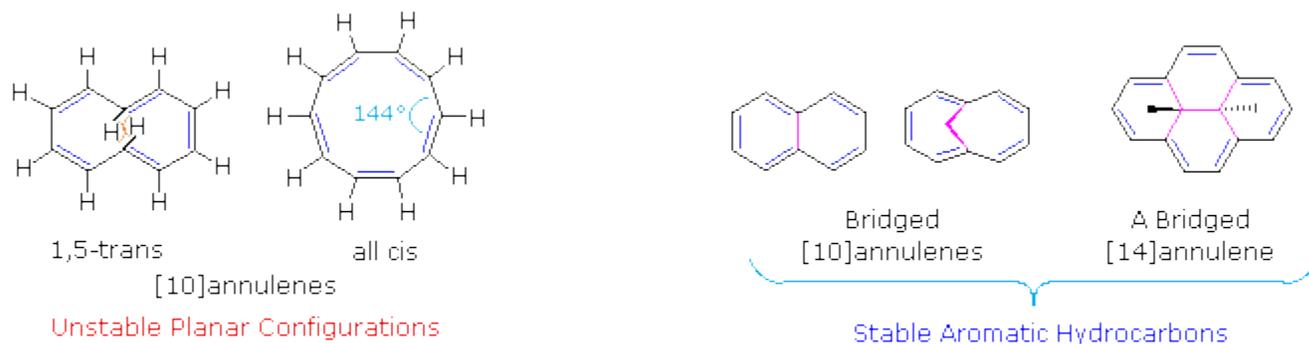


# Annulenes, Barrelene, Aromatic Ions and Antiaromaticity

## Annulenes

Monocyclic compounds made up of alternating conjugated double bonds are called **annulenes**. Benzene and 1,3,5,7-cyclooctatetraene are examples of annulenes; they are named [6]annulene and [8]annulene respectively, according to a general nomenclature system in which the number of pi-electrons in an annulene is designated by a number in brackets. Some annulenes are aromatic (e.g. benzene), but many are not due to non-planarity or a failure to satisfy the Hückel Rule. Compounds classified as [10]annulenes (a Hückel Rule system) serve to illustrate these factors. As shown in the following diagram, 1,3,5,7,9-cyclodecapentaene fails to adopt a planar conformation, either in the all cis-configuration or in its 1,5-trans-isomeric form. The transannular hydrogen crowding that destabilizes the latter may be eliminated by replacing the interior hydrogens with a bond or a short bridge (colored magenta in the diagram). As expected, the resulting 10  $\pi$ -electron annulene derivatives exhibit aromatic stability and reactivity as well as characteristic ring current anisotropy in the nmr. Naphthalene and azulene are [10]annulene analogs stabilized by a transannular bond. Although the  $\text{CH}_2$ bridged structure to the right of naphthalene in the diagram is not exactly planar, the conjugated 10  $\pi$ -electron ring is sufficiently close to planarity to achieve aromatic stabilization. The bridged [14]annulene compound on the far right, also has aromatic properties.



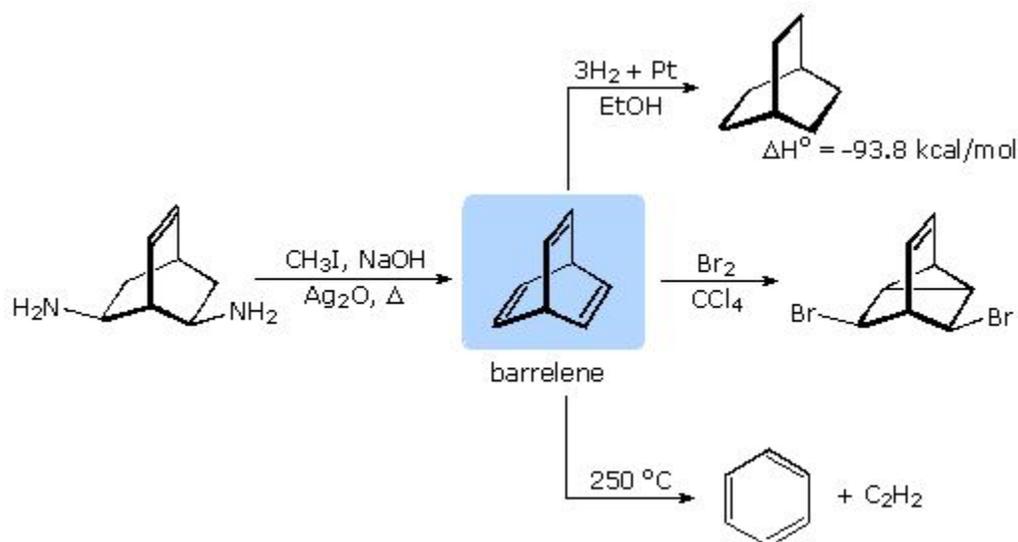
- transannular crowding in trans-isomer
- angle strain (  $240^\circ$  total ) in cis-isomer

## Barrelene

Formulation of the Hückel rule prompted organic chemists to consider the possible aromaticity of many unusual unsaturated hydrocarbons. One such compound was the 6  $\pi$ -electron bicyclic structure, now known as barrelene. Although the  $\pi$ -bonds in barrelene are not coplanar, it was believed that transannular overlap might still lead to aromatic

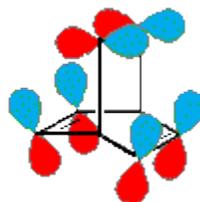
stabilization.

A synthesis of barrelene (bicyclo[2.2.2]-2,5,7-octatriene) was accomplished nearly fifty years ago by H. Zimmerman (Wisconsin), using a double Hofmann elimination. As shown in the following diagram, the chemical behavior of this triene confirmed it was not aromatic in the accepted sense of this term. Bromine addition took place rapidly with transannular bond formation, in the same fashion as with norbornadiene (bicyclo[2.2.1]-2,5-heptadiene). Pyrolysis of barrelene gave the expected cycloreversion products benzene and acetylene.



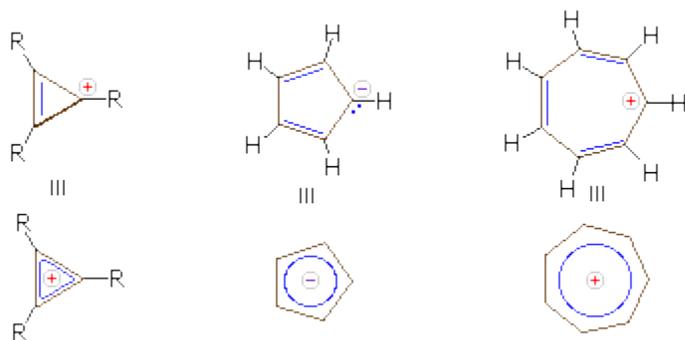
The heat of hydrogenation of barrelene reflects its thermodynamic stability. The value for cyclohexene is  $-28 \text{ kcal/mol}$ , significantly less than one third of the barrelene number. Furthermore, the first double bond of barrelene is reduced with the release of  $36.7 \text{ kcal/mol}$  heat, indicating destabilization rather than stabilization. The electronic spectrum of barrelene shows a  $\pi$ -electron interaction similar to that in related homoconjugated dienes. ( $\lambda_{\text{max}} \cong 220\text{-}230 \text{ nm}$ ).

An explanation for the lack of aromatic behavior in the case of barrelene may be found by comparing the orbital symmetry of the six component p-orbitals with those of benzene. Benzene is an annulene in which all six p-orbitals may be oriented with congruent overlapping phases. The cylindrical array of p-orbitals in barrelene cannot be so arranged, as shown in the diagram on the right. There will always be one region (a nodal plane) in which the transannular overlap is incongruent.



## Aromatic Ions

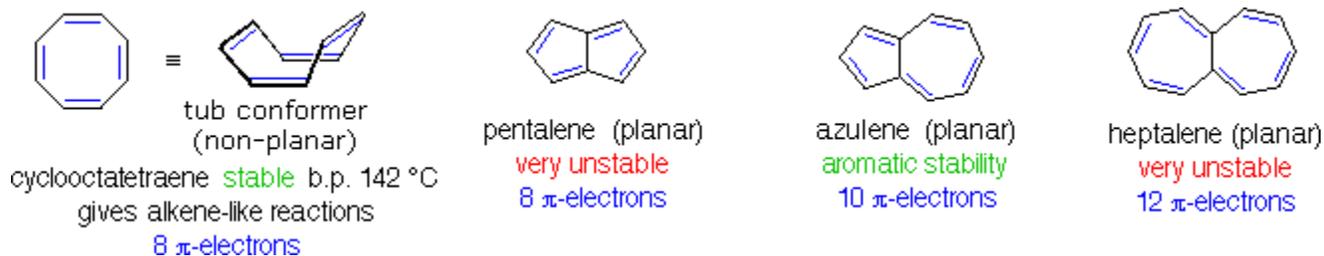
Carbanions and carbocations may also show aromatic stabilization. Some examples are:



The three-membered ring cation has 2  $\pi$ -electrons and is surprisingly stable, considering its ring strain. Cyclopentadiene is as acidic as ethanol, reflecting the stability of its 6  $\pi$ -electron conjugate base. Salts of cycloheptatrienyl cation (tropylium ion) are stable in water solution, again reflecting the stability of this 6  $\pi$ -electron cation.

## Antiaromaticity

Conjugated ring systems having  $4n$   $\pi$ -electrons (e.g. 4, 8, 12 etc. electrons) not only fail to show any aromatic properties, but appear to be less stable and more reactive than expected. As noted above, 1,3,5,7-cyclooctatetraene is non-planar and adopts a tub-shaped conformation. The compound is readily prepared, and undergoes addition reactions typical of alkenes. Catalytic hydrogenation of this tetraene produces cyclooctane. Planar bridged annulenes having  $4n$   $\pi$ -electrons have proven to be relatively unstable. Examples of 8 and 12- $\pi$ -electron systems are shown below, together with a similar 10  $\pi$ -electron aromatic compound.



The simple  $C_8H_6$  hydrocarbon pentalene does not exist as a stable compound, and its hexaphenyl derivative is air sensitive. The 12- $\pi$ -electron analog heptalene has been prepared, but is also extremely reactive (more so than cyclooctatetraene). On the other

hand, azulene is a stable 10- $\pi$ -electron hydrocarbon that incorporates structural features of both pentalene and heptalene. Azulene is a stable blue crystalline solid that undergoes a number of typical aromatic substitution reactions. The unexpected instability of  $4n$   $\pi$ -electron annulenes has been termed "**antiaromaticity**". Other examples may be cited. Thus, all attempts to isolate 1,3-cyclobutadiene have yielded its dimer, or products from reactions with other compounds introduced into the reaction system. Similarly, cyclopentadienyl cation (4  $\pi$ -electrons) and cycloheptatrienyl anion (8  $\pi$ -electrons) show very high reactivity when forced to form.

Source:<http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/react3.htm#rx10>