PHA284

Organic Chemistry II

Ankara University
Faculty of Pharmacy
Department of Pharmaceutical Chemistry

AROMATIC COMPOUNDS

The Discovery of Benzene

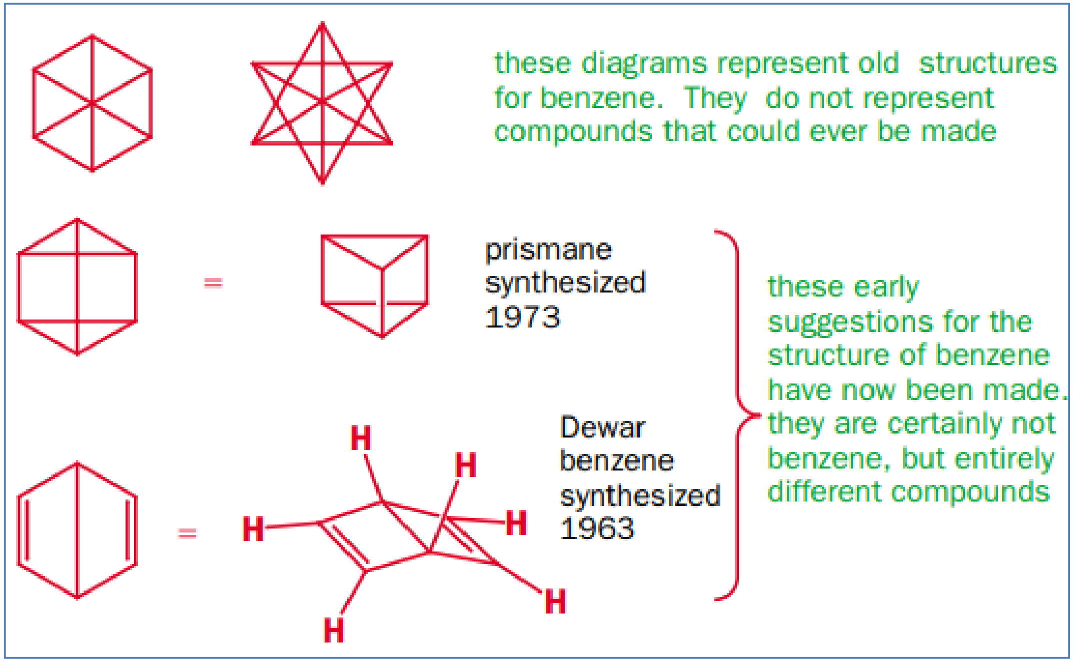
*In 1825, Michael Faraday (English chemist) isolated a pure compound of boiling point 80°C from the oily mixture that condensed from illuminating gas, the fuel burned in gaslights. Faraday named the new compound "bicarburet of hydrogen.

*Eilhard Mitscherlich synthesized the same compound in 1834 by heating benzoic acid, isolated from gum benzoin, in the presence of lime.

Since the new compound was derived from gum benzoin, he named it «**benzine**», now called «**benzene**».

The Structure of Benzene

It was worked out that the formula was C_6H_6, but how were these atoms arranged? Some strange structures were suggested until Kekulé proposed the correct structure in 1865.

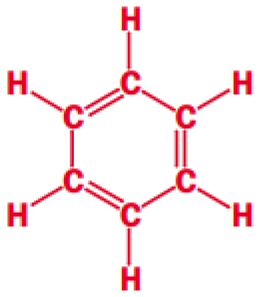


these diagrams represent old structures for benzene. They do not represent compounds that could ever be made

prismane synthesized 1973

Dewar benzene synthesized 1963

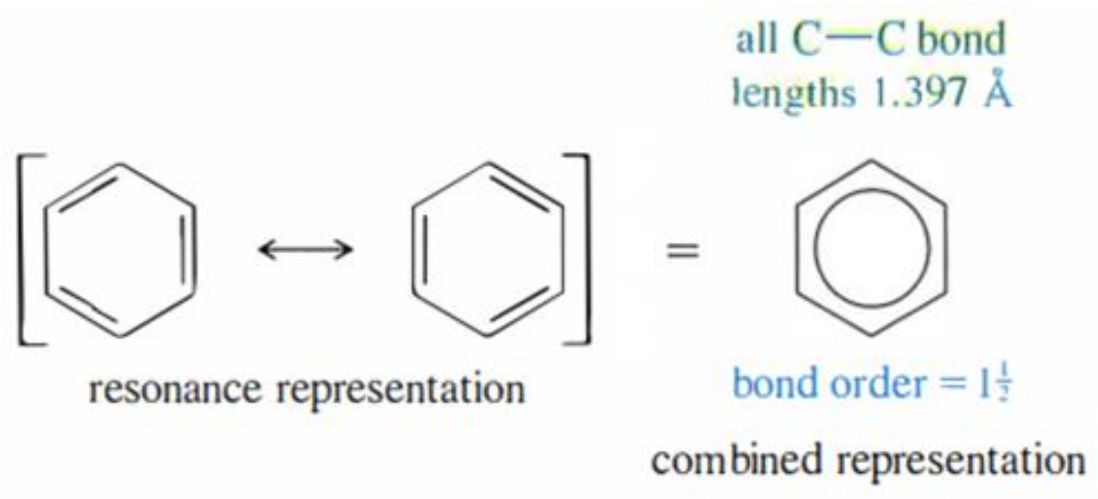
these early suggestions for the structure of benzene have now been made. they are certainly not benzene, but entirely different compounds



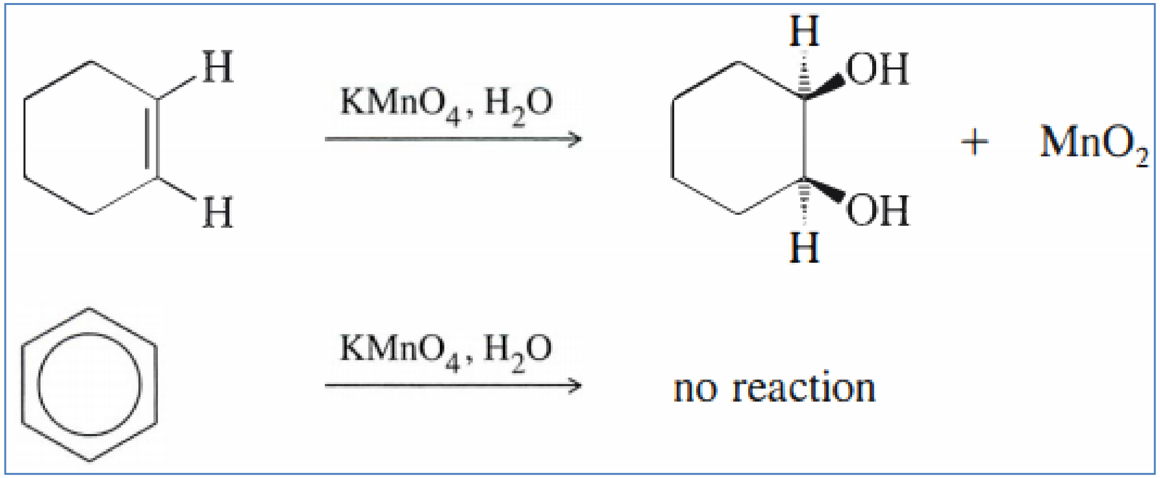
Kekulé's structure for benzene

The Resonance Representation:

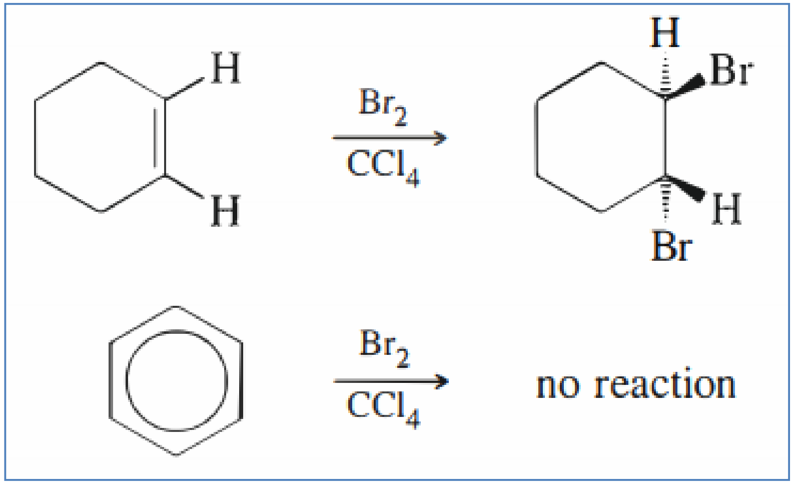
Benzene is actually a resonance hybrid of the two Kekule structures. This representation implies that the pi electrons are delocalized between adjacent carbon atoms. The carbon-carbon bond lengths in benzene are shorter than typical single-bond lengths, yet longer than typical double-bond lengths.



The Unusual Reactions of Benzene



The Unusual Reactions of Benzene



The Unusual Stability of Benzene

The Resonance Theory: Benzene's reluctance to undergo typical alkene reactions suggests that it must be unusually stable. By comparing molar heats of hydrogenation, we can get a quantitative idea of its stability.

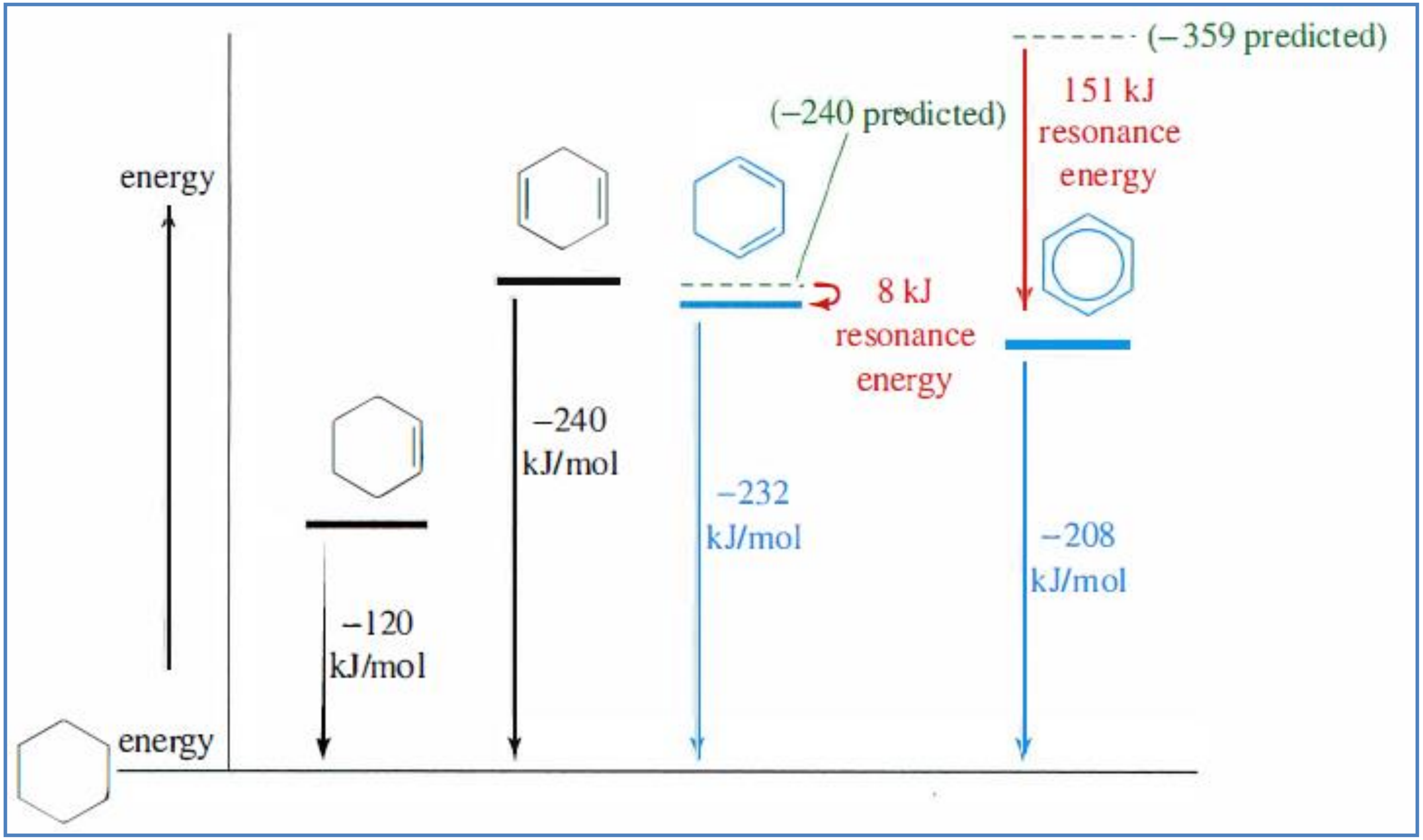
1. Hydrogenation of cyclohexene is exothermic by 120 kJ/mol.

2. Hydrogenation of 1,4-cyclohexadiene is exothermic by 240 kJ/mol, about twice the heat of hydrogenation of cyclohexene. The resonance energy of the isolated double bonds in 1,4-cyclohexadiene is about zero.

3. Hydrogenation of 1,3-cyclohexadiene is exothermic by 232 kJ/mol, about 8 kJ less than twice the value for cyclohexene. A resonance energy of 8 kJ is typical for a conjugated diene.

4. Hydrogenation of benzene requires higher pressures of hydrogen and a more active catalyst. This hydrogenation is exothermic by 208 kJ/mol, about 151 kJ less than 3 times the value for cyclohexene.

The Unusual Stability of Benzene



Annulenes

Cyclic hydrocarbons with alternating single and double bonds are called annulenes. For example, benzene is the six-membered annulene, so it can be named [6]annulene. Cyclobutadiene is [4]annulene, cyclooctatetraene is [8]annulene, and larger annulenes are named similarly.

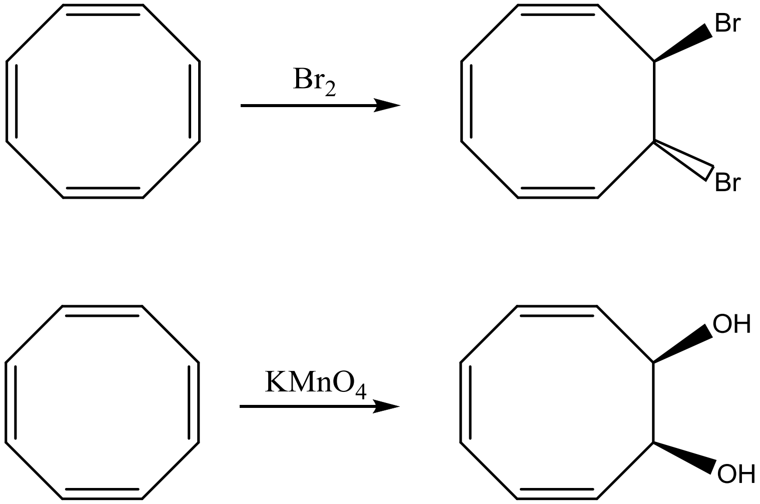

cyclobutadiene
[4]annulene


benzene
[6]annulene


cyclooctatetraene
[8]annulene


cyclodecapentaene
[10]annulene

In 1911, Richard Willstätter synthesized cyclooctatetraene and found that it reacts like a normal polyene. Bromine adds readily to cyclooctatetraene, and permanganate oxidizes its double bonds.



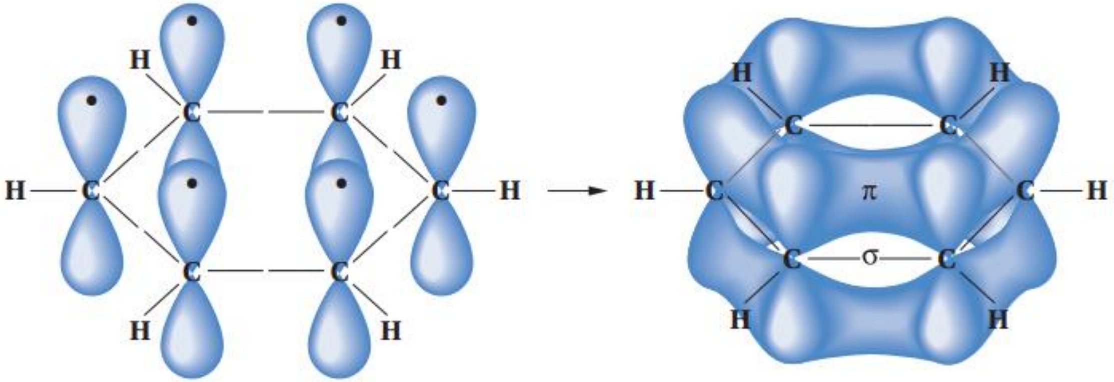
Cyclobutadiene and cyclooctatetraene have alternating single and double bonds similar to those of benzene. These compounds were mistakenly expected to be aromatic.

Visualizing benzene as a resonance hybrid of two Kekule structures cannot fully explain the unusual stability of the aromatic ring.

As we have seen with other conjugated systems, **molecular orbital theory** provides the key to understanding aromaticity and predicting which compounds will have the stability of an aromatic system.

Orbital theory, which is so useful in rationalizing the geometries of alkanes, alkenes, and alkynes, is also useful in explaining the structure of benzene.

- Each carbon atom in benzene is connected to only three other atoms.
- Two *sp*^{2} orbitals of each carbon atom overlap with similar orbitals of adjacent carbon atoms to form the sigma bonds of the hexagonal ring.
- The third *sp*^{2} orbital of each carbon overlaps with a hydrogen 1s orbital to form the C-H sigma bonds.
- Perpendicular to the plane of the three *sp*^{2} orbitals at each carbon is a *p* orbital containing one electron, the fourth valence electron.
- The *p* orbitals on all six carbon atoms can overlap laterally to form pi orbitals that create a ring or cloud of electrons above and below the plane of the ring.

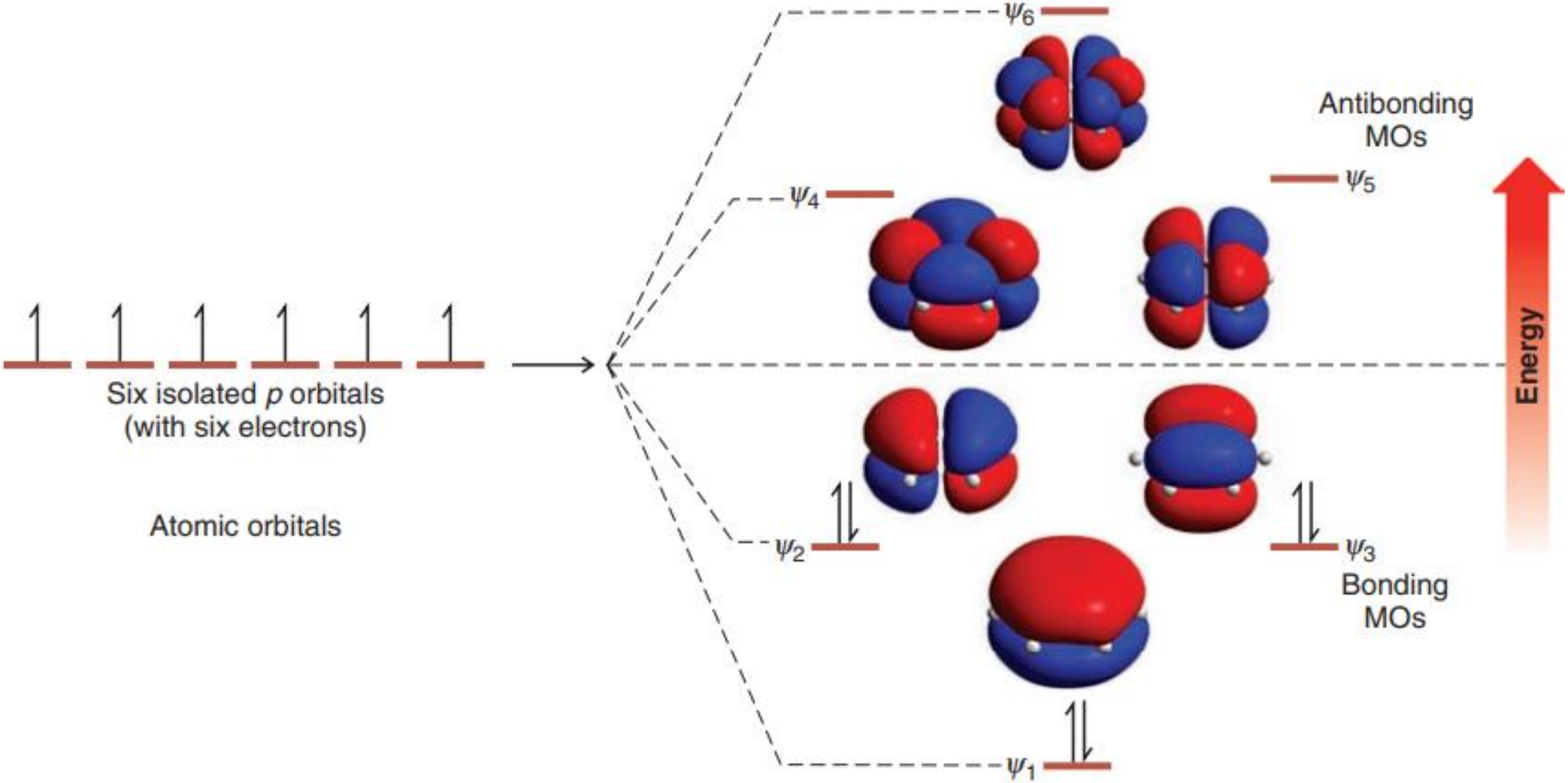


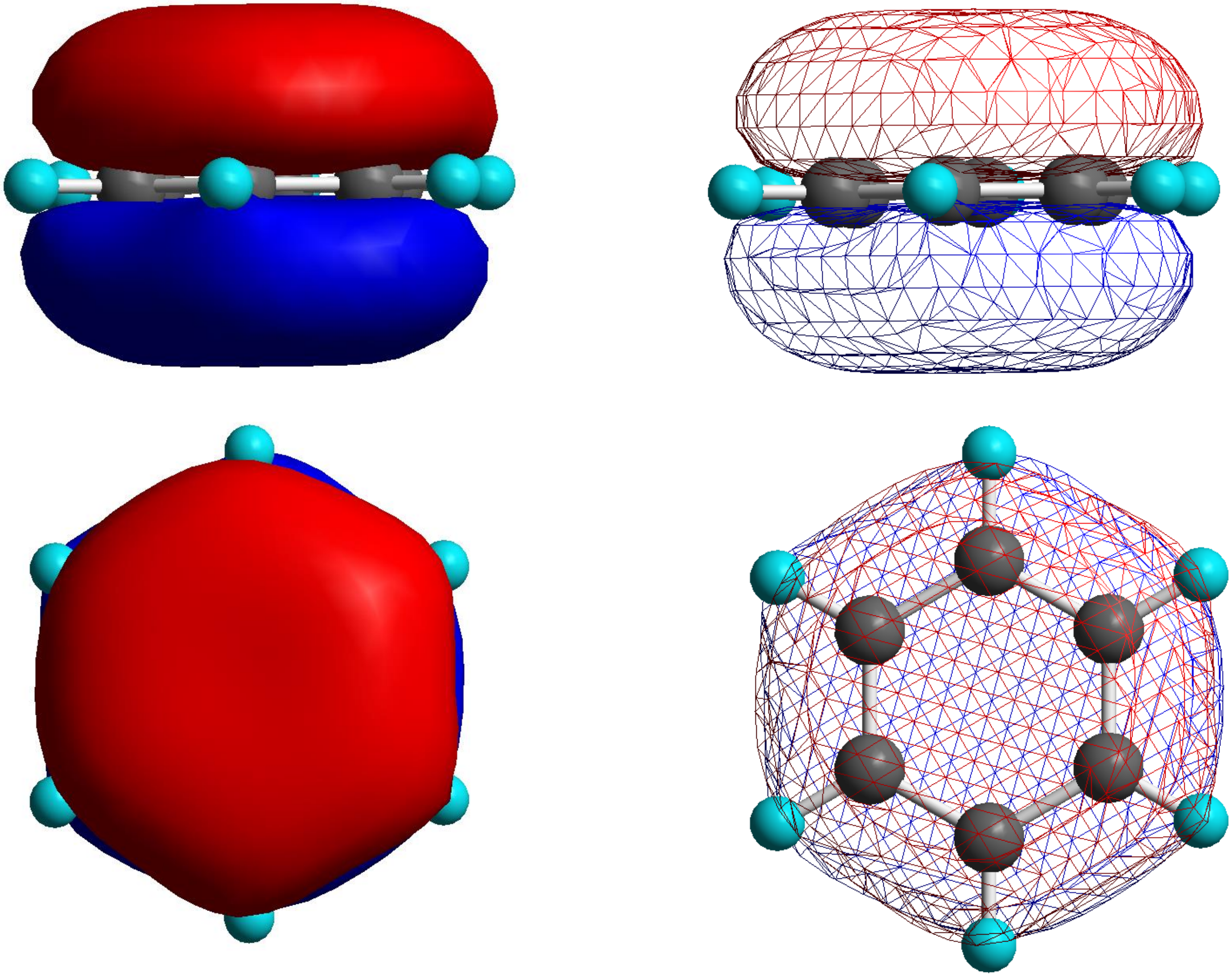
The Molecular Orbitals of Benzene

A two-dimensional cyclic system requires two-dimensional MOs, with the possibility of two distinct MOs having the same energy.

We can still follow the same principles in developing a molecular orbital representation for benzene, however.

1. There are six atomic *p* orbitals that overlap to form the benzene pi system. Therefore, there must be six molecular orbitals.
2. The lowest-energy molecular orbital is entirely bonding, with constructive overlap between all pairs of adjacent p orbitals. There are no vertical nodes in this lowest-lying MO.
3. The number of nodes increases as the MOs increase in energy.
4. The MOs should be evenly divided between bonding and antibonding MOs, with the possibility of nonbonding MOs in some cases.
5. We expect that a stable system will have filled bonding MOs and empty antibonding MOs.


ψ_6
Antibonding MOs
ψ_4
ψ_5
Energy
Six isolated *p* orbitals (with six electrons)
Atomic orbitals
ψ_2
ψ_3
Bonding MOs
ψ_1



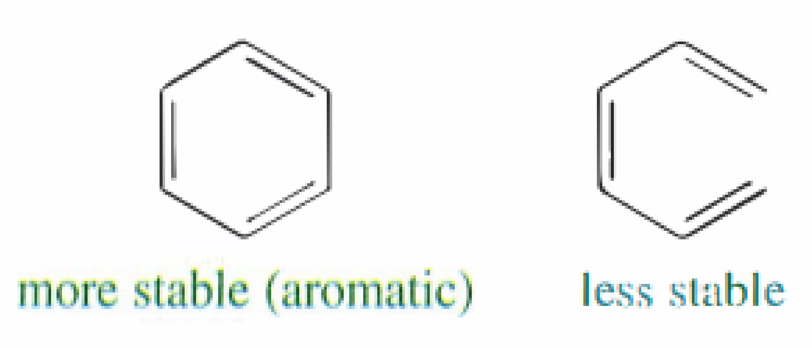
- **Aromatic,**
- **Antiaromatic, and**
- **Nonaromatic Compounds**

Aromatic compounds are those that meet the following criteria:

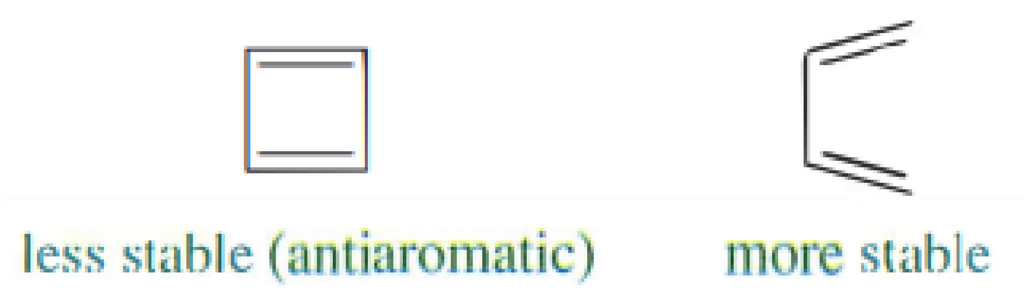
1. The structure must be cyclic, containing some number of conjugated pi bonds.
2. Each atom in the ring must have an unhybridized p orbital. (The ring atoms are usually *sp*^{2} hybridized or occasionally *sp* hybridized.)
3. The unhybridized p orbitals must overlap to form a continuous ring of parallel 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.

Benzene is aromatic.

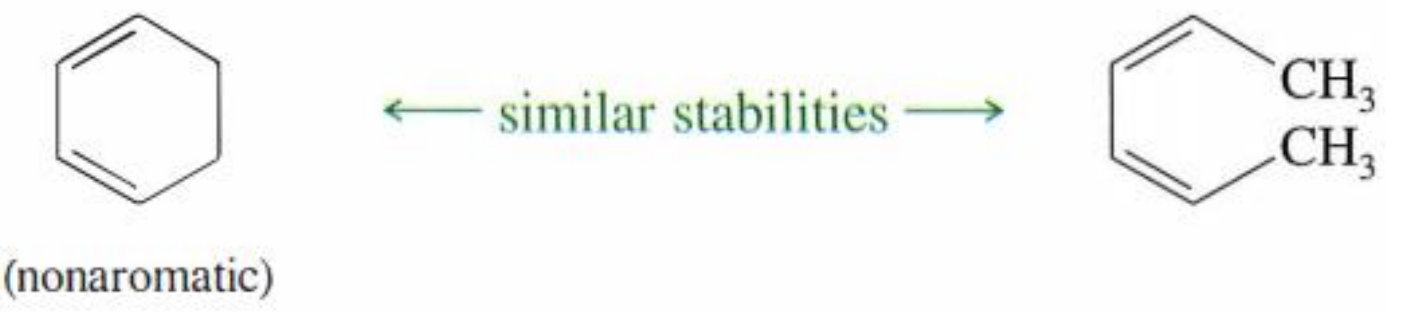


Cyclobutadiene is antiaromatic.



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.

For example,



Hückel's Rule

Erich Hückel developed a shortcut for predicting which of the annulenes and related compounds are aromatic and which are antiaromatic.

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 sytem is:
(4n + 2), the system is aromatic;
(4n), the system is antiaromatic,
where n is an integer (n= 0,1,2,3, …).

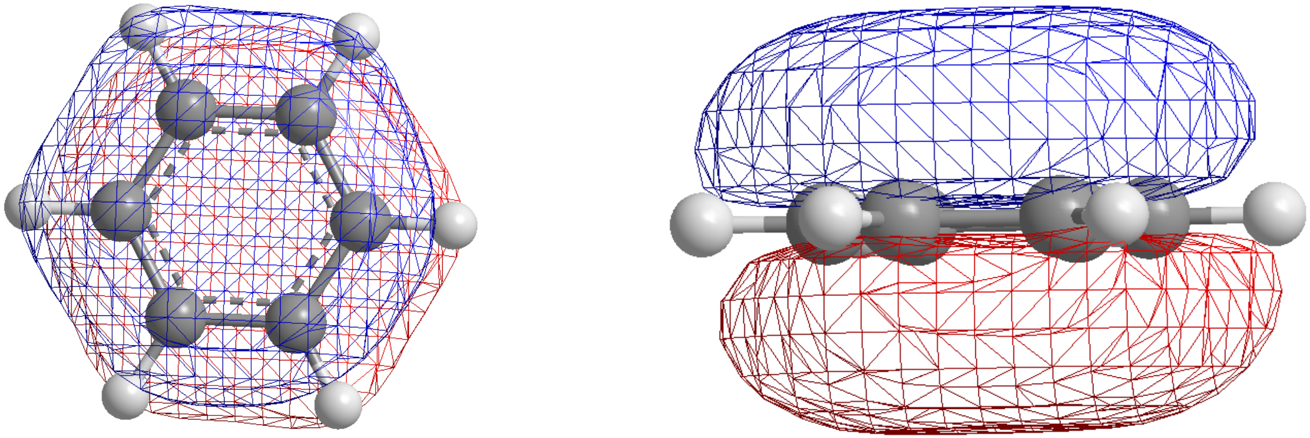
In other words, Hückel’s rule states that;

Planar
cyclic rings
with 2, 6, 10, 14,…, delocalized electrons

should be aromatic.

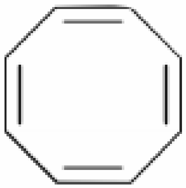
Benzene is

- [6]annulene,
- cyclic,
- planar
- 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). Hückel's rule predicts cyclobutadiene to be antiaromatic.

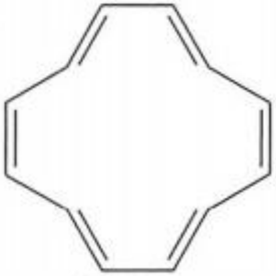
- Cyclooctatetraene is [8]annulene, with **eight** pi electrons (four double bonds) in the classical structure. It is a 4n system, with n = 2. If Hückel's rule were applied to cyclooctatetraene, it would predict antiaromaticity. However, cyclooctatetraene is a stable hydrocarbon with a boiling point of 153°C. It does not show the high reactivity associated with antiaromaticity, yet it is not aromatic either. Its reactions are typical of alkenes.



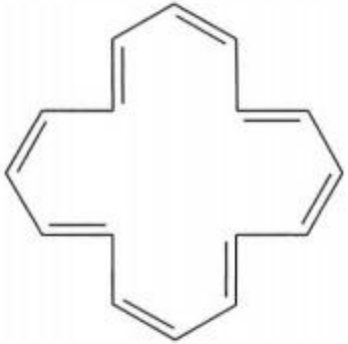
eight pi electrons

Large -Ring Annulenes

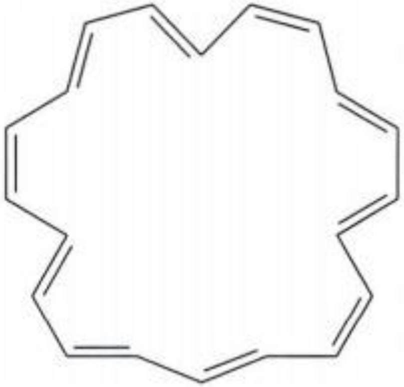
Like cyclooctatetraene, larger annulenes with 4n systems do not show antiaromaticity because they have the flexibility to adopt nonplanar conformations.



[12]annulene



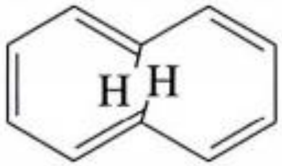
[16]annulene



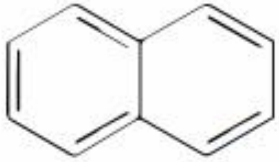
[20]annulene

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.

all-cis
nonaromatic



two trans
nonaromatic



naphthalene
aromatic

Aromatic Ions

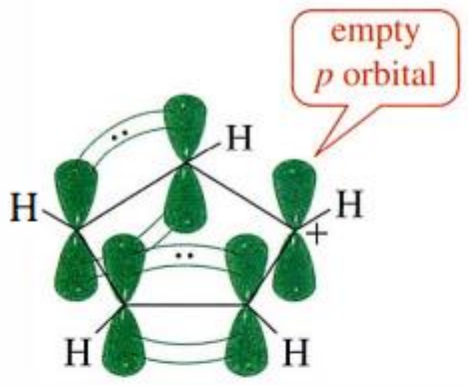
The Cyclopentadienyl Ions

We can draw a five-membered ring of *sp*^{2} -hybrid carbon atoms with all the unhybridized *p* orbitals lined up to form a continuous ring.

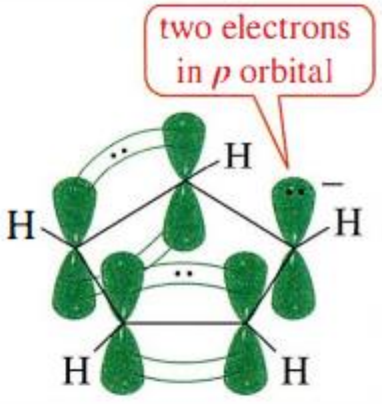
*With five pi electrons, this system would be neutral, but it would be a radical because an odd number of electrons cannot all be paired.

*With four pi electrons (a cation), Hückel's rule predicts this system to be antiaromatic.

*With six pi electrons (an anion), Hückel's rule predicts aromaticity.

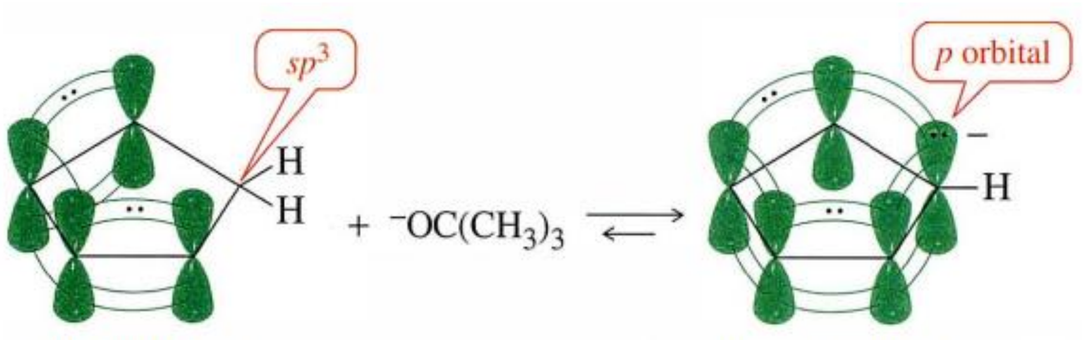


four electrons
cyclopentadienyl cation



six electrons
cyclopentadienyl anion

- Since the **cyclopentadienyl anion** (six pi electrons) is aromatic, it is unusually stable compared with other carbanions.

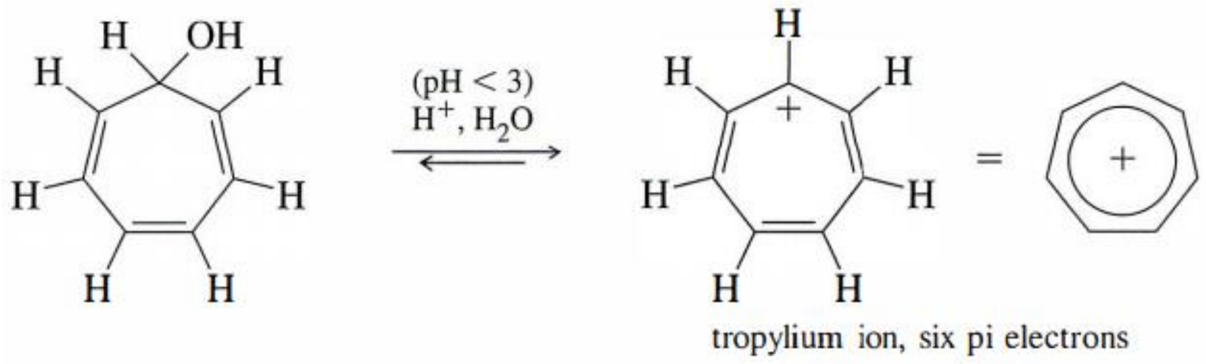


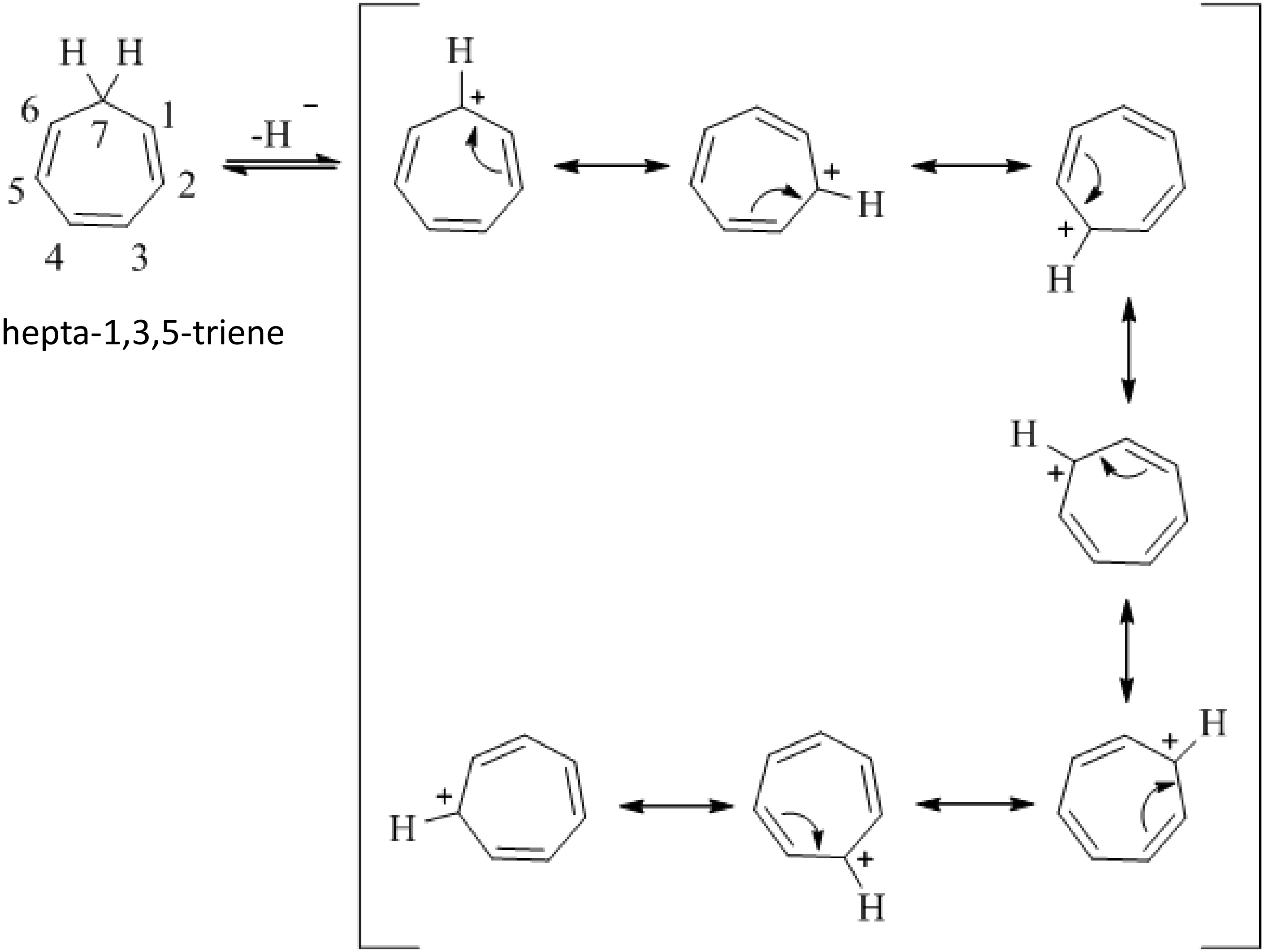
cyclopentadiene
nonaromatic

cyclopentadienyl anion
aromatic

The Cycloheptatrienyl Ions

As with the five-membered ring, we can imagine a flat seven-membered ring with seven ***p*** orbitals aligned. **The cation has six pi electrons**, and the **anion has eight pi electrons**.





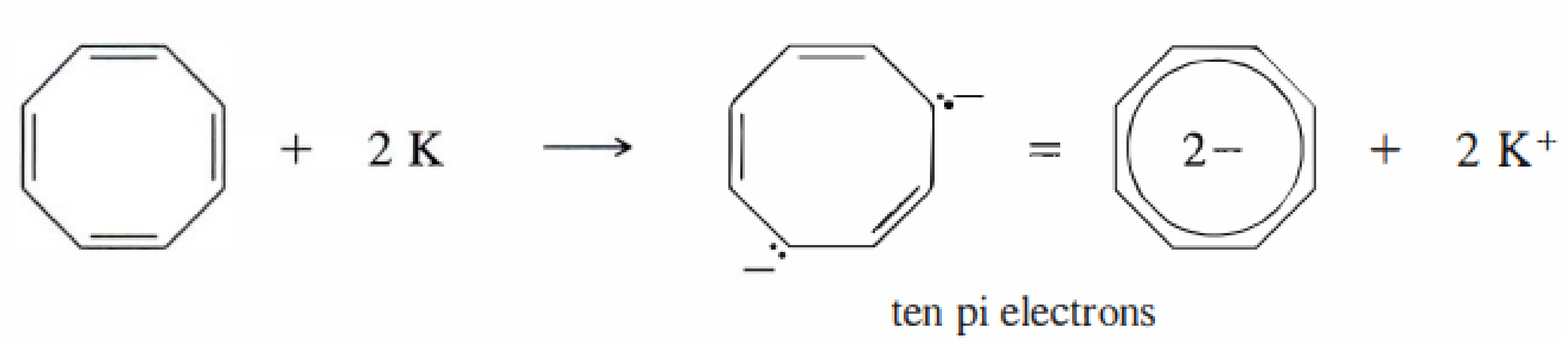
cyclohepta-1,3,5-triene

tropylium ion

The Cyclooctatetraene Dianion

Dianions of hydrocarbons are rare and are usually much more difficult to form.

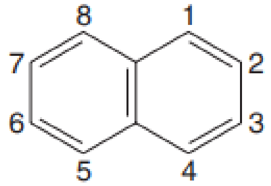
The cyclooctatetraene dianion is easily prepared because it is aromatic.



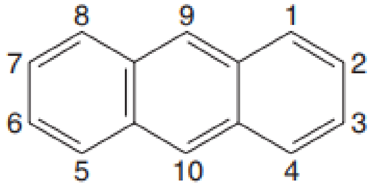
Other Aromatic Compounds

A- Benzenoid Aromatic Compounds

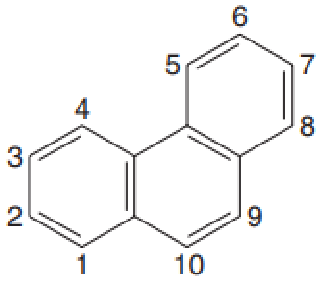
Representatives of one broad class of benzenoid aromatic compounds, called polycyclic aromatic hydrocarbons (**PAH**), are;



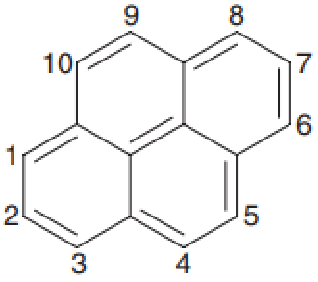
Naphthalene
$C_{10}H_8$



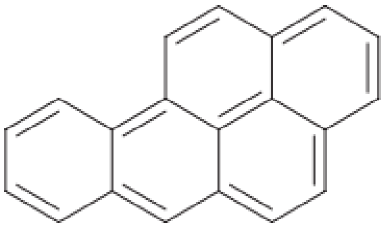
Anthracene
$C_{14}H_{10}$



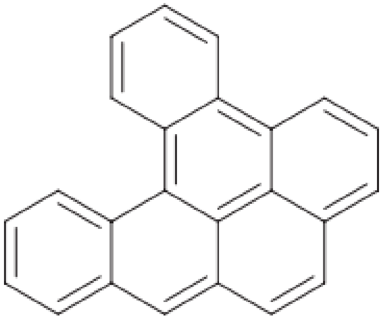
Phenanthrene
$C_{14}H_{10}$



Pyrene
$C_{16}H_{10}$



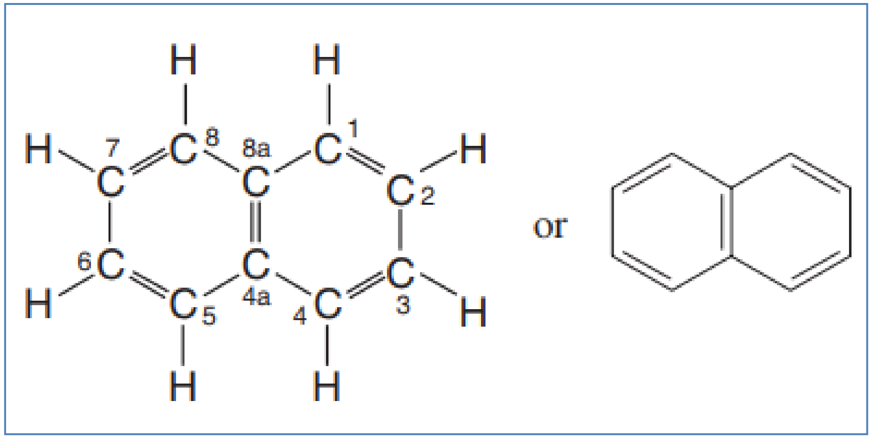
Benzo[*a*]pyrene
$C_{20}H_{12}$

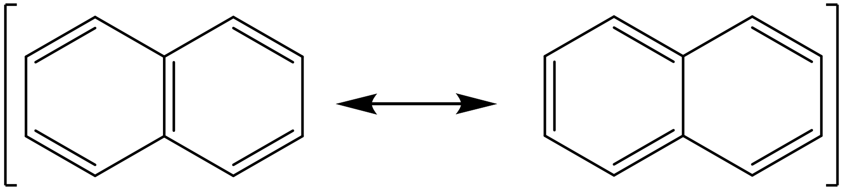


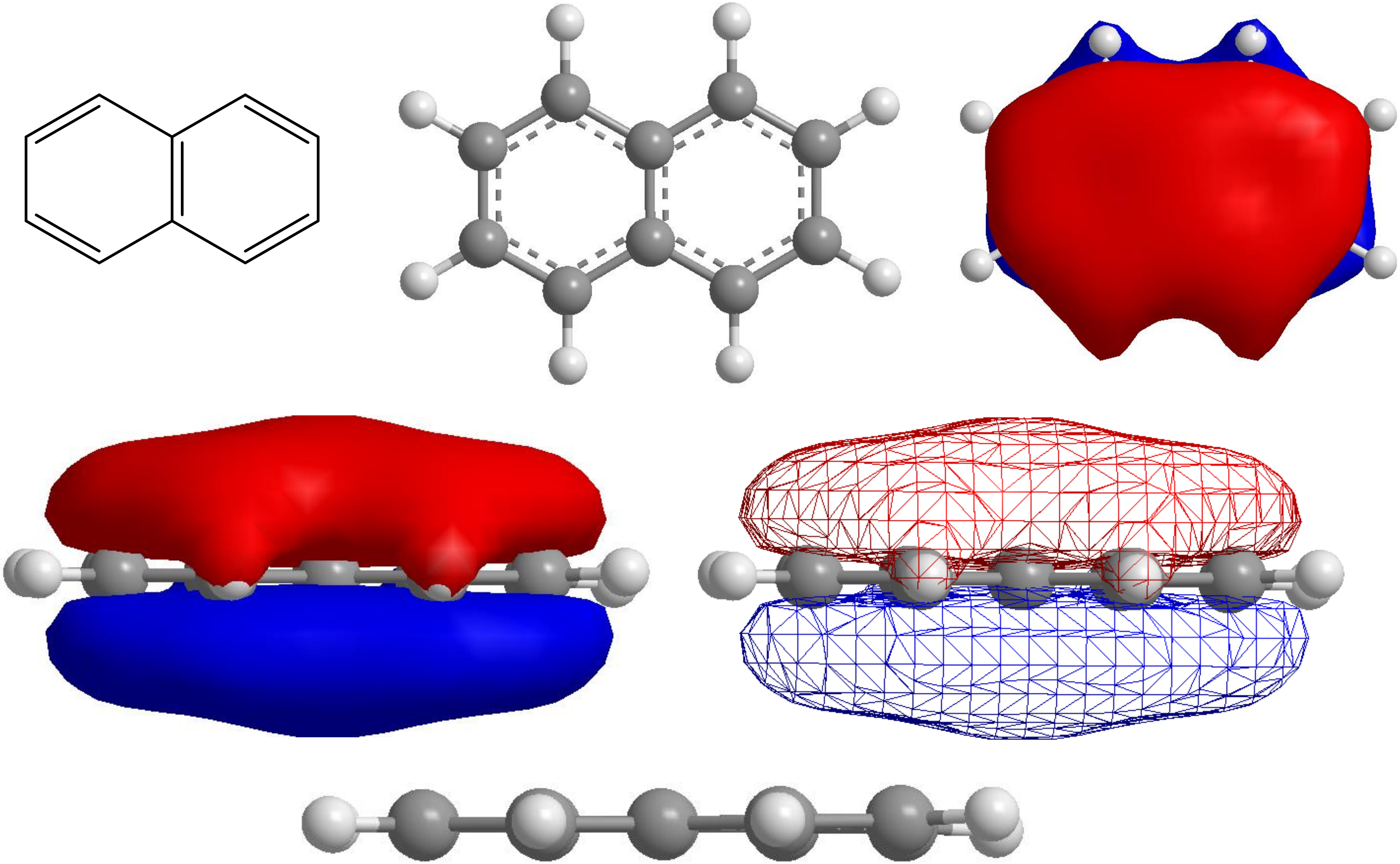
Dibenzo[*a,l*]pyrene
$C_{24}H_{14}$

Naphthalene, $C_{10}H_8$, was the first pure compound to be obtained from the higher boiling fractions of coal tar.

Naphthalene is a planar molecule with two fused benzene rings.

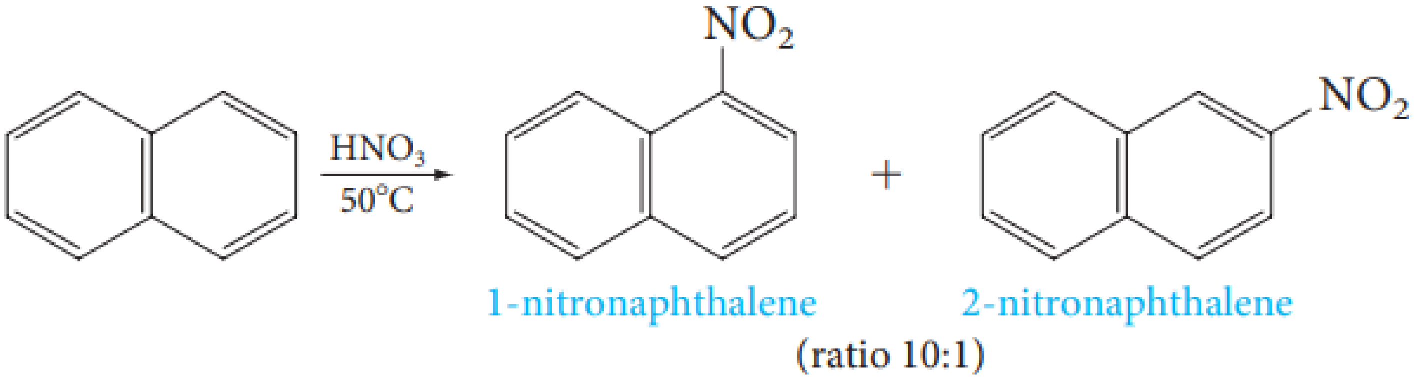






Naphthalene

- Like benzene, naphthalene undergoes electrophilic substitution reactions (halogenation, nitration, and so on), usually under somewhat milder conditions than benzene.



B- Nonbenzenoid Aromatic Compounds

Naphthalene, phenanthrene, and anthracene are examples of benzenoid aromatic compounds. On the other hand,

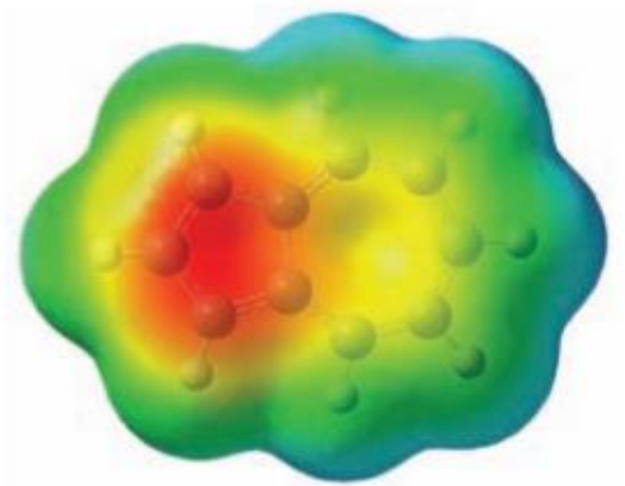
the cyclopentadienyl anion,

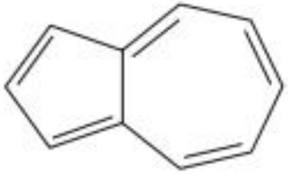
the cycloheptatrienyl cation,

and the aromatic annulenes (except for [6]annulene)

are classified as nonbenzenoid aromatic compounds.

Another example of a nonbenzenoid aromatic hydrocarbon is the compound azulene.

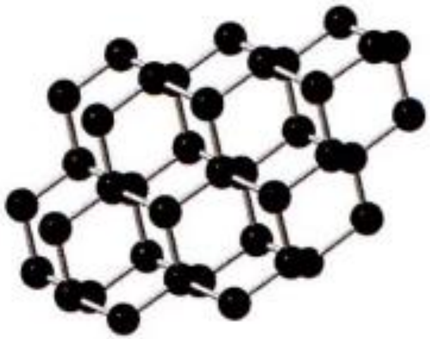




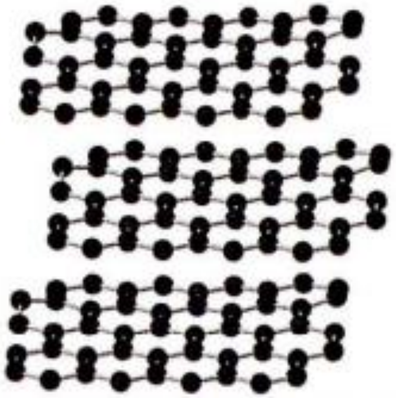
Azulene

C-Fullerenes

Allotropes of Carbon: Diamond and Graphite and Fullerenes



diamond



graphite

Around 1985, Kroto, Smalley, and Curl (Rice University) isolated a molecule of formula C_{60}

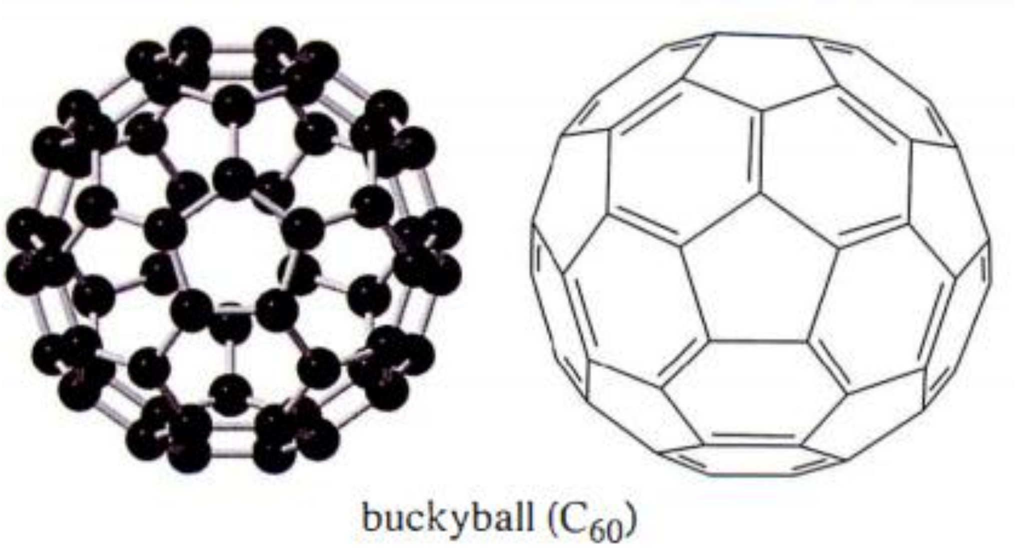
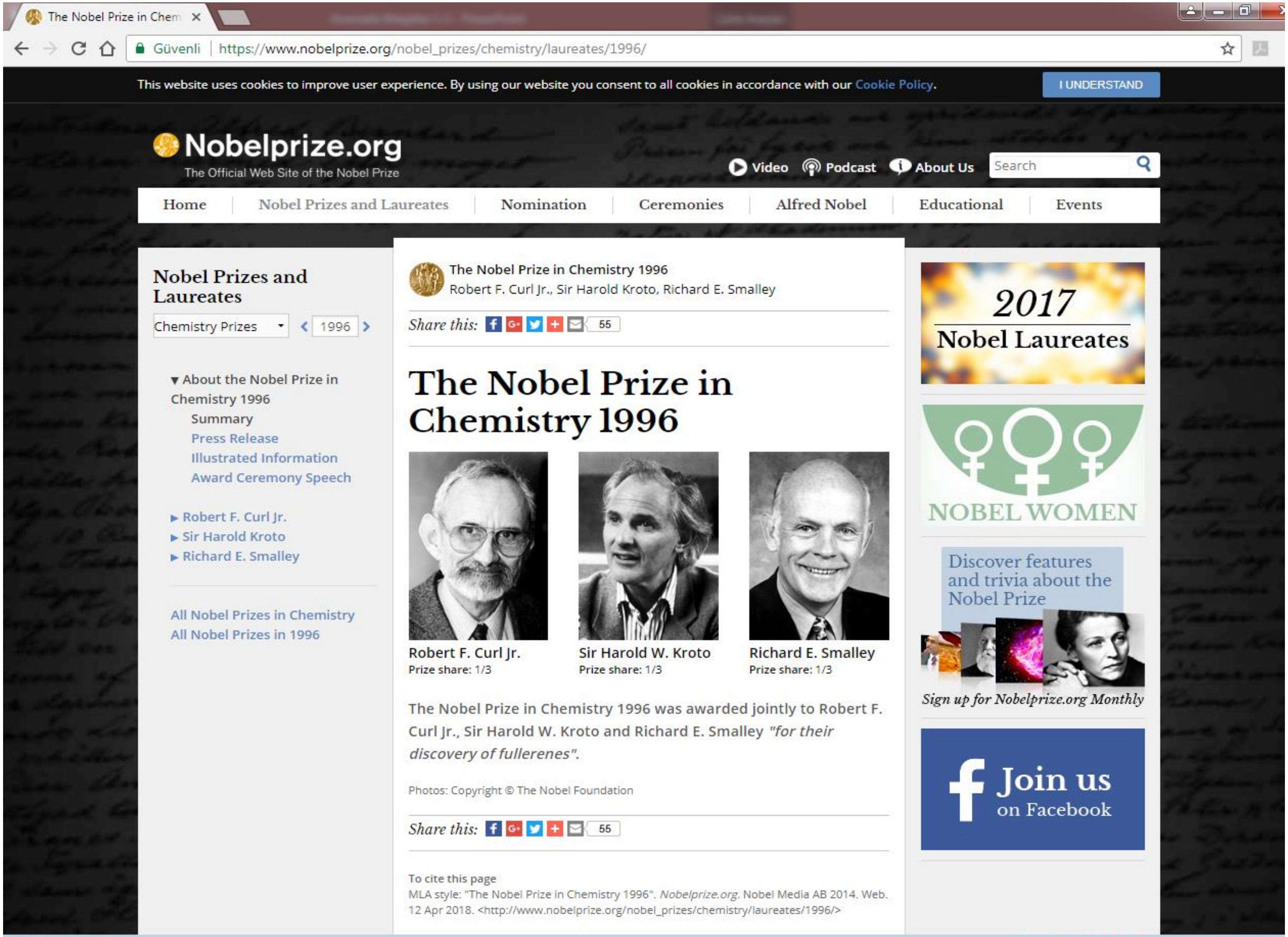

buckyball (C_{60})

Figure shows the structure of C_{60}, which was named buckminsterfullerene in honor of the American architect R. Buckminster Fuller, whose geodesic domes used similar five- and six-membered rings to form a curved roof. The C_{60} molecules are sometimes called "buckyballs," and these types of compounds (C_{60} and similar carbon clusters) are called **fullerenes.**

The Nobel Prize in Chemistry was awarded in 1996 to Professors Curl, Kroto, and Smalley for their discovery of fullerenes.



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  - Award Ceremony Speech
- ▸ Robert F. Curl Jr.
- ▸ Sir Harold Kroto
- ▸ Richard E. Smalley

All Nobel Prizes in Chemistry
All Nobel Prizes in 1996

The Nobel Prize in Chemistry 1996
Robert F. Curl Jr., Sir Harold Kroto, Richard E. Smalley

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The Nobel Prize in Chemistry 1996

Robert F. Curl Jr.	Sir Harold W. Kroto	Richard E. Smalley
Prize share: 1/3	Prize share: 1/3	Prize share: 1/3

The Nobel Prize in Chemistry 1996 was awarded jointly to Robert F. Curl Jr., Sir Harold W. Kroto and Richard E. Smalley *"for their discovery of fullerenes".*

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Physical Properties of Benzene and Its Derivatives

The melting points, boiling points, and densities of benzene and some derivatives are given in Table.

- Benzene derivatives have higher melting points than similar aliphatic compounds.
- The relative boiling points of many benzene derivatives are related to their dipole moments.

Physical Properties of Benzene and Its Derivatives

- Benzene and other aromatic hydrocarbons are slightly denser than the nonaromatic analogues, but they are still less dense than water.
- The halogenated benzenes are denser than water.
- Aromatic hydrocarbons and halogenated aromatics are generally insoluble in water, although some derivatives with strongly polar functional groups (phenol, benzoic acid, etc.) are moderately soluble in water.

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