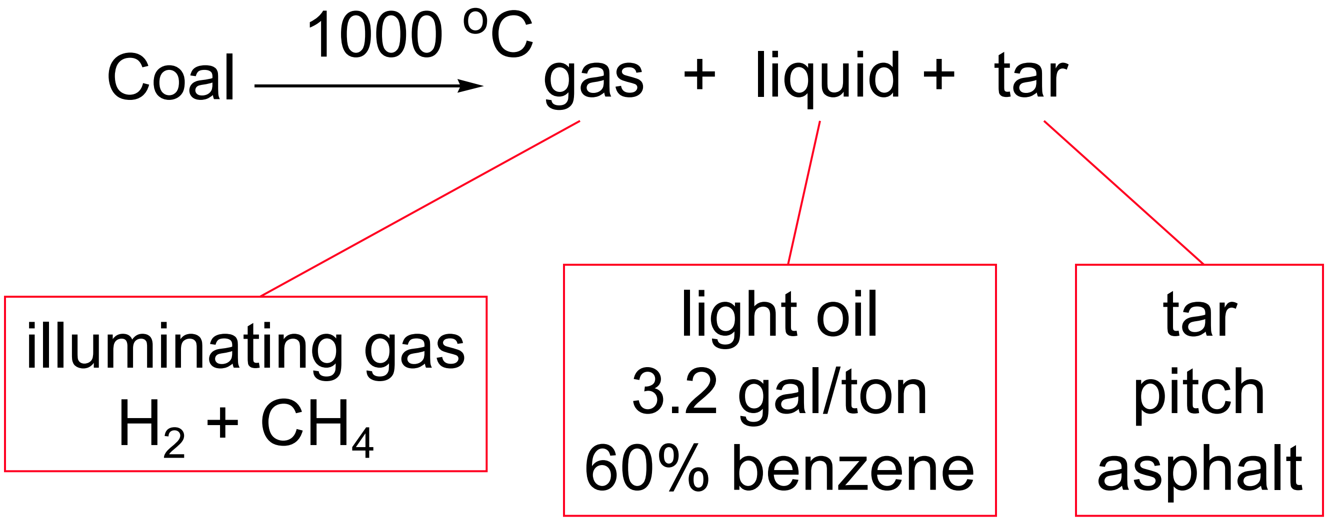
Aromaticity

Coal as a Source of Benzene

1675 - Bituminous coal is distilled to form tars



$$\text{Coal} \xrightarrow{1000\ ^{o}\text{C}} \text{gas} + \text{liquid} + \text{tar}$$

illuminating gas
$H_2 + CH_4$

light oil
3.2 gal/ton
60% benzene

tar
pitch
asphalt

Faraday Isolates Bicarburetted Hydrogen

Michael Faraday
(1791-1867)

1825 - Michael Faraday isolates "bicarburetted hydrogen" ($C_{12}H_6$) from liquid residue in a cylinder of illuminating gas. [C = 6, H = 1]

"One Christmas was so much like another, in those years around the sea-town corner now and out of all sound except the distant speaking of the voices I sometimes hear a moment before sleep, that I can never remember whether it snowed for six days and six nights when I was twelve or whether it snowed for twelve days and twelve nights when I was six."

"A Child's Christmas in Wales" --- Dylan Thomas

The Preparation, Naming and Correct Formula of Benzene

Eilhard Mitscherlich
(1794-1863)

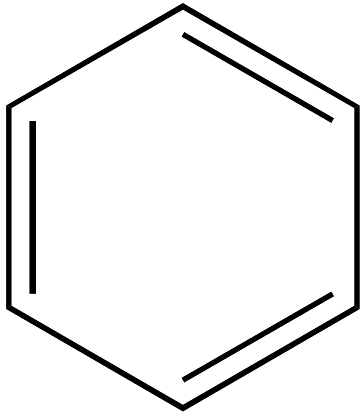
1834 - Mitscherlich prepares benzene (C_6H_6) from benzoic acid by heating with CaO. Benzoic acid was prepared from gum benzoin resin from *Styrax benzoin*.

Kekulé's First Structure of Benzene

August Kekulé

(1829-1896)

1865 - Proposes a cyclic structure for benzene with alternating single and double bonds

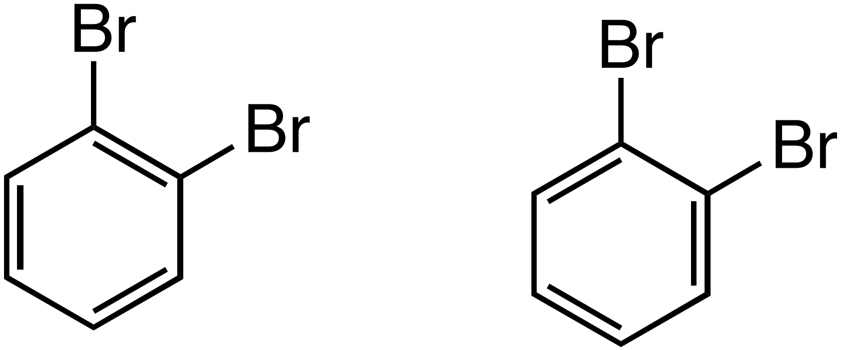


1890- Benzene Fest - Kekulé's Dream

Ladenburg's Riposte

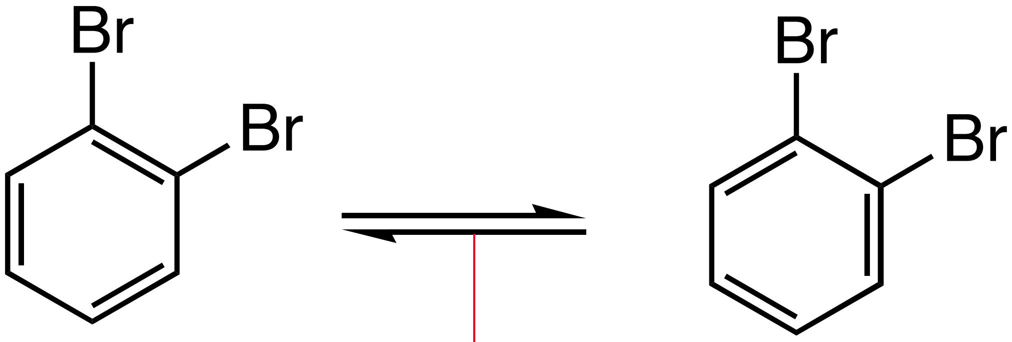
Albert Ladenburg
(1842 - 1911)

Ladenburg, a former student of Kekulé's, objects to his mentor's formula for benzene because only one o-dibromobenzene is known, not two.



Kekule’s Response

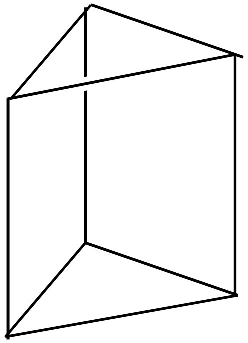
1872 - Kekulé revises his theory, suggesting that the single bonds are changing places with the double bonds.



not resonance - barrier implied

Ladenburg's Prismane Structure

1869 - Ladenburg proposes the prismane structure for benzene.



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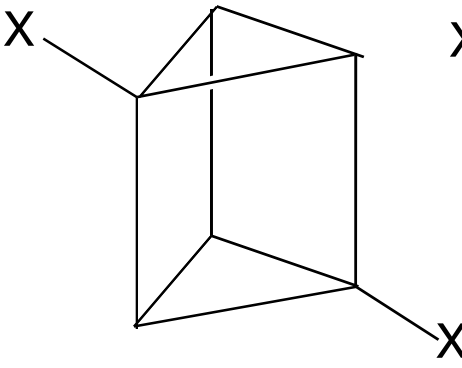
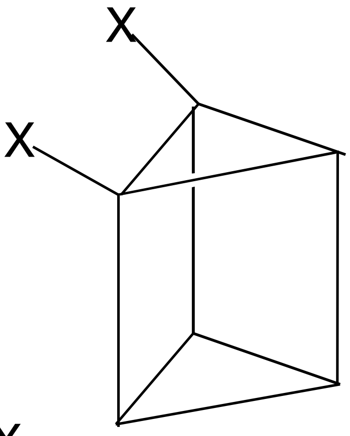
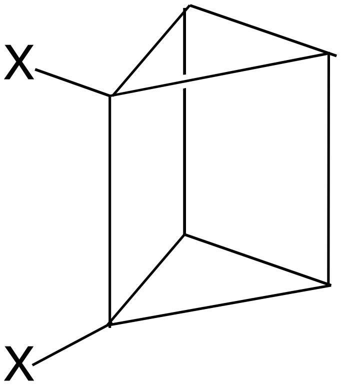


ortho



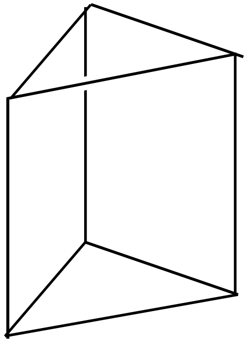
para



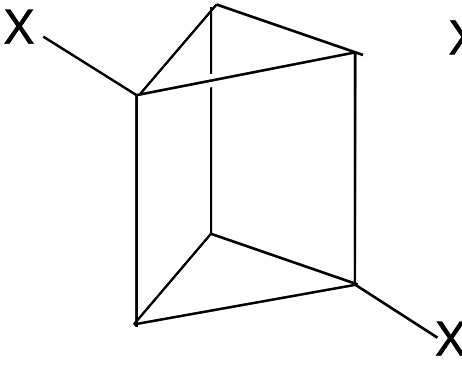
meta

Van't Hoff's Objection

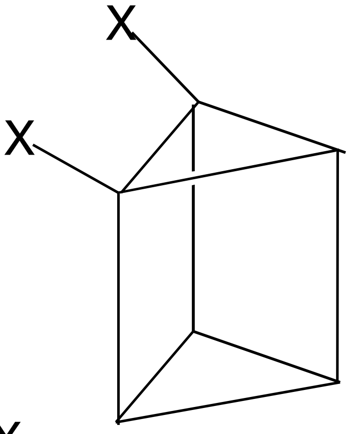
1869 - Ladenburg proposes the prismane structure for benzene.



Van't Hoff objects to Ladenburg's prismane structure because the ortho isomer is chiral and should be resolvable.



ortho



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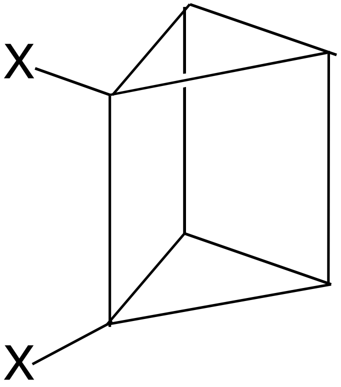
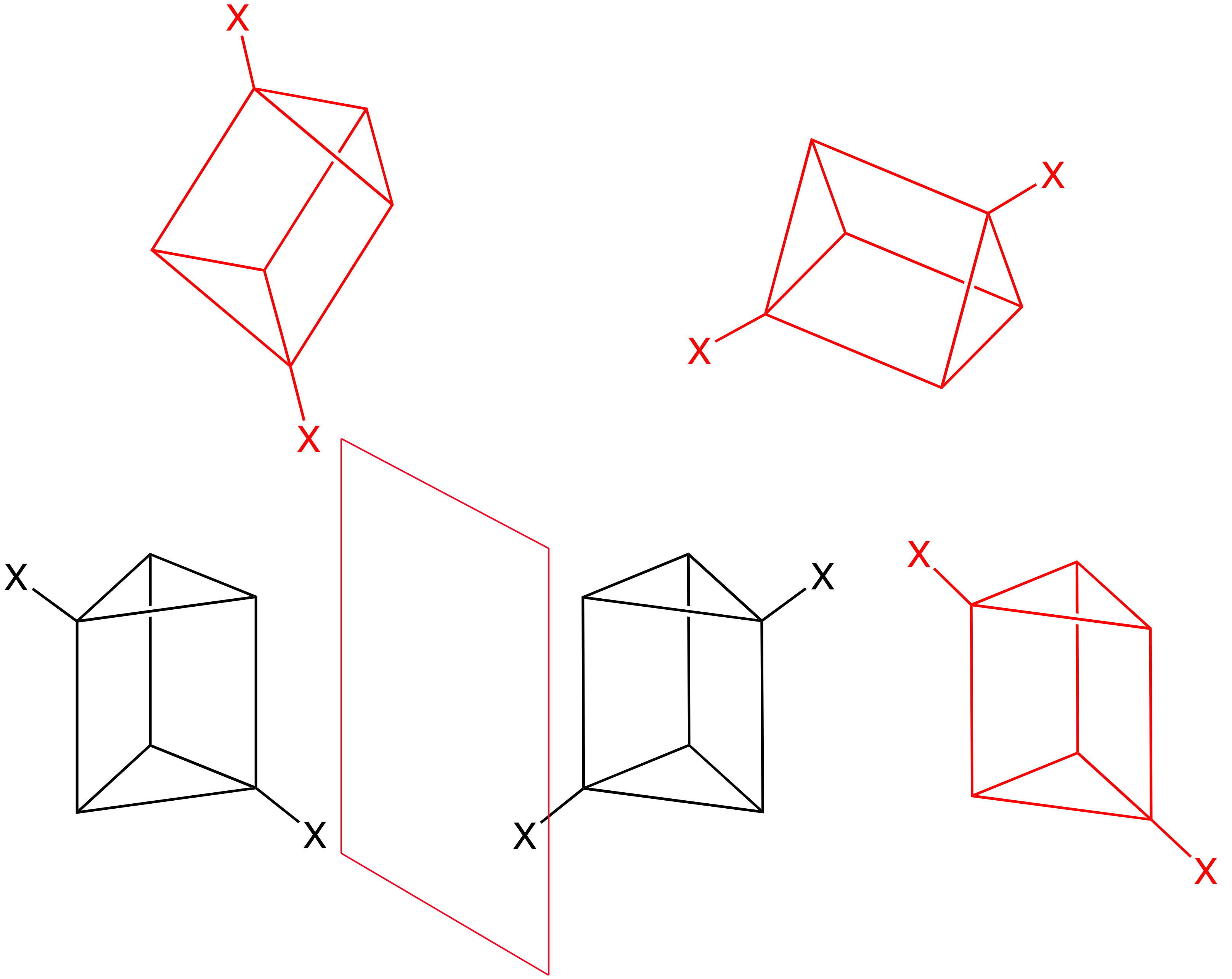


meta

The ortho-Isomer

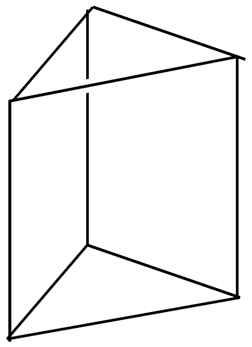


104 Years Later…

1973 - Acton and Katz synthesize prismane.

.

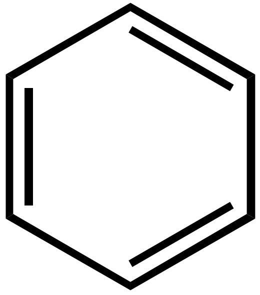
Prismane



^{1}H NMR: δ 2.28, s

^{13}C NMR: 30.6 ppm

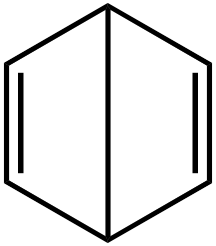
Benzene



^{1}H NMR: δ 7.34, s

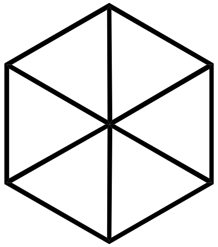
^{13}C NMR: 128.4 ppm

Other Benzenes

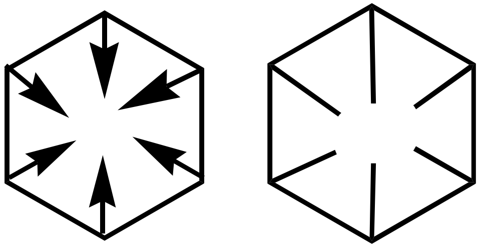


“Dewar benzene”

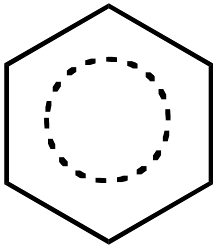
Dewar (1867)
Stadeler (1868)
Wichelhaus (1869)



Claus (1867)

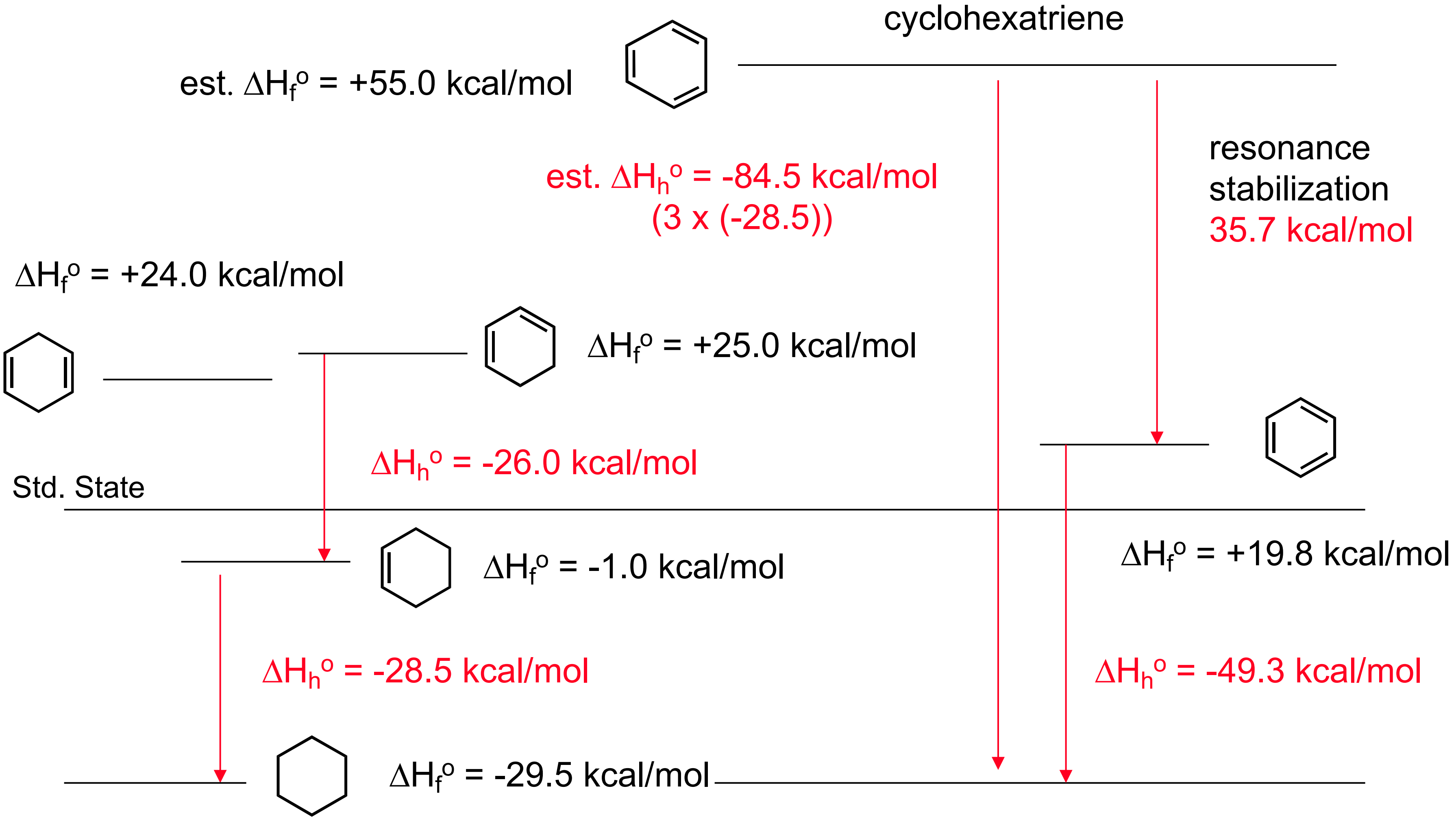


Armstrong-Baeyer (1887)



Thiele (1899)

Cyclohexatriene vs. Benzene



cyclohexatriene

est. ΔH_f^o = +55.0 kcal/mol

est. ΔH_h^o = -84.5 kcal/mol
(3 x (-28.5))

resonance
stabilization
35.7 kcal/mol

ΔH_f^o = +24.0 kcal/mol

ΔH_f^o = +25.0 kcal/mol

ΔH_h^o = -26.0 kcal/mol

Std. State

ΔH_f^o = -1.0 kcal/mol

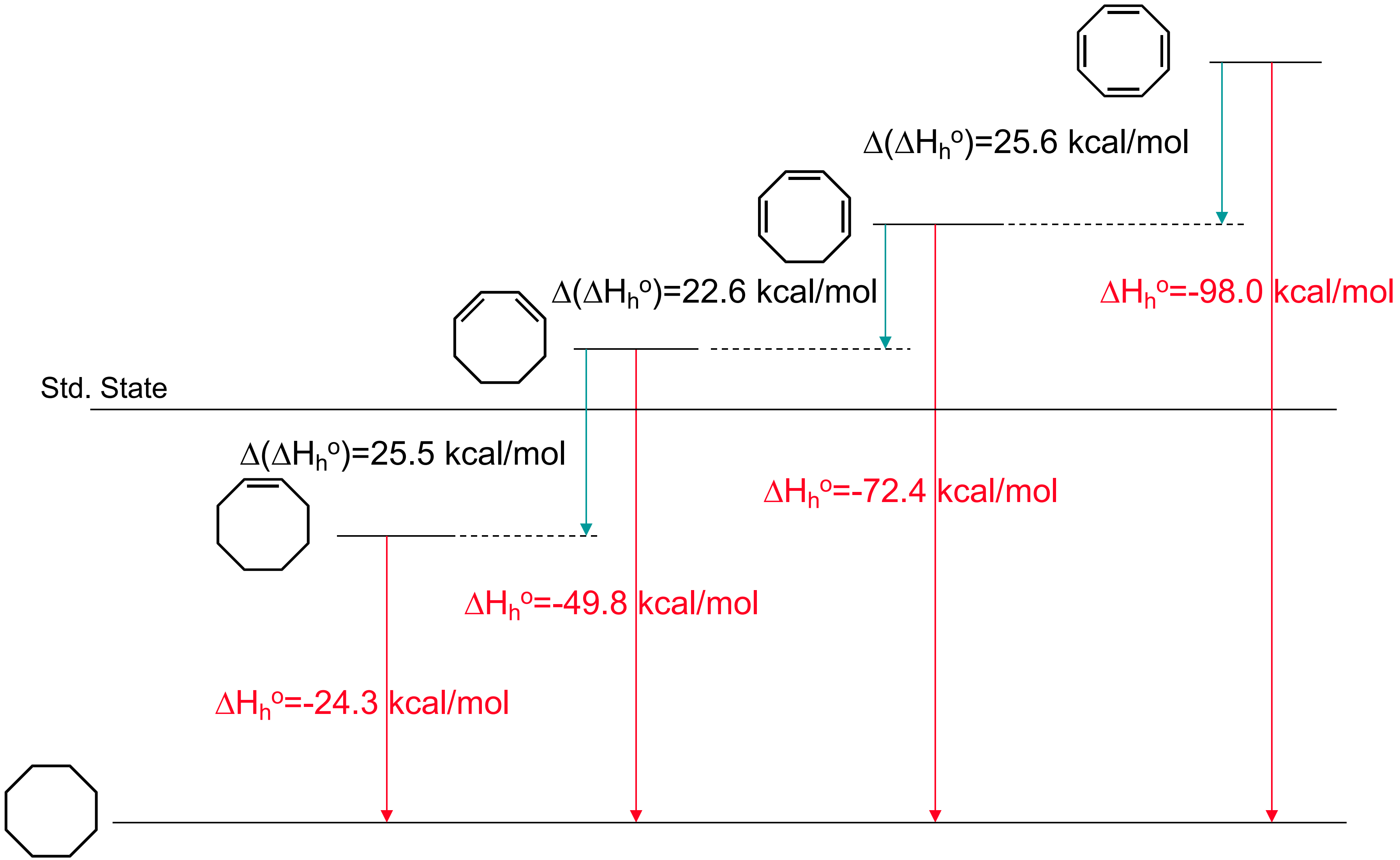
ΔH_f^o = +19.8 kcal/mol

ΔH_h^o = -28.5 kcal/mol

ΔH_h^o = -49.3 kcal/mol

ΔH_f^o = -29.5 kcal/mol

Is Cyclooctatetraene Aromatic?



$\Delta(\Delta H_h^o)$=25.6 kcal/mol

ΔH_h^o=-98.0 kcal/mol

$\Delta(\Delta H_h^o)$=22.6 kcal/mol

Std. State

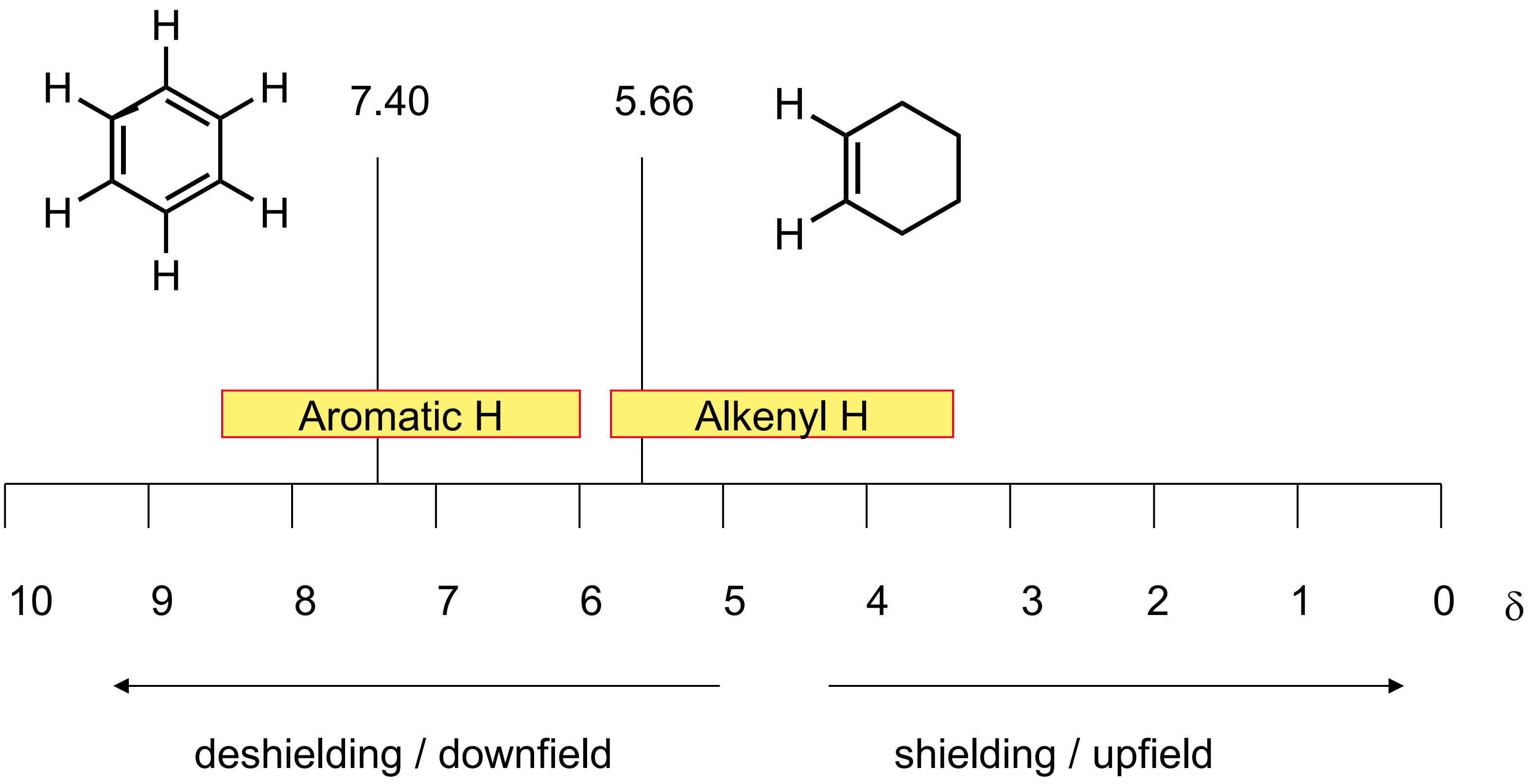
$\Delta(\Delta H_h^o)$=25.5 kcal/mol

ΔH_h^o=-72.4 kcal/mol

ΔH_h^o=-49.8 kcal/mol

ΔH_h^o=-24.3 kcal/mol

^{1}H NMR: Aromatic vs. Alkenyl Hydrogens



7.40

5.66

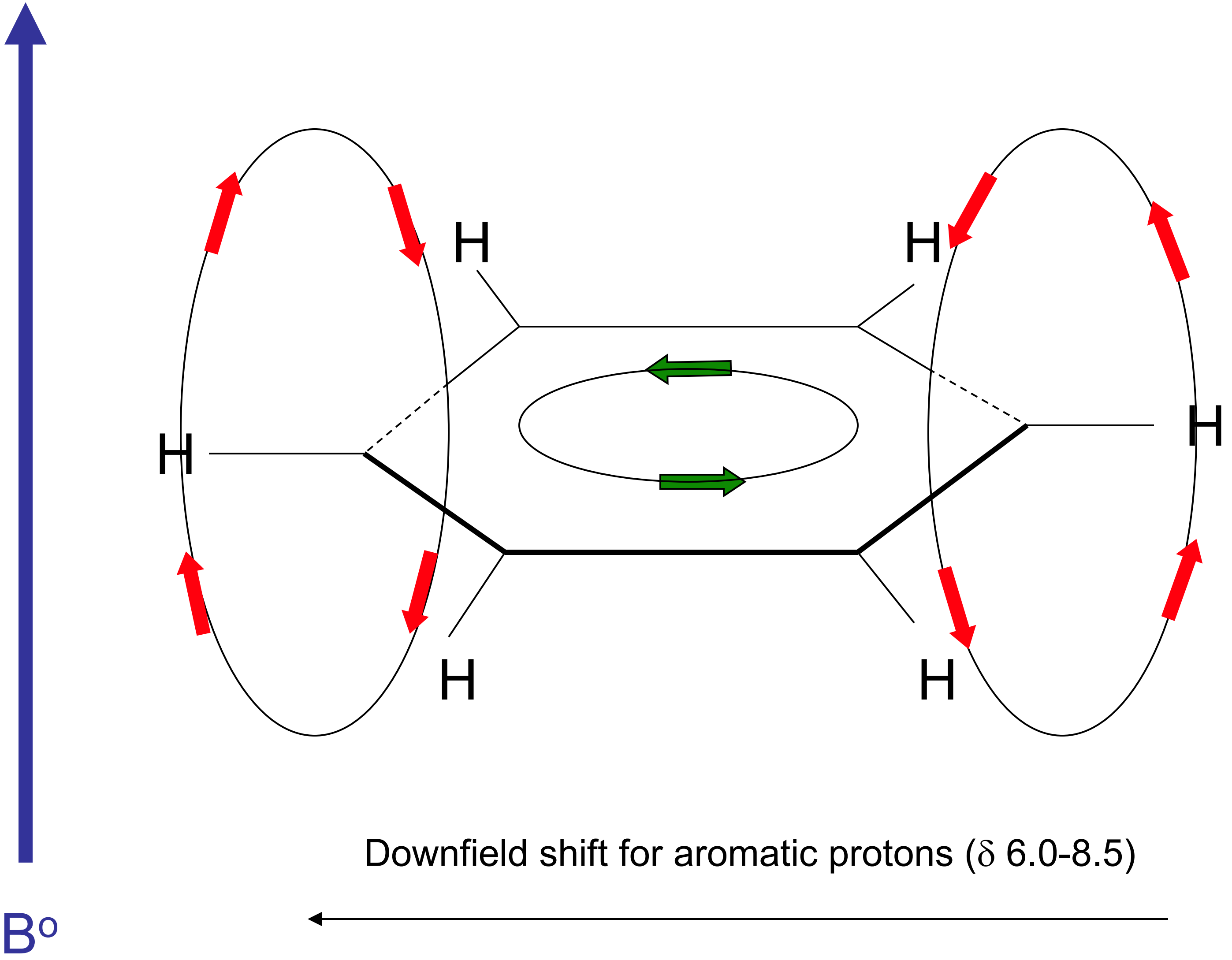
Aromatic H

Alkenyl H

deshielding / downfield

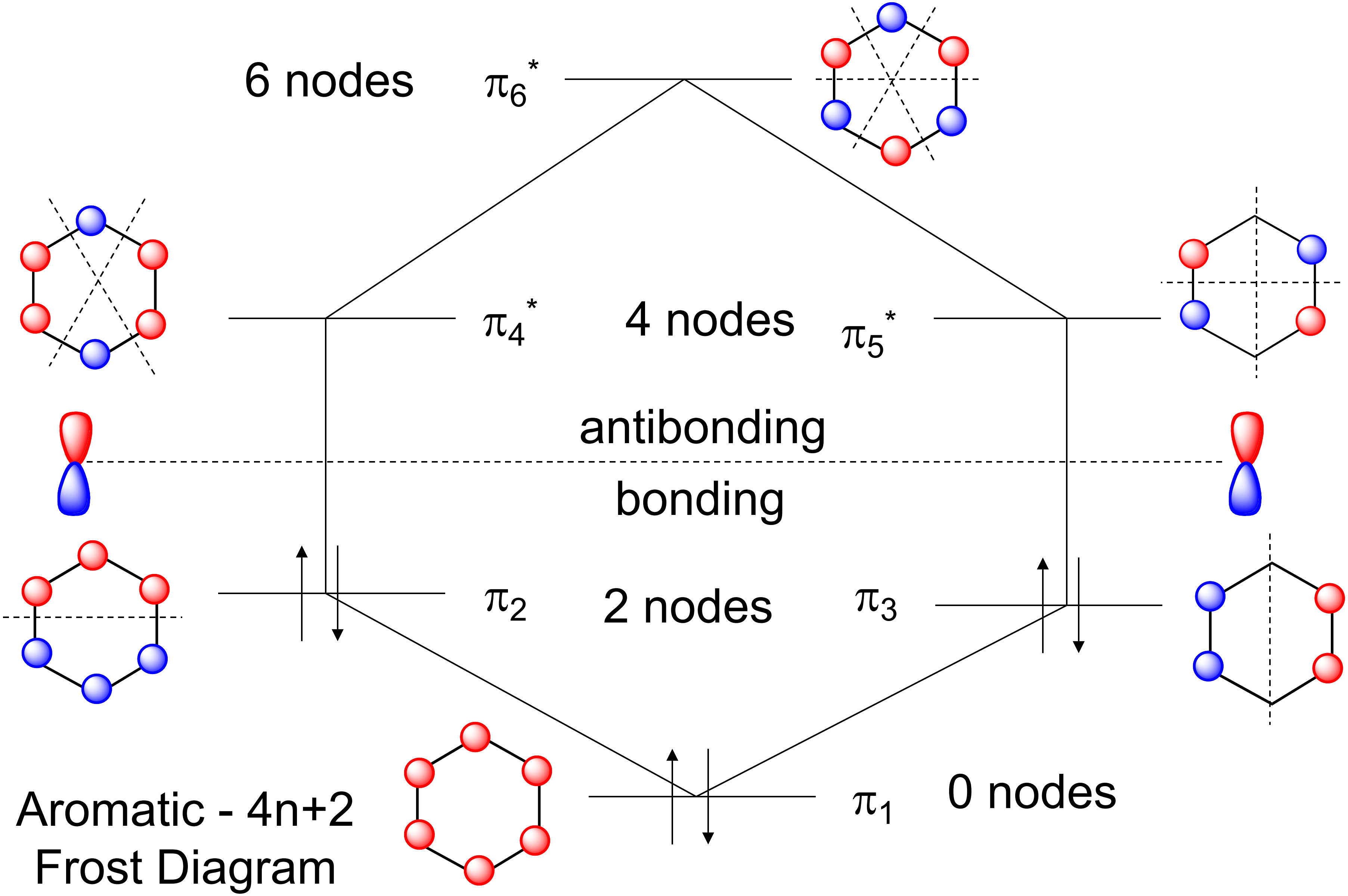
shielding / upfield

Magnetic Anisotropy



Downfield shift for aromatic protons (δ 6.0-8.5)

Molecular Orbitals of Benzene



6 nodes π_6^*

π_4^* 4 nodes π_5^*

antibonding

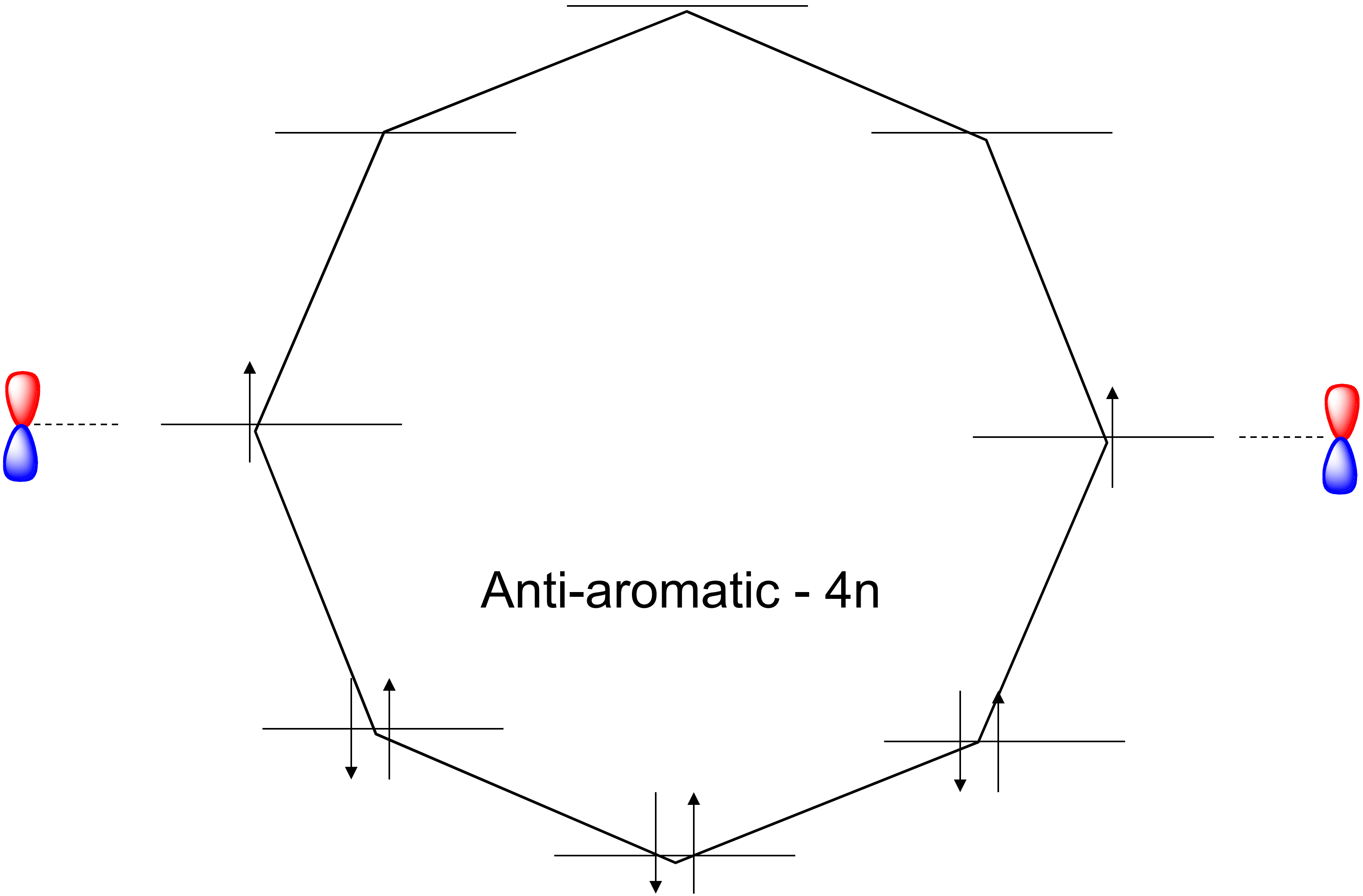
bonding

π_2 2 nodes π_3

π_1 0 nodes

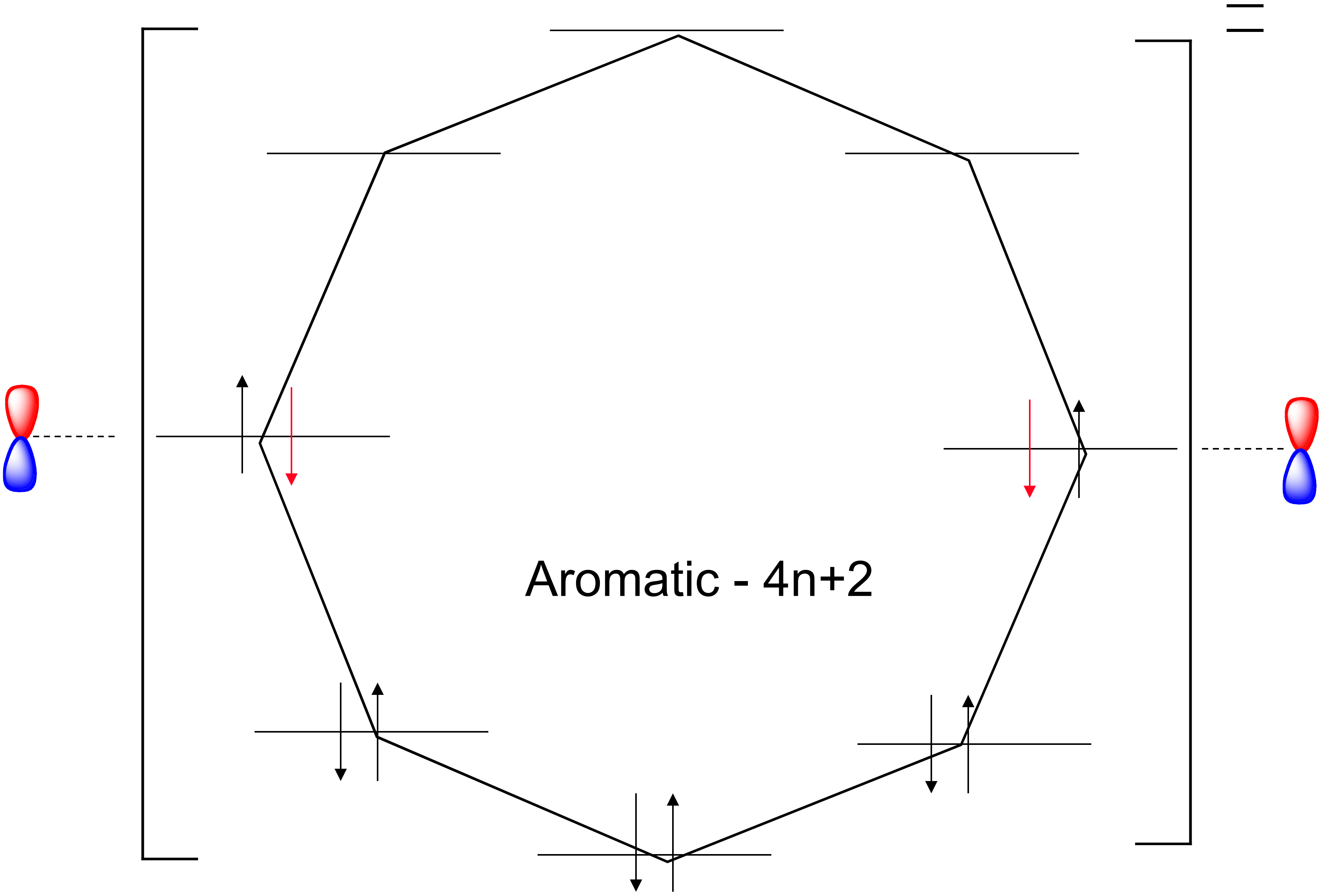
Aromatic - 4n+2
Frost Diagram

Molecular Orbitals of Cyclooctatetraene



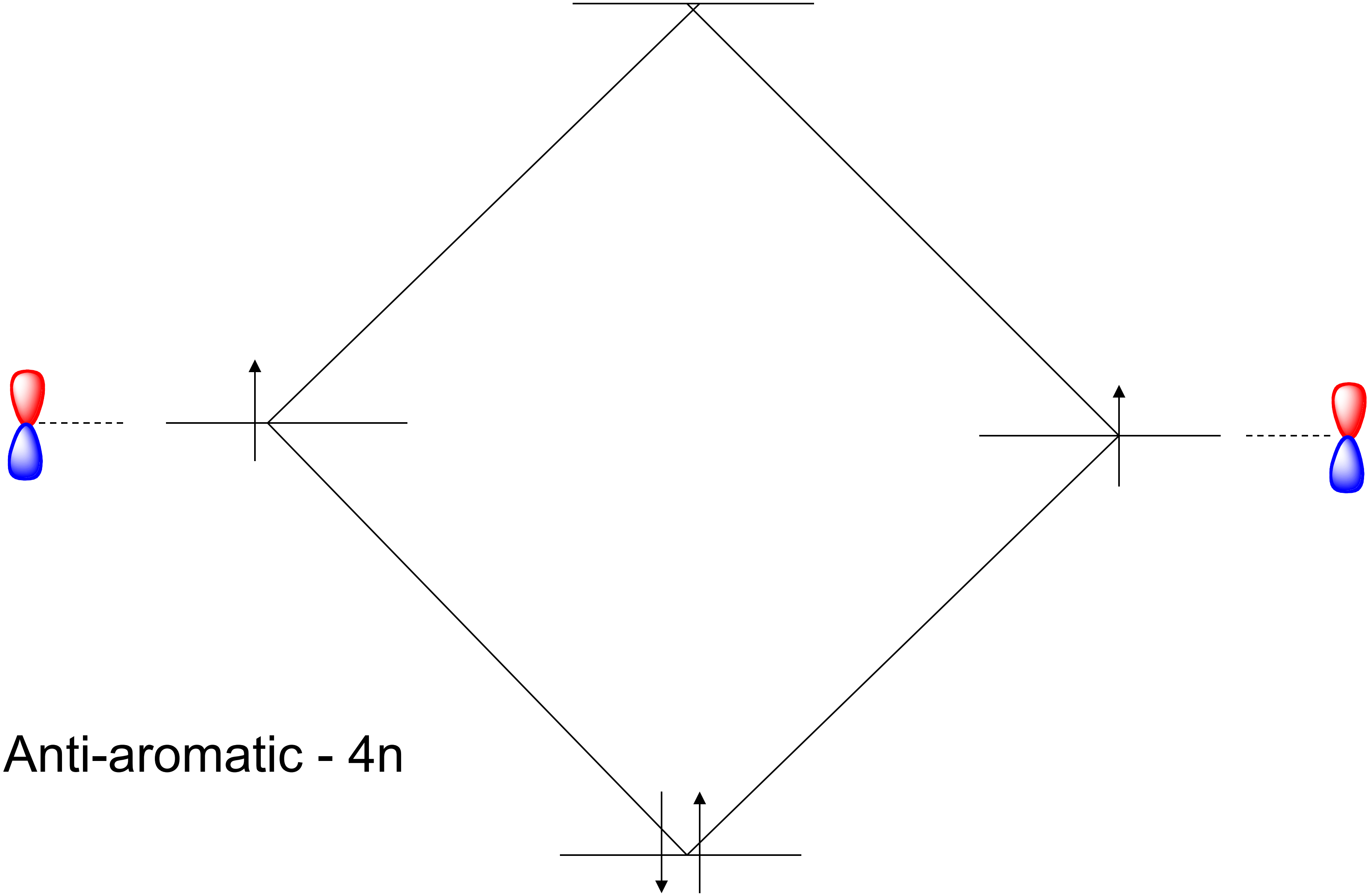
Anti-aromatic - 4n

Molecular Orbitals of Cyclooctatetraene Dianion



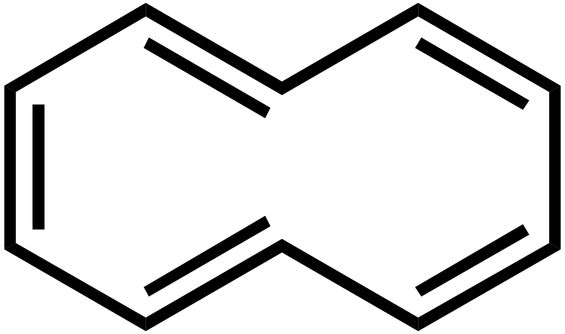
Aromatic - 4n+2

Molecular Orbitals of Cyclobutadiene

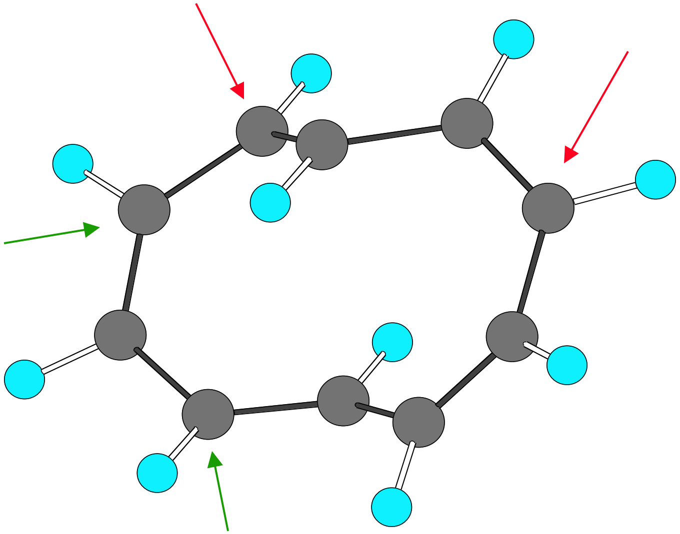


Anti-aromatic - 4n

4n + 2 (E,Z,Z,E,Z)-Cyclodecapentaene



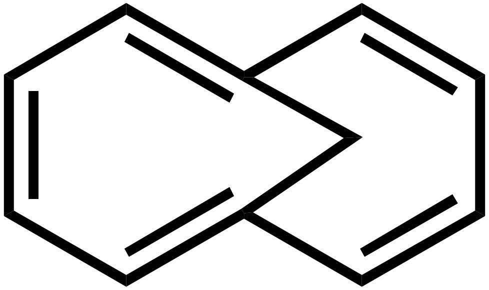
(E,Z)-Dihedral angle = 48°

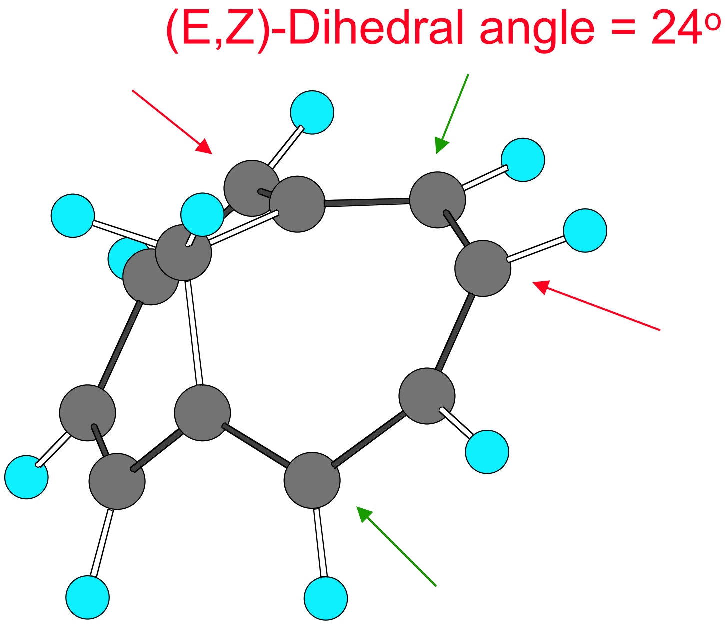


(Z,Z)-Dihedral angle = 31°

4n + 2, non-planar; non-aromatic!

1,6-Methano-(E,Z,Z,E,Z)-Cyclodecapentaene



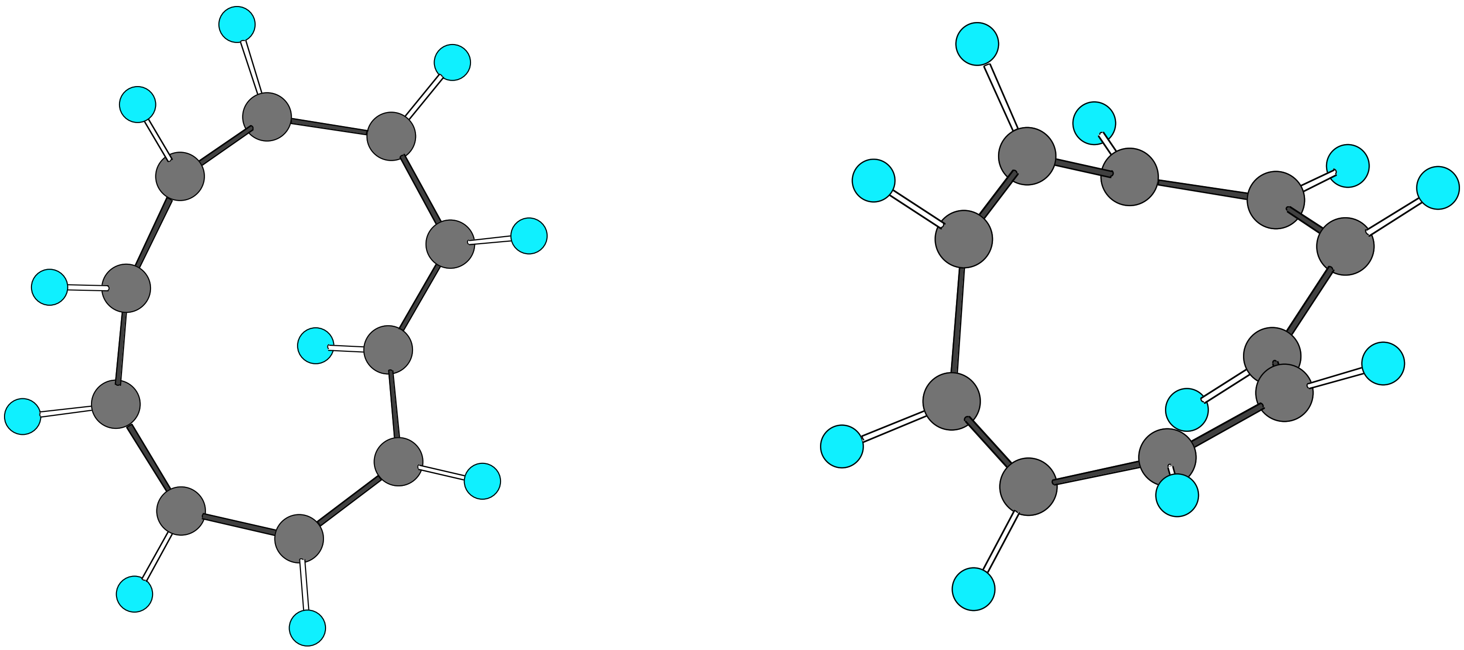


(E,Z)-Dihedral angle = 24°

(Z,Z)-Dihedral angle = 0.5°

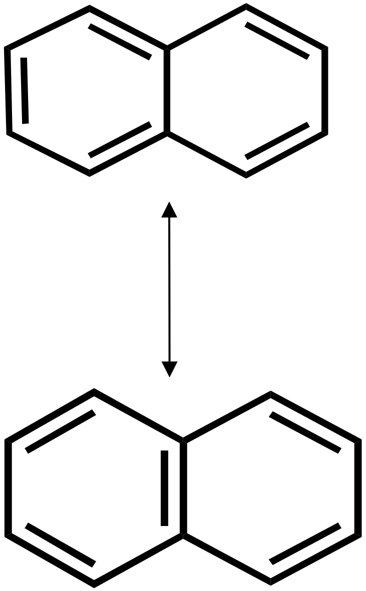
4n + 2, “planar”; aromatic

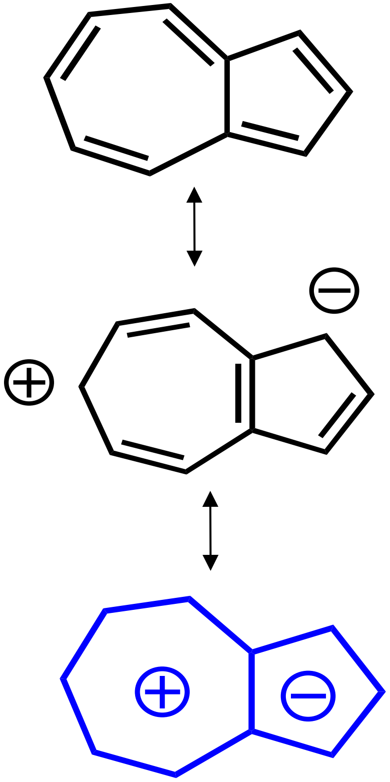
(E,Z,Z,Z,Z,Z)-Cyclodecapentaene



4n + 2, non-planar; non-aromatic

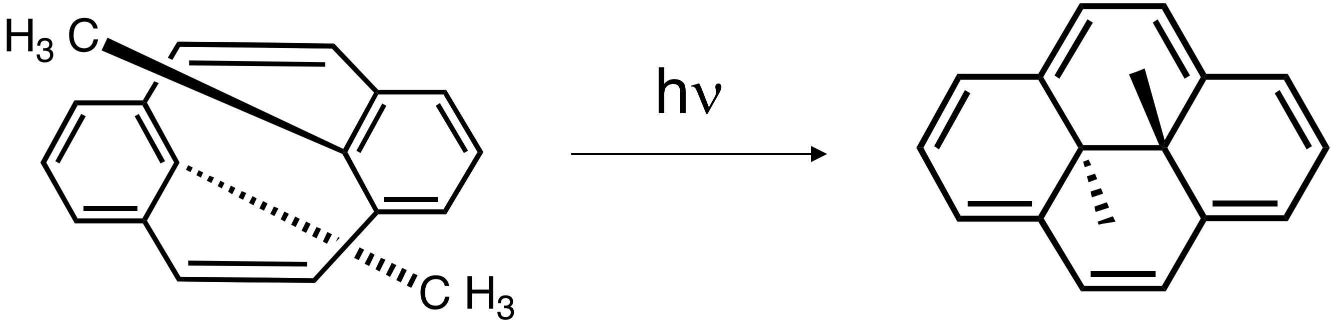
Naphthalene and Azulene



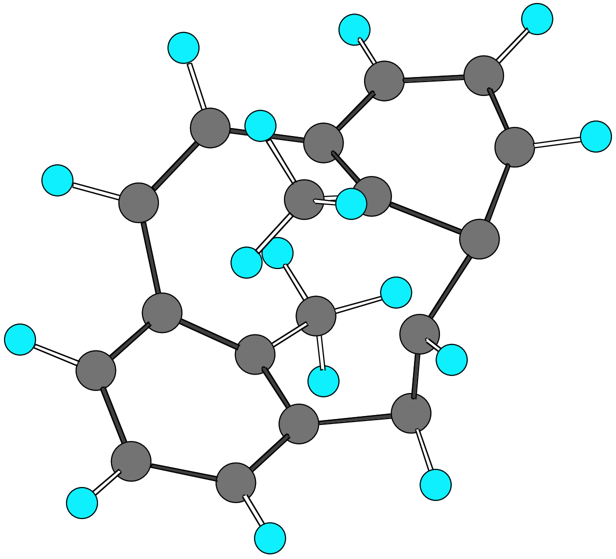


4n + 2, planar; aromatic

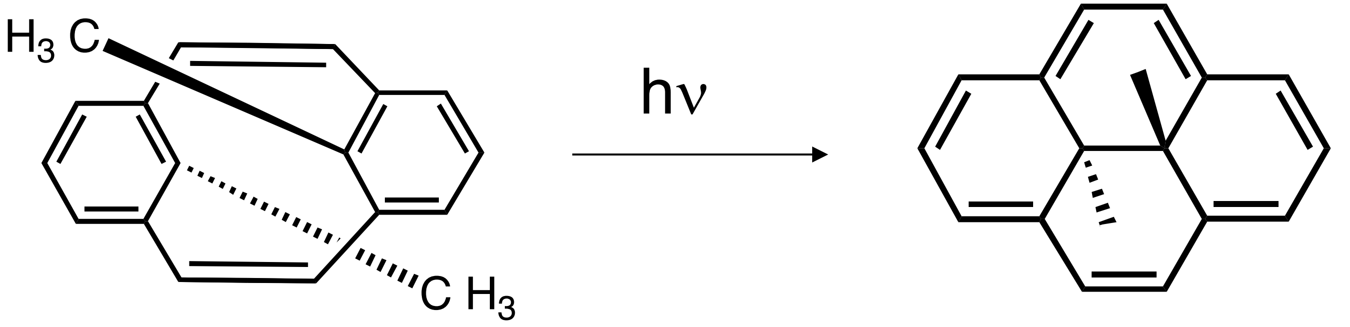
Pyrenes



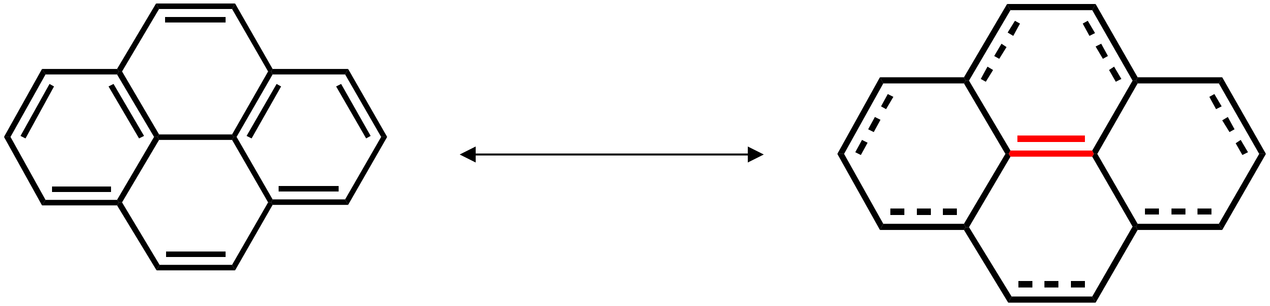
14e: aromatic



Pyrenes



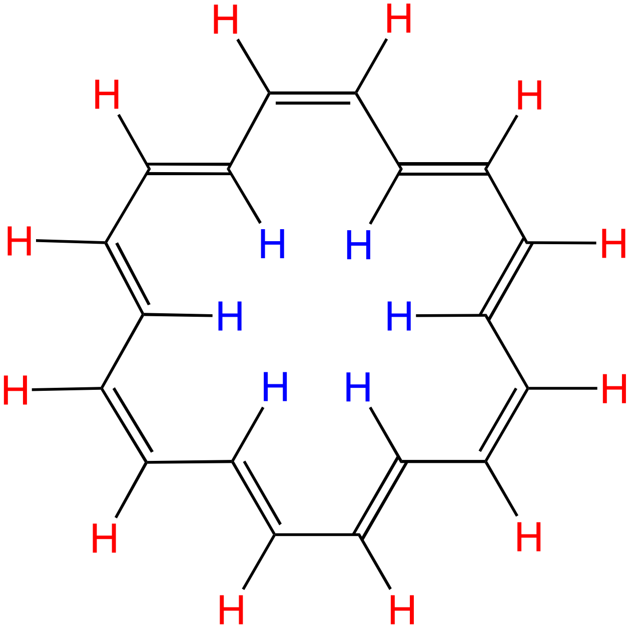
14e: aromatic

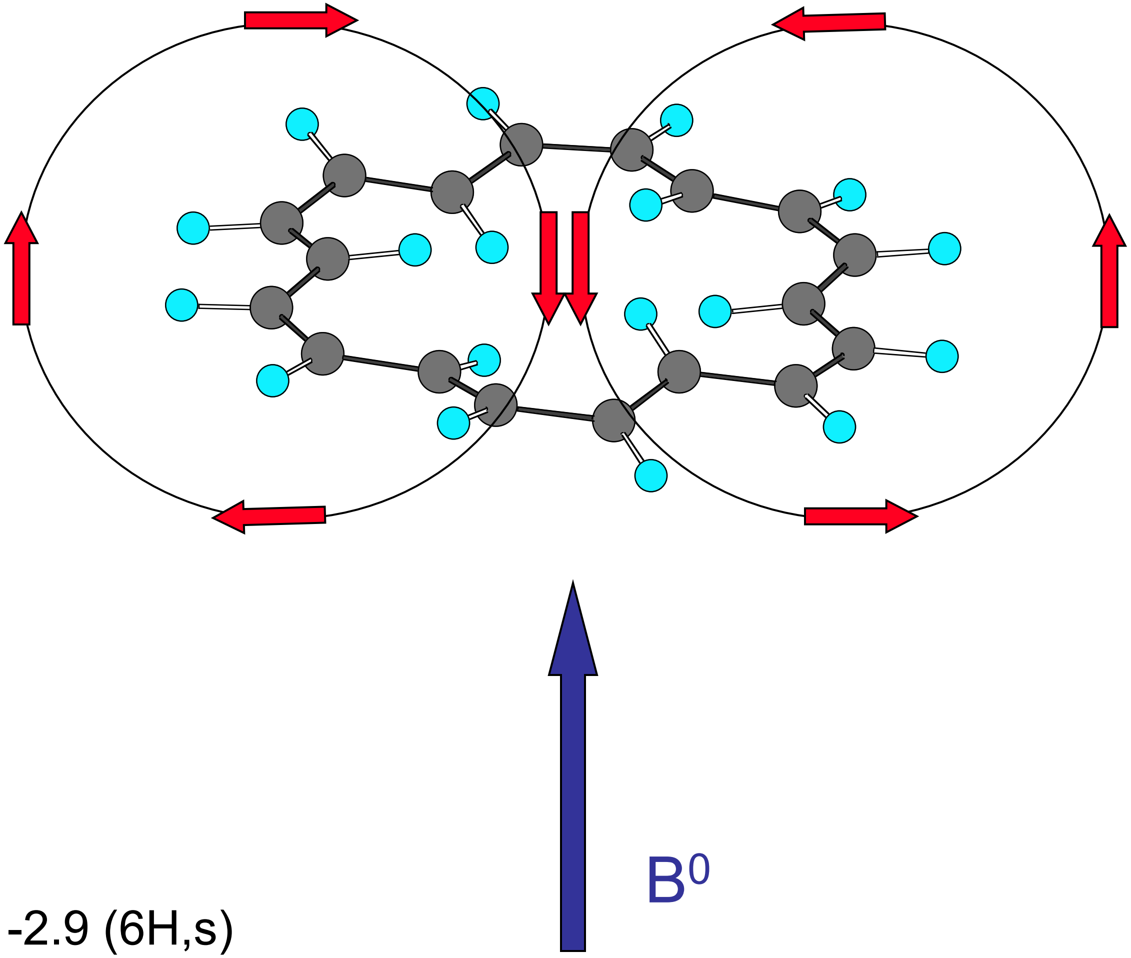


16e: anti-aromatic?

14e: aromatic!

[18]-Annulene



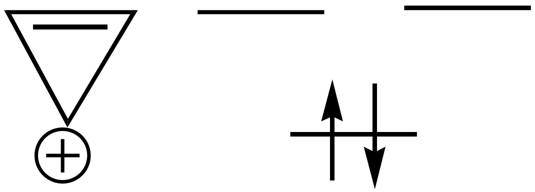


^{1}H NMR:

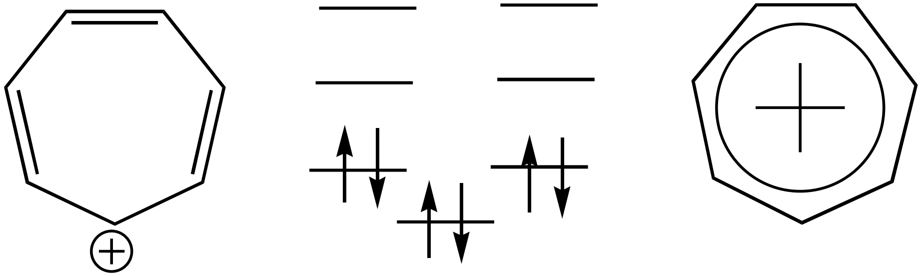
120^{O}C; δ5.45 (18H,s)

-60^{o}C; δ9.25 (12H,s), -2.9 (6H,s)

Aromatic Cations

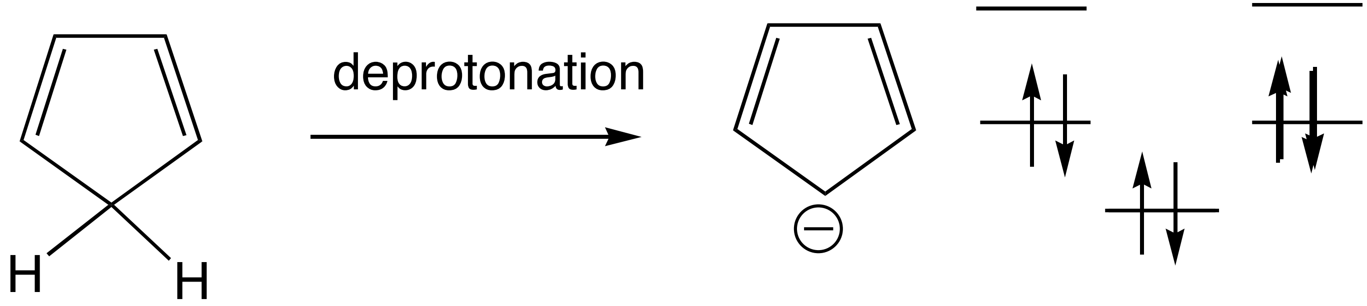


Cyclopropenium cation



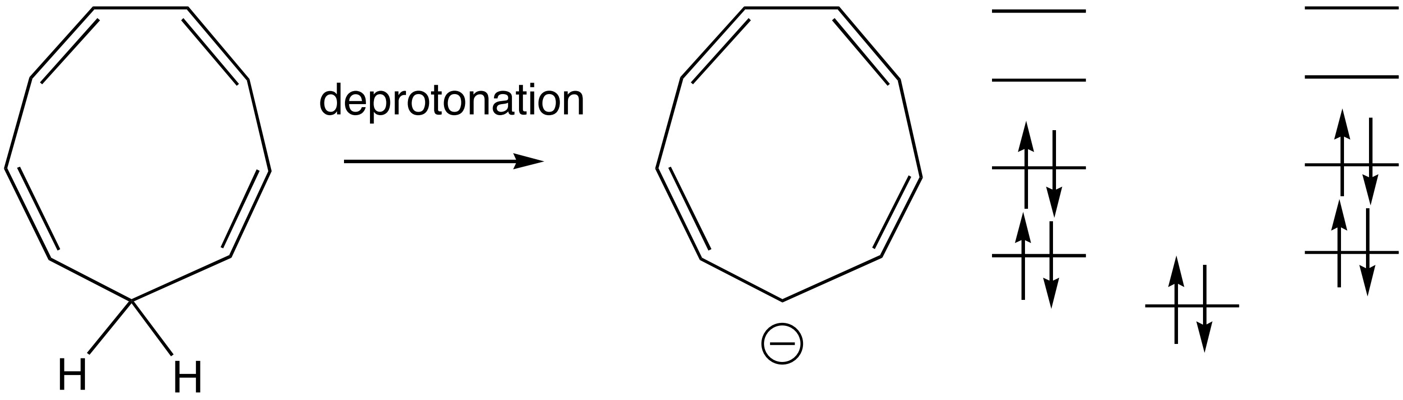
Tropylium cation
^{1}H NMR: δ9.17, singlet

Aromatic Anions



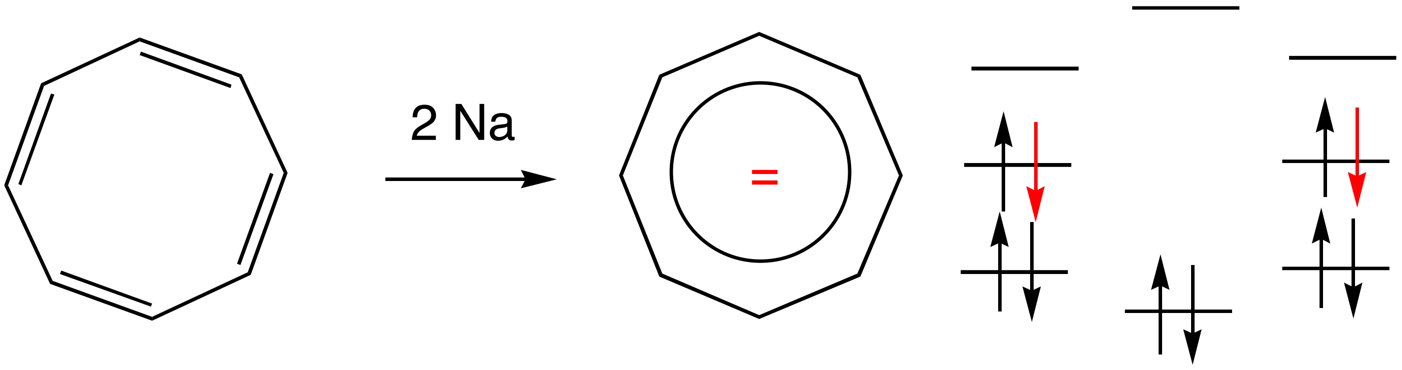
pKa = 16

Cyclopentadienyl anion



Cyclononatetraenyl anion

Aromatic Dianions I



Cyclooctatetraene

anti-aromatic

tub-shaped

^{1}H NMR: δ6.75, singlet

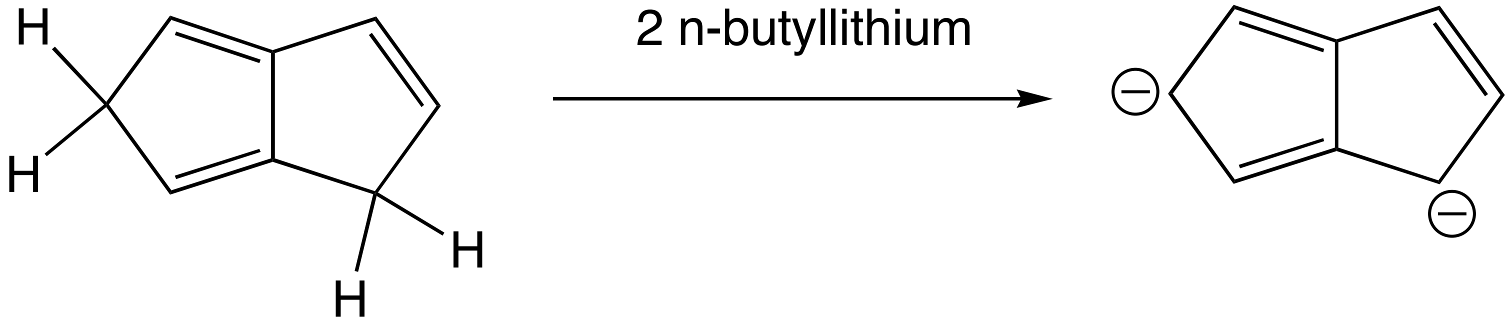
Cyclooctatetraenyl anion

aromatic

planar

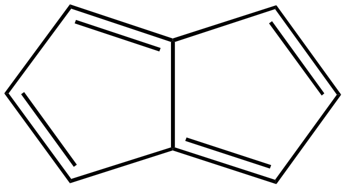
^{1}H NMR: δ5.56, singlet

Aromatic Dianions II

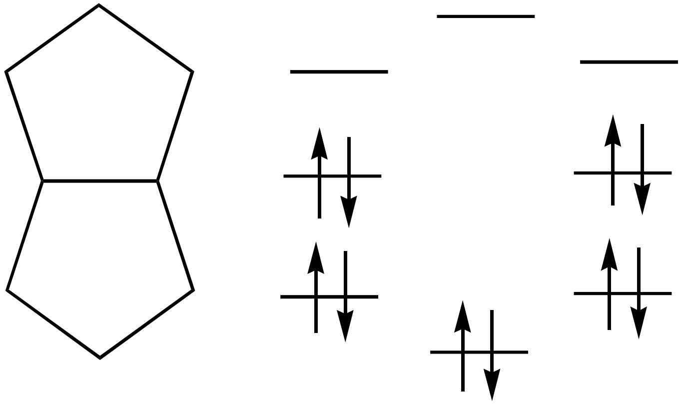


Dihydropentalene

Pentalene dianion



Pentalene



The End