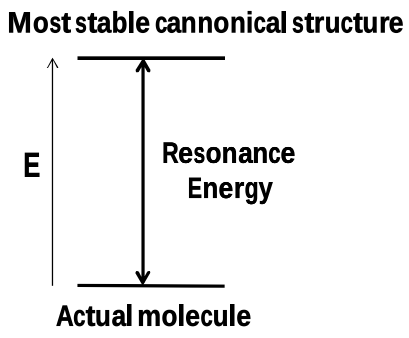
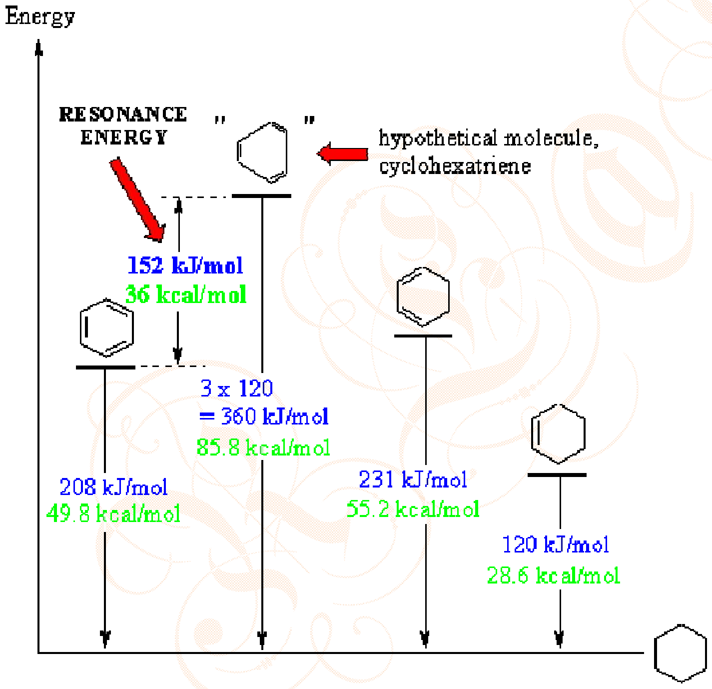
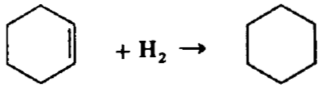
Resonance Energy

The energy difference between the actual molecule and the most stable canonical form (structure) of lowest energy is called ***resonance energy***. The resonance energy is represented by following way:



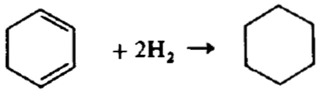


The resonance energy is calculated mainly from heat of hydrogenation (ΔH) data. The heat of hydrogenation of cyclohexene and 1,3 cyclohexadiene are -28.6 Kcal/mole and -55.6 Kcal/mole (nearly twice the cyclohexane). Thus, the heat of hydrogenation of three double bond in Kekule structure i.e for benzene should be -28.6 x 3 = -85.8 Kcal/mole. But when ‘real’ benzene is hydrogenated, only -49.8 Kcal/mole energy is evolved. ‘Real’ benzene is thermodynamically -85.8 – (-49.8) = -36 Kcal/mole energy stable than the hypothetical ‘cyclohexatriene’ by resonance. This compares only 4.0 Kacl/mole energy by which a conjugated diene is stabilized; with respect to its analogue in which there is no interaction between electrons and double bonds. In spite of planar, conjugated structure, the hexatriene has heat of hydrogenation is much higher (about 80.2 Kcal/mole) than benzene indicating the difference in delocalization energy for which the delocalization energy is termed as resonance energy in case aromatic compounds.



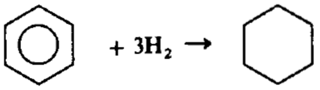
(7)

$\Delta H = -120\ \text{kJ}\ (-28{\cdot}6\ \text{kcal})\ \text{mol}^{-1}$

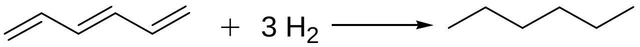


(8)

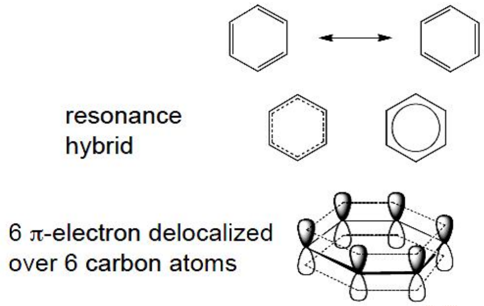
$\Delta H = -232\ \text{kJ}\ (-55{\cdot}6\ \text{kcal})\ \text{mol}^{-1}$



$\Delta H = -208\ \text{kJ}\ (-49{\cdot}8\ \text{kcal})\ \text{mol}^{-1}$

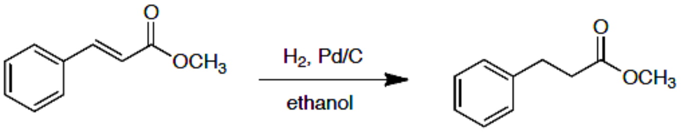


+ 80.2 Kcal /mole

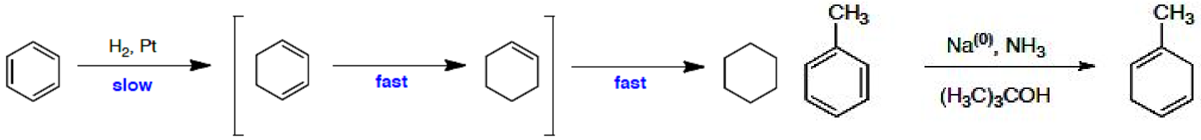


The following examples account why the resonance energy is preserved and the inertness of aromatic ring if other reactive groups are present. Benzene ring normally does not sacrifice its resonance energy because the actual molecule of benzene is energetically much different from its most stable canonical form which is supposed to participate in the reaction. Such energy difference is comparatively small for analogous acyclic molecules.

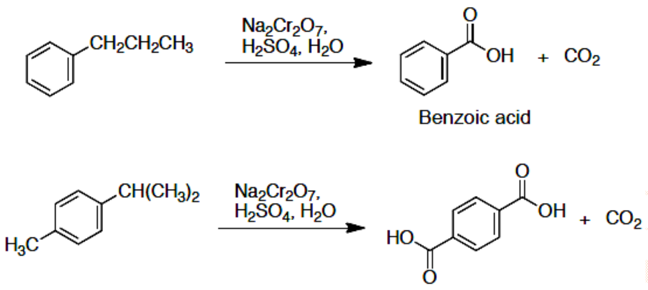
Example-1: The following reaction clearly suggests that the aromatic ring is unaffected by hydrogenation reaction implying high resonance energy as compared to αβ—unsaturated double bond.



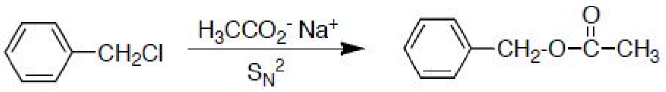
Example-2: Rather the hydrogenation of benzene requires drastic reaction condition like high pressure and temperature or high active catalyst. One of such reaction in benzene is Birch reduction.



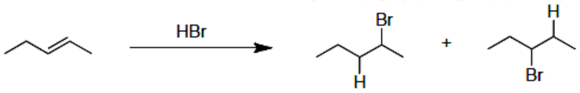
Example-3: Benzene rings do not react with strong oxidant such as $KMnO_4$ or $Na_2Cr_2O_7$; rather it activates benzylic position for oxidation to carboxylic acid.



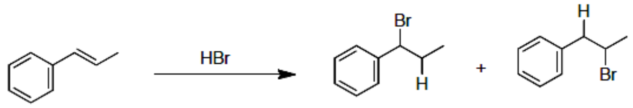
Example-4: The $S_N{}^2$ substitution reaction takes place without affecting the benzene rings.



Example-5: Benzene can influence the addition reaction without directly involving into it.

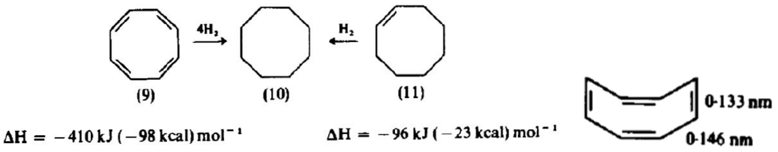


both products observed



not observed

In marked contrast to benzene, the heat of hydrogenation of cyclooctatetraene to cyclooctane is -98 Kcal/mole while that of cyclooctene is -23 Kcal/mole. The difference between ΔH for cyclooctatetraene and 4 x ΔH for cyclooctene is only -98 – (-4 x 23) = -6 Kcal/mole. So, unlike benzene, cyclooctatetraene exhibits no characteristics stabilization when compared with relevant hypothetical cyclic polyene i.e not aromatic.



23 Kcal/mol **49 Kcal/mol** **72 Kcal/mol** **98 Kcal/mol**

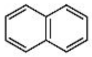
The lack of aromatic character is due to requirement of flat structure of p orbital overlap with a consequent C-C-C bond angle of 135^{o}; resulting considerable ring strain for an array of sp^2 hybridised carbons. Such strain can be relieved by puckering of the ring; but only at the expense of sacrificing the possibility of all p orbitals overlap. The puckering is observed in X-ray crystallography and the cyclooctatetraene is said to be in tub shape.

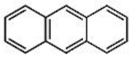
Condition necessary for cyclic polyene to gain resonance energy (or aromatic character is):

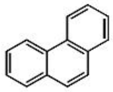
a) The molecule should be flat to allow of cyclic overlap of p orbitals
b) All bonding orbitals should be completely filled
c) It should posses $(4n+2)\pi$ electron system according to Huckel rule.

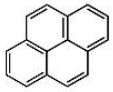
As the number of ring in polyene increases, the resonance energy also increases and hence the reactivity decreases. For example, the rate of nitration /sulfonation/ halogenations / Friedel Craft alkylation in naphthalene is slower than benzene.

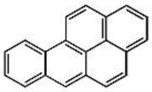

benzene

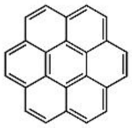

naphthalene

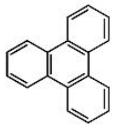

anthracene


phenanthrene


pyrene


benzo[a]pyrene


coronene


triphenylene

<u>Calculation of resonance energy from heat of atomization and heat of hydrogenation</u>

Resonance energy of benzene = Energy of cyclohexatriene — Energy of benzene

<u>Heat of atomization of cyclohexatriene</u>:

From heat of atomization data, in cyclohexatriene, there are three C=C, three C—C and six C—H bonds.

3 x C=C Bond energy (from Cyclohexene) = 3 x 148.8 =446.4 Kcal/mole

3 x C—C Bond energy (from Cyclohexene) = 3 x 81.8 =245.4 Kcal/mole

3 x C—H Bond energy (from Cyclohexene) = 6 x 99.5 =597 Kcal/mole

Total Bond energy (from Cyclohexene) = 1288.8 Kcal/mole

Energy of cyclohexatriene +1288.8 Kcal/mole = 6 x Energy of C + 6 x Energy of H ....(1)

Heat of atomization of benzene:

By using heat of combustion data of benzene, it can be calculated the heat of atomization of benzene which is found to be 1322.8 Kcal/mole.

Energy of benzene +1322.8 Kcal/mole = 6 x Energy of C + 6 x Energy of H ....(2)

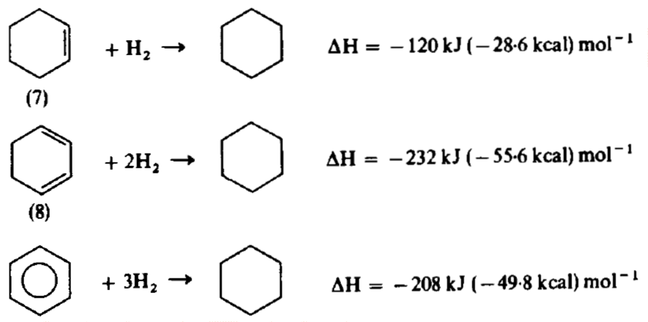
From equation (1) and (2),

Energy of cyclohexatriene +1288.8 Kcal/mole = Energy of benzene +1322.8 Kcal/mole

Energy of cyclohexatriene — Energy of benzene = 1322.8—1288.8 = 34 Kcal/mole

Thus, the resonance energy of benzene = 34 Kcal/mole

Heat of hydrogenation of cyclohexatriene:



Heat of hydrogenation of cyclohexene = —28.6 Kcal/mole

Heat of hydrogenation of Cyclohexatriene = -28.6 x 3 = 85.8 Kcal/mole

Energy of cyclohexatriene + 3 x Energy of H_2 = Energy of cyclohexane + 85.8 Kcal/mole ....(3)

Heat of hydrogenation of benzene:

Heat of hydrogenation of benzene was determined as —49.8 Kcal/mole

Energy of benzene + 3 x Energy of H_2 = Energy of cyclohexane + 49.8 Kcal/mole ....(4)

From equation (3) and (4),

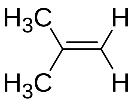
Energy of cyclohexatriene — Energy of benzene = 85.8 — 49.8 = 36 Kcal/mole

From both heat of atomization and heat of hydrogenation render very close value of resonance energy of benzene. The calculation of resonance energy predicts a hypothetical structure of benzene with most stable canonical forms. Usually, the resonance energy of benzene is considered as 36 Kcal/mole.

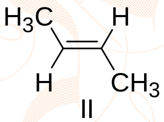
Rule of resonance

The actual structure of the molecule is assumed to be the hybrid of several possible structures arising out of delocalization of electron in bonds. The canonical form has no practical existence except in our imagination. Certain rules guide the resonance:

1. All cannonical form must be bonafied Lewis structure (no five carbon bonds).
2. Only electron movement is allowed. The nuclei in each cannonical form must be the same relative position. Structure II does not contribute the structure of isobutylene I.

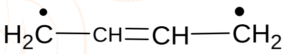


I



II

3. All cannonical forms must have same number of unpaired electrons. Thus the following is not valid for the structure of butadiene.



$H_2\dot{C}-CH=CH-\dot{C}H_2$

4. All the atoms participating in delocalization must lie in a plane or nearly planar.
5. The energy of actual molecule (resonance hybrid) is lower than the energy that might be estimated from the contributing structure.
6. All resonance structures do not contribute equally to the hybrid. Each form contributes to proportion to its stability; thus most stable cannonical form contributes most. Equivalent cannonical structures contribute identically.

Frost Diagram: 'The polygon rule'

In 1953, A. A. Frost demonstrated a simplified approach to determine the relative energies of π— MOs in planar cyclic conjugated systems.

1) Draw a circle

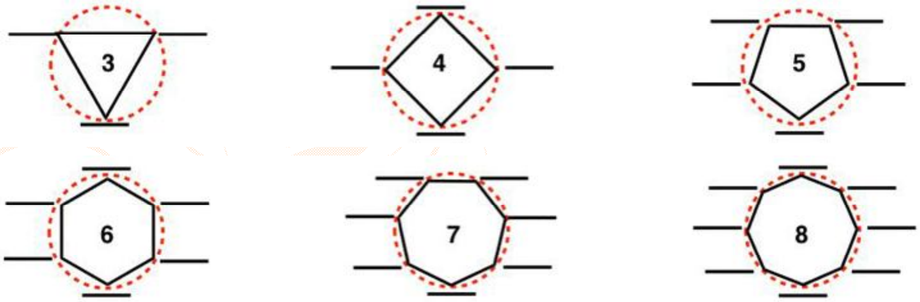
2) Connect the carbon atoms to the circle to form polygon ring such that one atom is always pointed at the bottom. Each point of the polygon that touches the circle represents a discrete energy level.

3) Draw a dotted line through the middle of the circle. It represents the nonbonding MO. Energy levels above this boundary level is called bonding MOs and below the boundary level is called antibonding MOs.

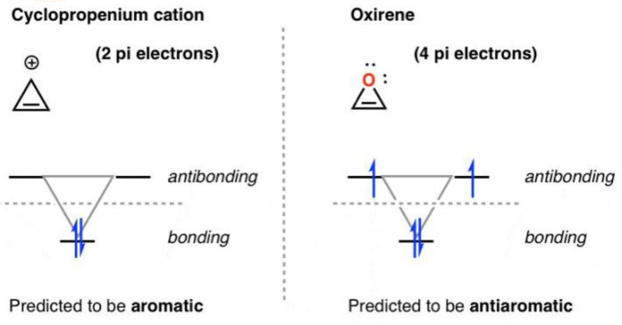
4) Filled the energy levels (orbitals) with the correct number of π—electrons obeying Hund's rule i.e. the lowest energy orbital is filled first.

According to Frost's circle, an aromatic compounds will have all occupied molecular orbitals completely filled where as antiaromatic compounds would have incompletely filled orbitals.

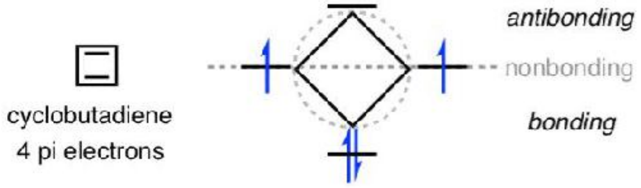
Useful mnemonic for drawing energy level in cyclic π system



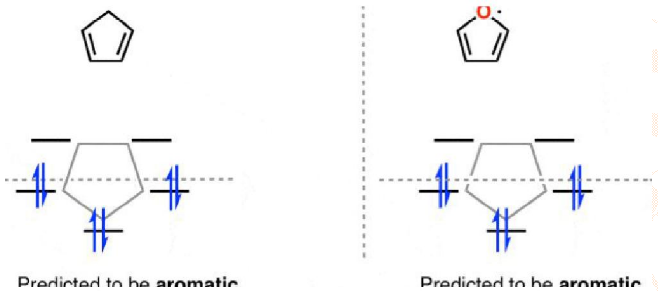
3-membered ring



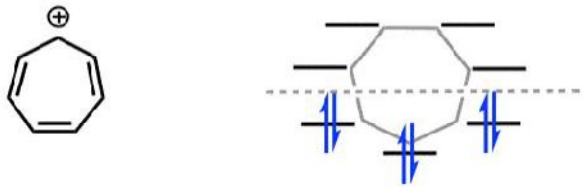
4-membered ring



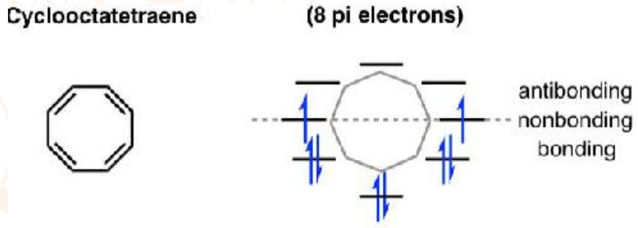
5-membered ring



7-membered ring

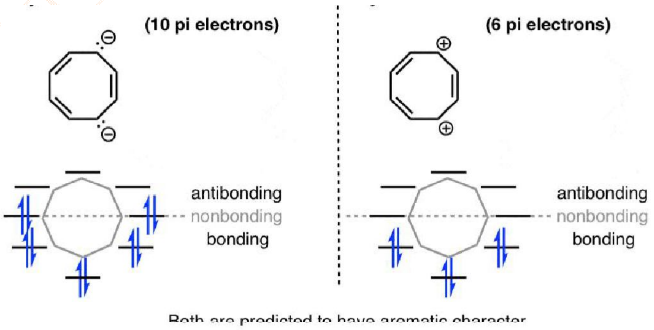


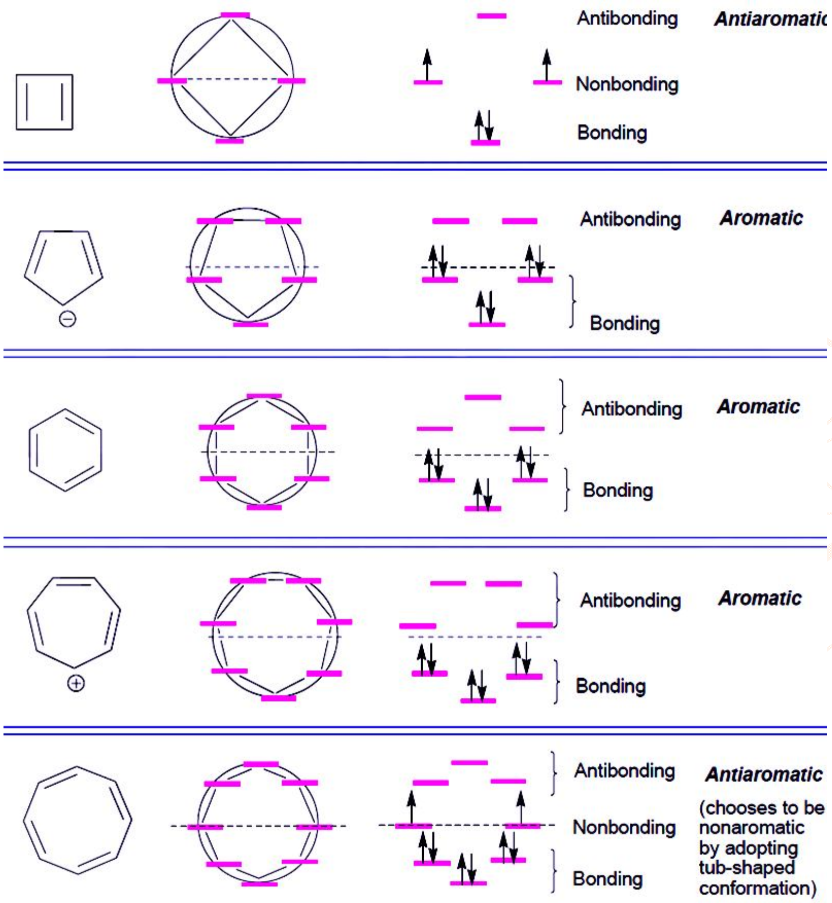
8-membered ring



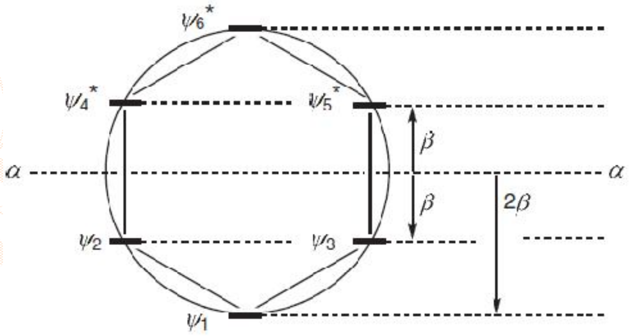
Predicted to be **antiaromatic**

6π and 10π- electron system

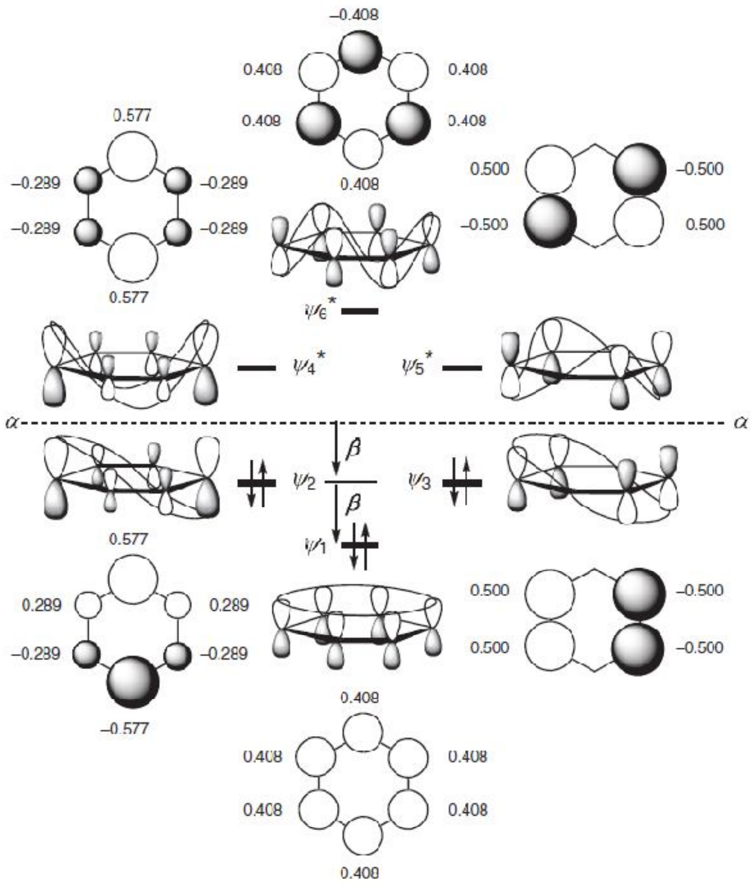




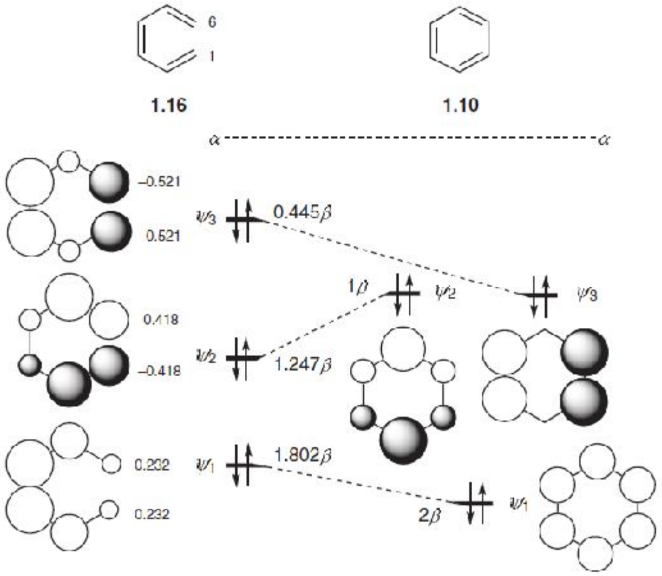
The energies of π—MOs of benzene



Molecular Orbitals of Benzene



The drop in p energy in going from hexatriene to benzene



The energies and coefficients of the p molecular orbitals of the cyclopentadienyl system