Benzene And Aromaticity

from chapter(s) _____ in the recommended text

A. Introduction

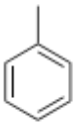
B. Common Aromatic Compounds

aromatic compounds tend *to* smell. They also react *differently to* aliphatic compounds. Industrially they can be formed by distillation from *oil*, or by heating petroleum to a high temperature over *a catalyst*.

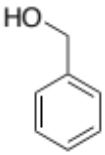
benzene

pyridine

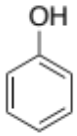
furan



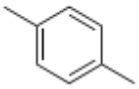
toluene



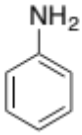
benzyl alcohol



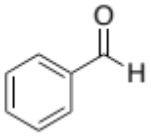
phenol



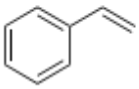
para-xylene



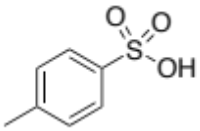
aniline



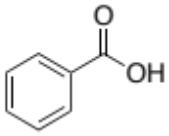
benzaldehyde



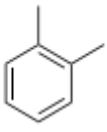
styrene



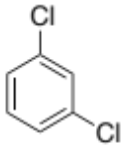
tosic acid



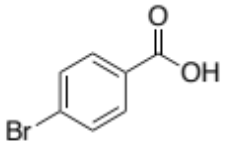
benzoic acid



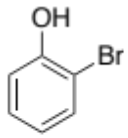
1,2-dimethylbenzene



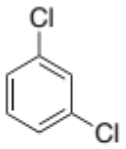
meta-dichlorobenzene



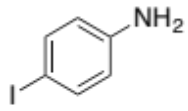
para-bromobenzoic acid



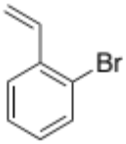
ortho-bromophenol



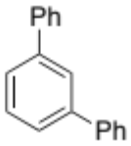
1,3-dichlorobenzene



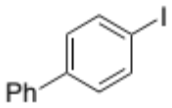
4-iodoaniline



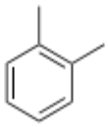
2-bromostyrene



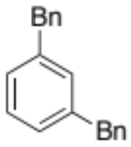
1,3-diphenylbenzene



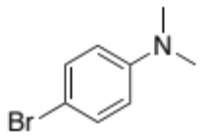
para-phenyliodobenzene



ortho-$Me_2C_6H_4$

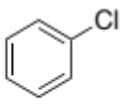


1,3-$Bn_2C_6H_4$

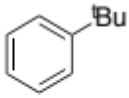


para-$(Me_2N)BrC_6H_4$

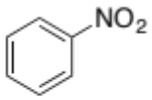
the substituent does not have more *C*-atoms than the benzene ring *ie* toluene.



chlorobenzene



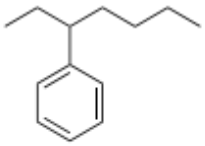
tert-butylbenzene



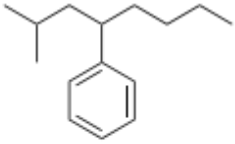
nitrobenzene

Benzenoid compounds *do not* contain heteroatoms in the ring.

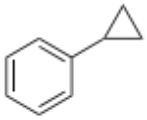
Benzene rings tend to make compounds containing *lipophilic* often leading to aggregation and insolubility



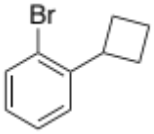
3-phenylheptane



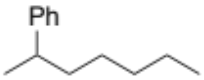
2-methyl-4-phenyloctane



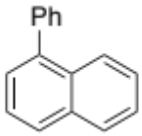
phenylcyclopropane



1-bromo-2-cyclobutylbenzene

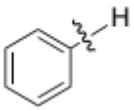


2-phenylheptane

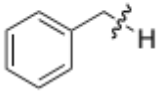


1-phenylnaphthalene

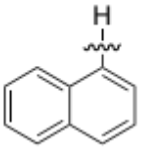
correct name: ____cycloproplybenzene_.



phenyl group in benzene



benzyl group in toluene



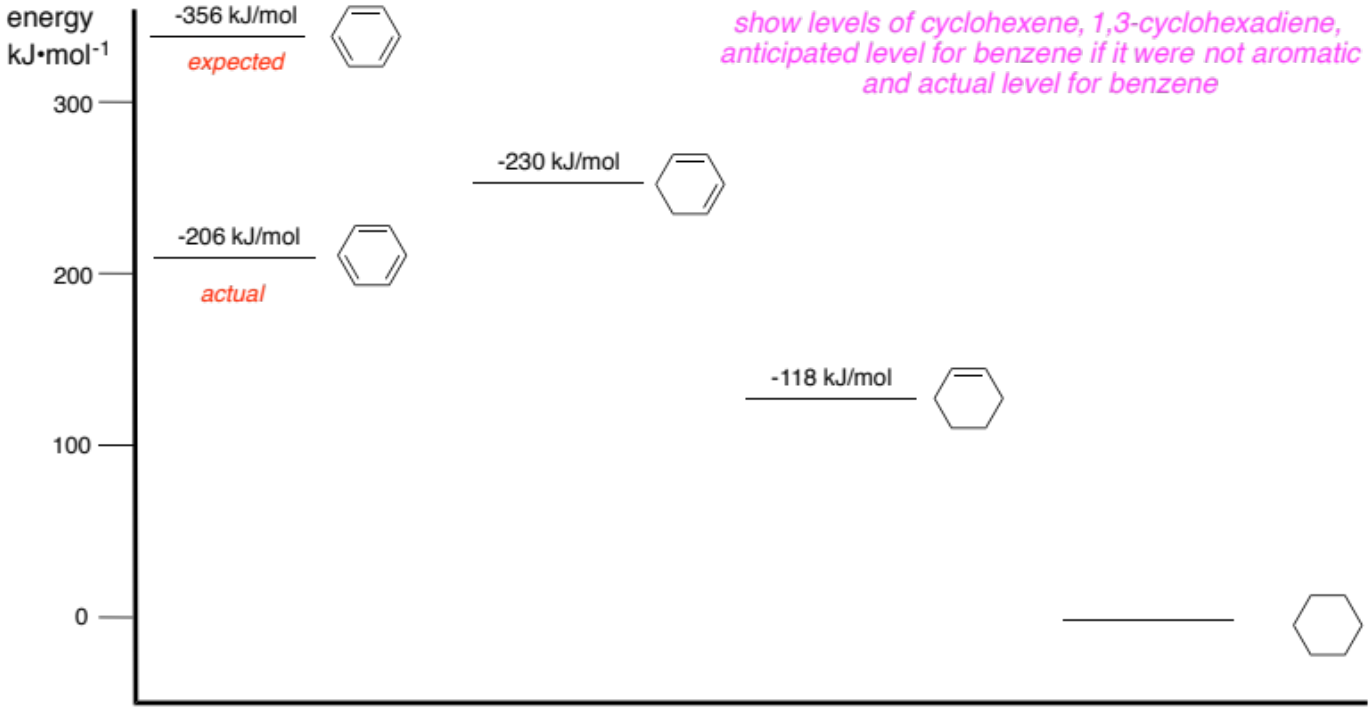
1-naphthyl group in naphthalene

C. Heats Of Hydrogenation And Aromaticity

Energy is *liberated* when hydrogen is added across a C=C bond.
different compounds to give *the same* product *can* be used to gauge the relative stabilities

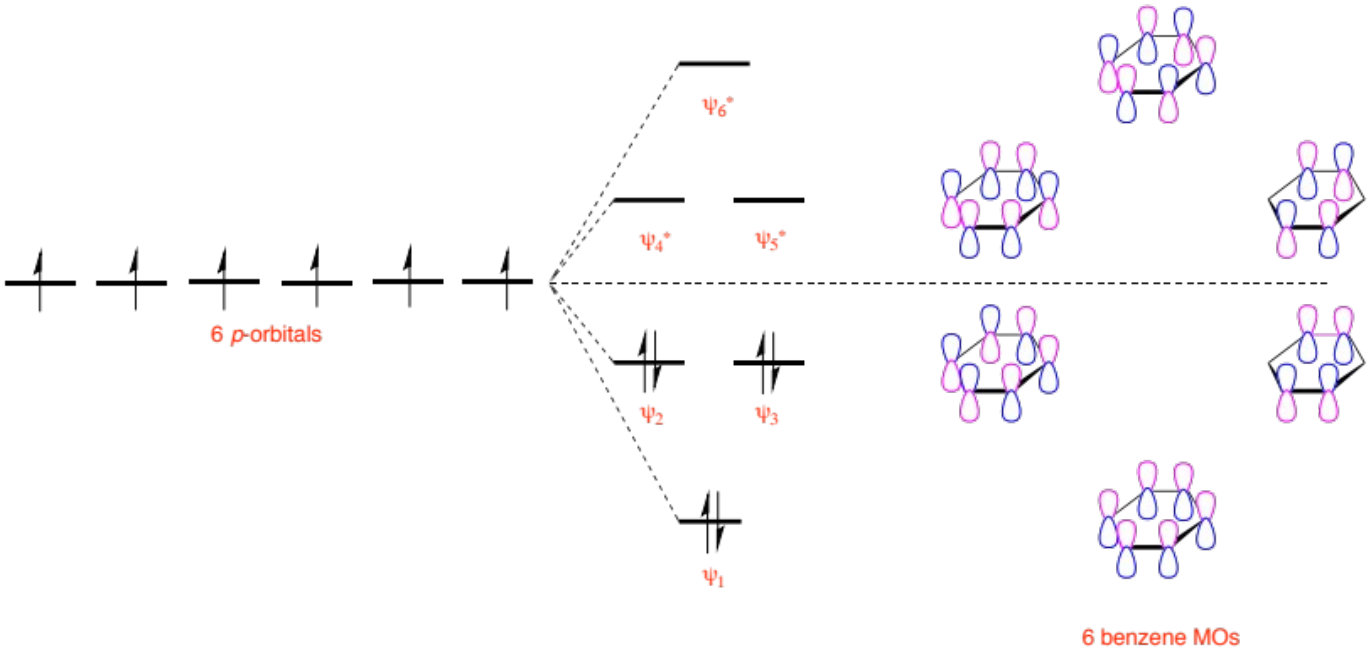
Benzene is *more* stable than expected from the heats of hydrogenation
the heat of hydrogenation of benzene (-206 kJ/mol) is *less* than expected.

Complete hydrogenation of all these molecules gives *cyclohexane*



and all the *C-C-C* bond angles are *120°*; each carbon is *sp^2-hybridized*, and has an empty *p*-orbital
Electron densities on the carbons are *equal*.

In molecular orbital theory, combination of 6 *p*-orbitals gives *6* molecular orbitals

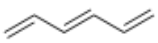


Aromatic molecules must be *cyclic*, *conjugated*, *planar* and they must have 4*n* + 2 -electrons (*n* = integer). This is called *The Hückel Rule.*

Based on the diagram above, explain why 4*n* + 2 might be a significant number for aromatic compounds:

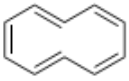
The number of electrons needed to fill HOMOs of aromatic compounds tends to follow the order 2, 6, 10, 14 in the molecular diagram above, so 4n + 2 electrons are required. This occurs because the HOMOs and LUMOs and all the other orbitals above the lowest and below the highest, are degenerate.

aromatic because it has {4(1)+2} = 6 π-electrons, follows Huckel Rule.



not aromatic because this is not cyclic compound.

aromatic because it has {4(1)+2} = 6 π-electrons, follows Huckel Rule.



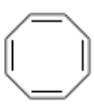
aromatic because because it has {4(2)+2} = 10 π-electrons, follows Huckel Rule.

not aromatic because it has 4 π-electrons, does not follow Huckel Rule.

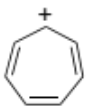
not aromatic because it has 4 π-electrons, does not follow Huckel Rule.

not aromatic because it has 4 π-electrons, does not follow Huckel Rule.

not aromatic because of nonplanarity of the methylene bridge



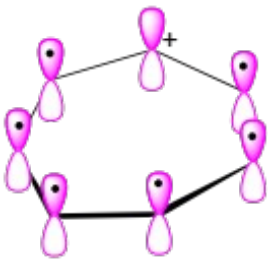
not aromatic because it has 8 π-electrons, does not follow Huckel Rule.



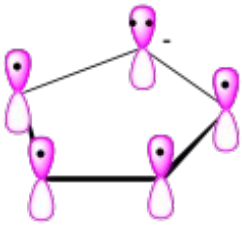
aromatic because the cation on methylene bridge gives planar structure and 6 π-electrons follow Huckel Rule.

D. Predicting Aromaticity

Carbocycles

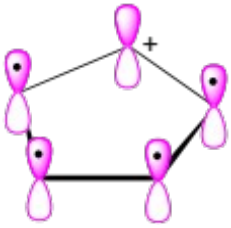


This ion is *aromatic*.

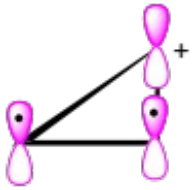


There are *5* resonance structures resonance structures for the 1-ethyl-2-methylcyclopentadienyl anion

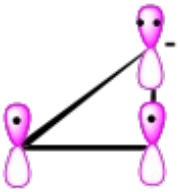
This ion is *non-aromatic*.

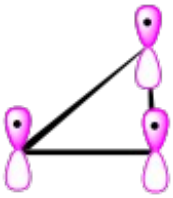


This ion is *aromatic*.

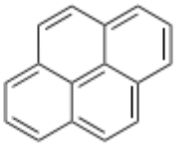


There are *3* resonance structures for the 2-ethyl-1-methylcyclopropenyl cation, and it is *flat*.

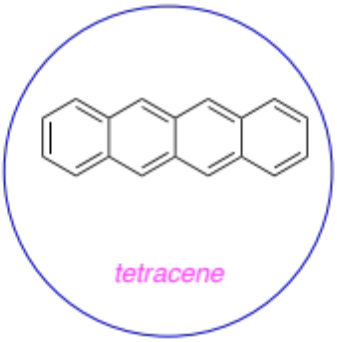
This ion is *non-aromatic*. 

This radical is *non-aromatic*. 

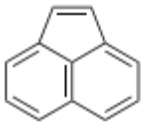
C_{60}



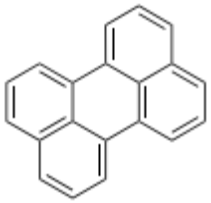
pyrene



tetracene



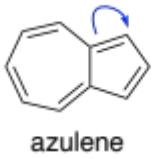
acenaphthalene



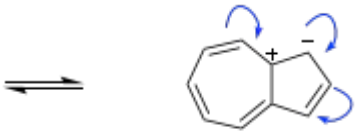
perylene

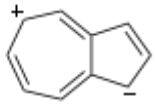
The 4*n* + 2 rule *is not* inviolable.

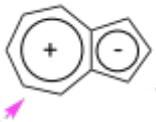
Draw the structure of azulene and resonance structures that account for the observation that it is polar, with a negative charge in the five-membered ring and a positive one in the six.



azulene







aromatic cycloheptatrienium cation

aromatic cyclopentadienyl anion