CHEM 222 section 01

LECTURE #16 Thurs., Oct.25, 2007

Lecture topics & readings

Today's class
- aromaticity & describing benzene: Ch. 14.1-8

Before next class – important
- practice drawing resonance structures for aromatics (*e.g.,* furan, cyclopentadienyl anion, benzyl cation…)

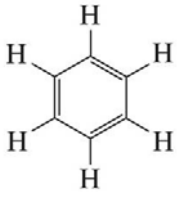
Next class
- rxns of benzene: Ch. 14 continued…

Midterm exam: Tues. Oct. 30 (some mult.choice, some written) everything to end of NMR…

Aromatic compounds & their reactivity (Ch.14-15)

Benzene

represents



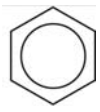
Localized-e⁻ Kekulé structure:
- alternating *C-C* & *C=C* bonds
- expected: 1.54 Å *vs* 1.33 Å

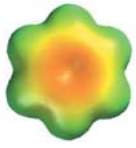
Notable characteristics:
- all Hs chemically equivalent
- all Cs chemically equivalent
- low reactivity, high stability

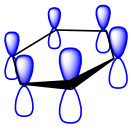
See textbook for:
7.1-7.2: how structure deduced
& 14.1: more on stability

Real structure:
- all C-C bonds same: 1.39 Å
- 6 σ-bonds PLUS…
- delocalized, cyclic array of 6 π-e⁻s
  ⇨ particularly stable: "aromatic"

represents AND represented as

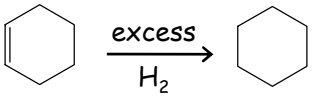
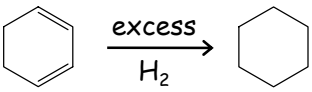
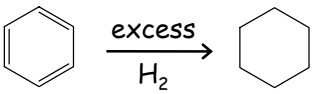






14.1 The unusual stability of aromatic compounds

Benzene hydrogenation much less exothermic than "cyclohexatriene":

	# double bonds	$\Delta H_{H2'n}$ expected	$\Delta H_{H2'n}$ observed
	1	-118 kJ/mol	-118 kJ/mol
	2	2x(-118 kJ/mol) = -236 kJ/mol	-230 kJ/mol
		Conjugation increases stability a bit…	
	3	3x(-118 kJ/mol) = -354 kJ/mol "cyclohexatriene"	**-206 kJ/mol** benzene

IMPLICATION: Cyclic delocalization increases stability HUGELY…

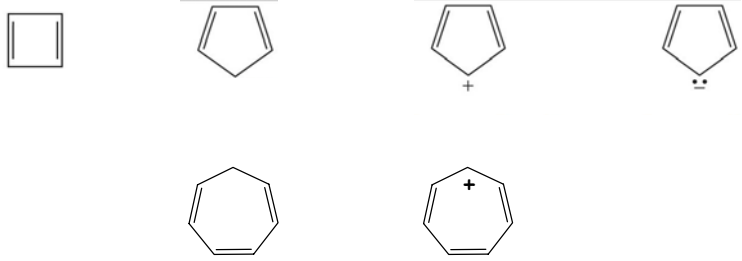
14.2-3 The criteria for aromaticity: Hückel's rule

To be aromatic (= to have unusually large resonance stabilization), **a compound needs:**

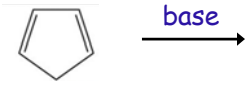
an uninterrupted, cyclic π-system containing an ODD # of e⁻ pairs

- every atom needs a p orbital
- molecule must be planar
- molecule must be cyclic
- (4n+2) π electrons
- where n is an integer

Aromatic or not? (& if not, why not?)



Draw the resonance structures of: cyclopentadienyl anion



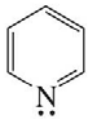
pK_a = 15…

Normal for H—C_{sp3} ?

Aromaticity is "super-resonance" (not a technical term!)…
& has profound effects on reactivity (see 14.5)

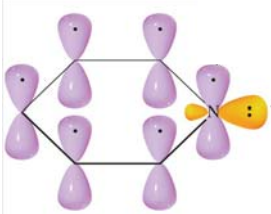
14.4 Aromatic heterocyclic compounds: same rules, but…

- if putting a lone pair into a p orbital would permit delocalization, atom will hybridize to allow it ⇨ *aromaticity is strongly favourable!*



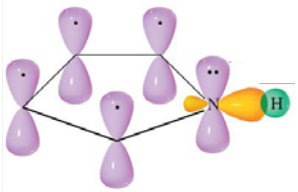
pyridine

- Aromatic
- only involves π-bonds
- lone pair not involved
- lone pair in sp^2 orbital



pyrrole furan thiophene

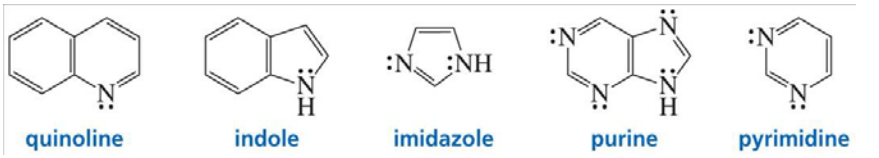
- Aromatic
- can explain ONLY by considering heteratom as sp^2 hybridized (not sp^3) such that lone pair in p-orbital



Task: Draw resonance structures to show lone pair being delocalized

Task: consider pyrrole
Draw resonance structures to show lone pair being delocalized

- Related aromatic heterocycles:



amino-acid sidechain

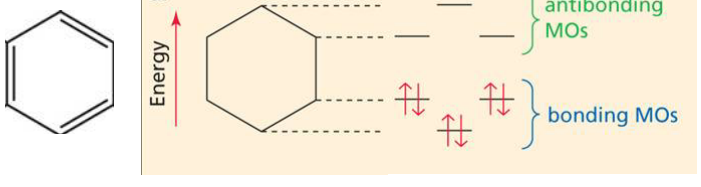
"bases" in DNA & RNA

(7)

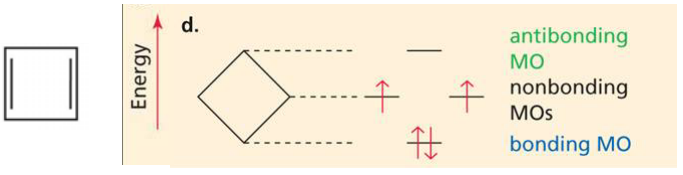
14.6-7 MOs help understand "4n+2 rule" *(for general info)*

- An aromatic compound = more stable than its localized-e⁻ cyclic analog.
  4n+2 π-electrons in an uninterrupted cyclic array
- An anti-aromatic compound = less stable than its localized-e⁻ analog
  4n π-electrons in an uninterrupted cyclic array

Frost's trick: # π MOs = # atoms in ring
use vertex positions to estimate Es → above = antibonding, midline = nonbonding, below = bonding



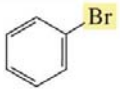
HOMOs filled
⇨ stable

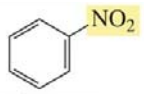


HOMOs only half-filled
⇨ LESS stable.

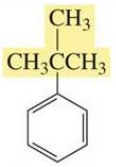
14.8 Naming monosubstituted benzenes

- Substituent + **benzene**

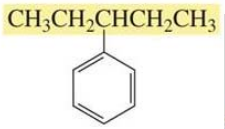


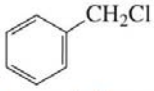


nitrobenzene



- As **phenyl** substituent:

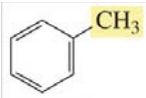




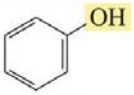
chloromethylbenzene
benzyl chloride

Benzyl group
= -CH_2-Ph

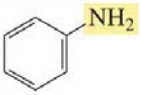
- **Common names** you should memorize:



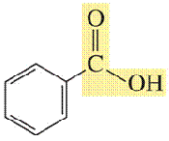
toluene



phenol



aniline



benzoic acid

- In general terms: benzene / substituted benzene = an *aryl group* (Ar)