California State Polytechnic University, Pomona
Organic Chemistry II, CHM 3150, Dr. Laurie S. Starkey
Chapters 17-18 Outline (Klein)
Aromaticity & Aromatic Substitution Reactions

I. Benzene (17.3)
II. Aromaticity
A) definition and rules (17.1, 17.4, **SB 17.2**)
B) common aromatic compounds (17.5, **SB 17.3**)
C) nomenclature (17.2, **SB 17.1**)
D) Bucky Balls and nanotubes (Practically Speaking sidebar)

Step 1

III. Electrophilic Aromatic Substitution, EAS (18.1, 18.15)
IV. EAS on substituted benzenes (18.7 – 18.11, **SB 18.1**, **SB 18.2**, **SB 18.3**)

Step 2

V. Electrophiles for EAS (18.2 – 18.6)
Br/Cl (18.2), sulfonation (18.3, **SB 18.4**),
nitration (18.4), Friedel-Crafts alkylation (18.5) and acylation (18.6)

Step 3

VI. Diazonium Salts, ArN_2^+ (22.10, 22.11)
VII. Aromatic synthesis (combination of IV – VI, 18.12, **SB 18.4, SB 18.5**, **SB 18.6**)
Protective groups (22.8) and blocking groups (**SB 18.4**)
VIII. Nucleophilic Aromatic Substitution, S_NAr (18.13, 18.15, **SB 18.7**)
IX. Reactions of benzylic carbon atoms (17.6, **SB 17.4**)

Step 4

SB = SkillBuilder

SKIP Sections: Spectroscopy (17.8), Birch Reduction (17.7, **SB 17.5**)
Benzyne (18.14), Oxidation of phenols (12.12)

Suggested textbook problems (Klein, 4th edition)

Ch. 17 Aromaticity problems 1–56, 60 (skip 7, 16, 20-23, 26-29, 43-46)

Ch. 18 Aromatic Reactions problems 1–80 (skip 1-3, 33, 34, 35a, 36, 56)
ADD problems from Chapters 20-22: 20.43, 20.50, 20.59, 21.34, 22.26, 22.66, 22.68c

Chapter 17 - Aromatic Compounds

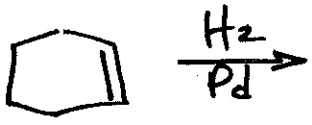
Benzene 

3D sketch: 

Features of benzene (17-3)

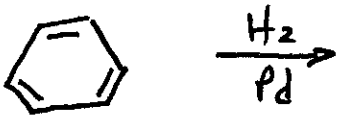
- → planar
- → symmetrical (all C-C bonds equal length)
- → very stable
- → doesn't react as an alkene
- → new class of compounds: aromatic (Ar)

How much resonance stabilization does benzene have?

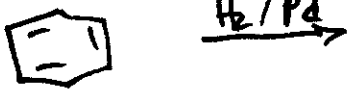


$\Delta H_{hydrogenation}$ (kcal/mol)

−28.6 (calculated)

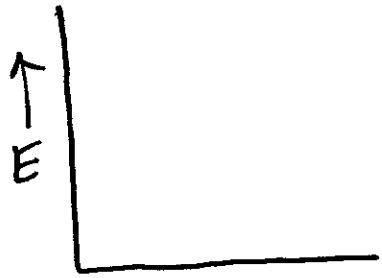


"cyclohexatriene"



benzene

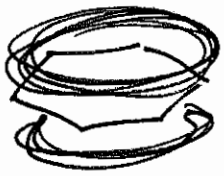
(experimental)



theoretical molecule assumes no interaction between π bonds

* Benzene is 36 kcal/mol more stable than expected *

Aromaticity Requirements (17.1, 17.4)



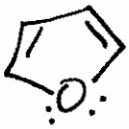
SkillBuilder 17.2

1) cyclic + planar
2) contiguous p orbitals
3) satisfy Hückel's Rule:
   # of electrons in p orbitals = 2, 6, 10, 14, 18, etc.

Common Aromatic Compounds (17.5)

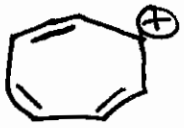
benzene

pyridine

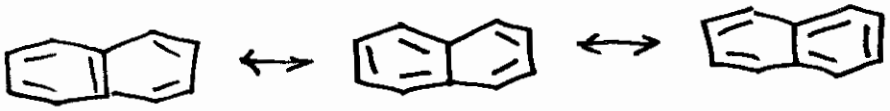


furan

pyrrole

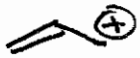


fused aromatic:



naphthalene

Aromatic?

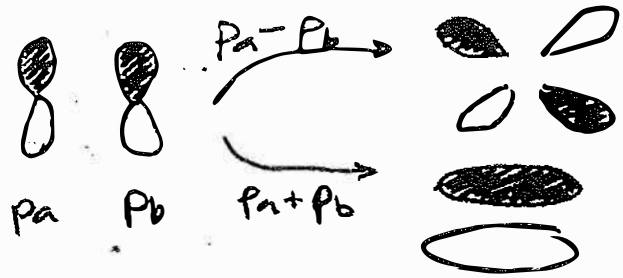


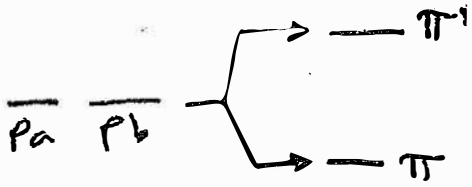
SkillBuilder 17.3

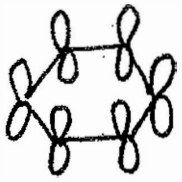
Aromatic Compounds... What's so special about "4n+2" electrons?
Molecular Orbital (MO) Theory (17.4)

Recall: form a π bond by overlapping p orbitals

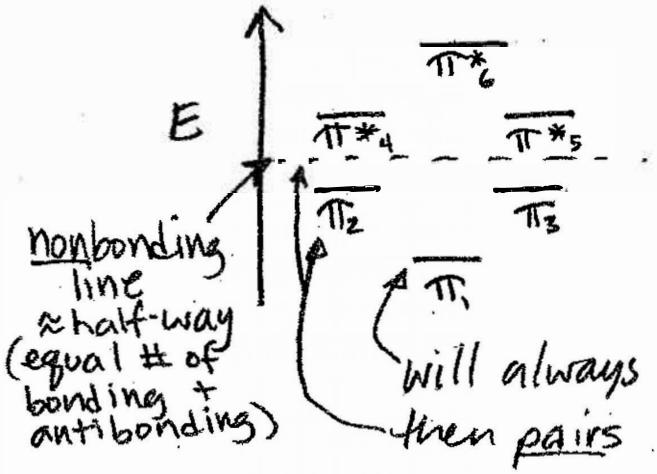
a molecular orbital (MO) ← an atomic orbital (AO)





Consider benzene  ≡  6 p orbitals → 6 new MO's (AO's)

MO Diagram:



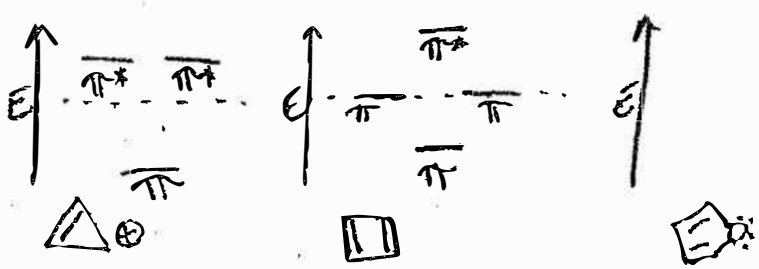
will always be one MO with lowest E

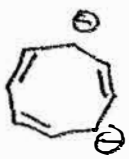
then pairs of MO's of equal E (degenerate)

"4n+2" electrons gives completely filled bonding MO's → very stabl → aromatic!

Note: # MO's = # AO's (p orbitals) = # atoms in ring (look for polygon)

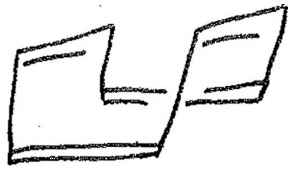
3-membring 4-membring 5-memb. ring 8-memb. ring





* If cyclic + contiguous p orbitals but $4n$ e⁻ then antiaromatic (unstable!)

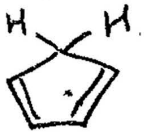
e⁻ are not delocalized

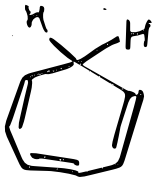


more stable if not planar

* Look for aromaticity as ultimate resonance stabilization

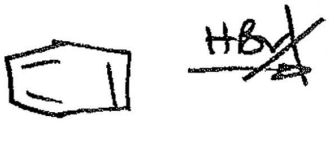
Which is more acidic?



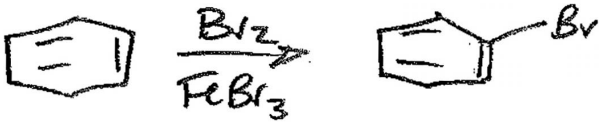


Which has the more basic N, pyrrole or pyridine?

N/R as alkenes (no addition rxns)



Instead, substitution reactions (Ch 18)



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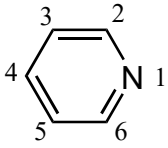
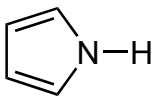
Nomenclature for Aromatic Compounds (Klein 17.2, SkillBuilder 17.1)

Common names (you will be tested on the ones in bold):

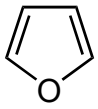
benzene



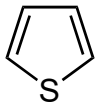
pyridine



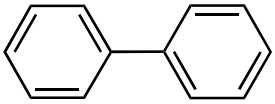
pyrrole



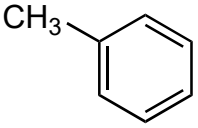
furan



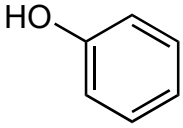
thiophene



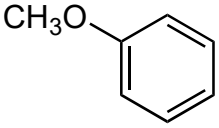
biphenyl (phenylbenzene)



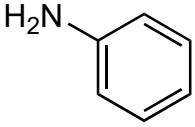
toluene (methylbenzene)



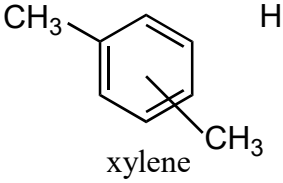
phenol (hydroxy-benzene)



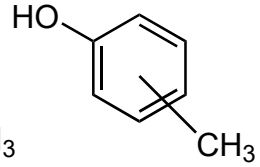
toluene (methoxy-benzene)



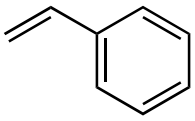
aniline (benzenamine)



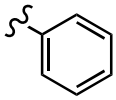
xylene (dimethyl-benzene)



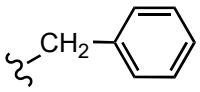
cresol (hydroxymethyl benzene)



styrene (vinylbenzene or phenylethene)

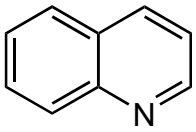


phenyl group (Ph)

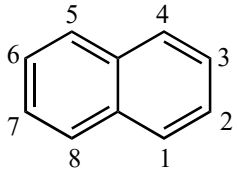


benzyl group (Bn)

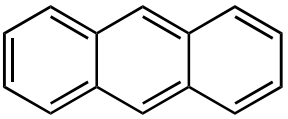
fused aromatic compounds:



quinoline



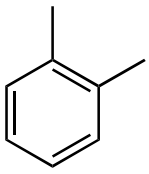
naphthalene



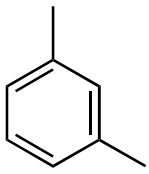
anthracene

Nomenclature:

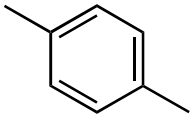
Disubstituted benzenes are usually named as *ortho, meta,* or *para*. Otherwise, number the benzene carbons.



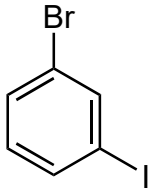
ortho (*o*-) 1,2-disubstituted



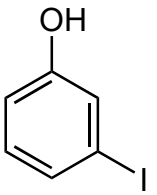
meta (*m*-) 1,3-disubstituted



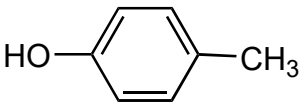
para (*p*-) 1,4-disubstituted



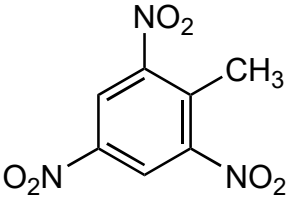
1-bromo-3-iodobenzene or *m*-bromoiodobenzene



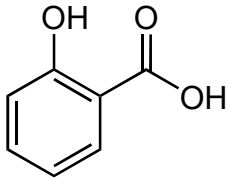
3-iodophenol or *m*-iodophenol



para-cresol or 4-methylphenol



2,4,6-trinitrotoluene (TNT)



ortho-hydroxybenzoic acid

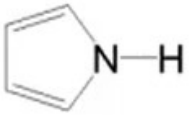
Try: 3-benzylpyridine, 1-phenyl-6-ethylnaphthalene, *p*-ethylnitrobenzene, tetrahydrofuran (THF)

Aromatic Nomenclature (skeleton notes for Educator Section 2, 1:05:02 – 1:16:34)
See Klein section 17.2 and ***SkillBuilder 17.1***

Aromatic compounds are named according to the parent ring.

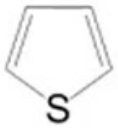

benzene

pyridine

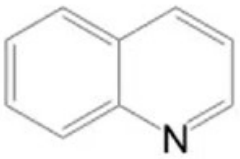


pyrrole

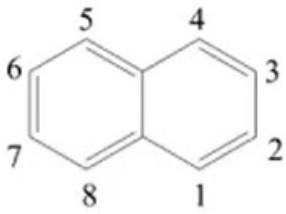
furan



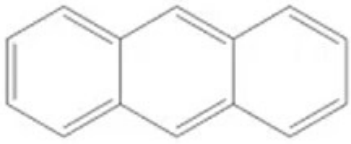
thiophene



quinoline



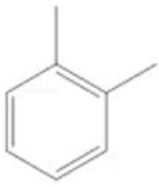
naphthalene

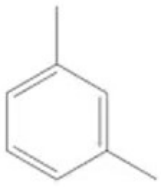

anthracene

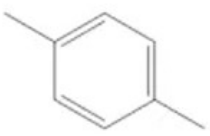

biphenyl

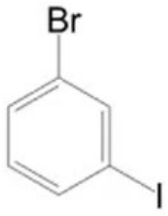
IUPAC:

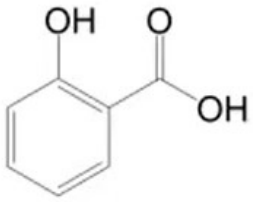
Numbering can be used as with cycloalkanes, but the terms *ortho, meta* and *para* are typically used for disubstituted benzene derivatives.

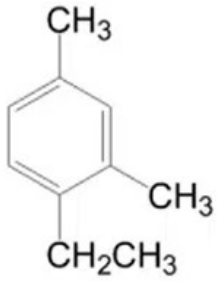

ortho (*o*-)
1,2-disubstituted


meta (*m*-)
1,3-disubstituted

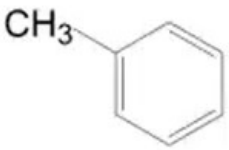

para (*p*-)
1,4-disubstituted



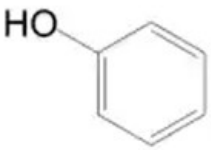




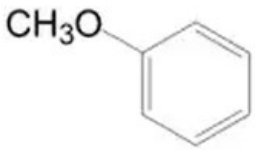
Many common names exist for simple, substituted aromatic compounds.



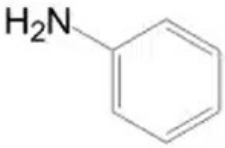
toluene
(methylbenzene)



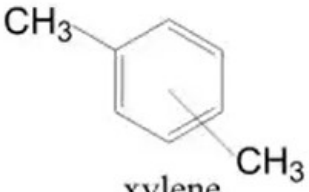
phenol
(hydroxy-
benzene)



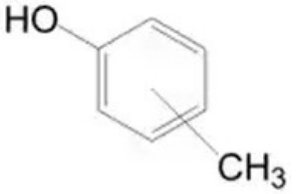
anisole
(methoxy-
benzene)



aniline
(benzenamine)



xylene
(dimethyl-
benzene)



cresol
(hydroxymethyl
benzene)