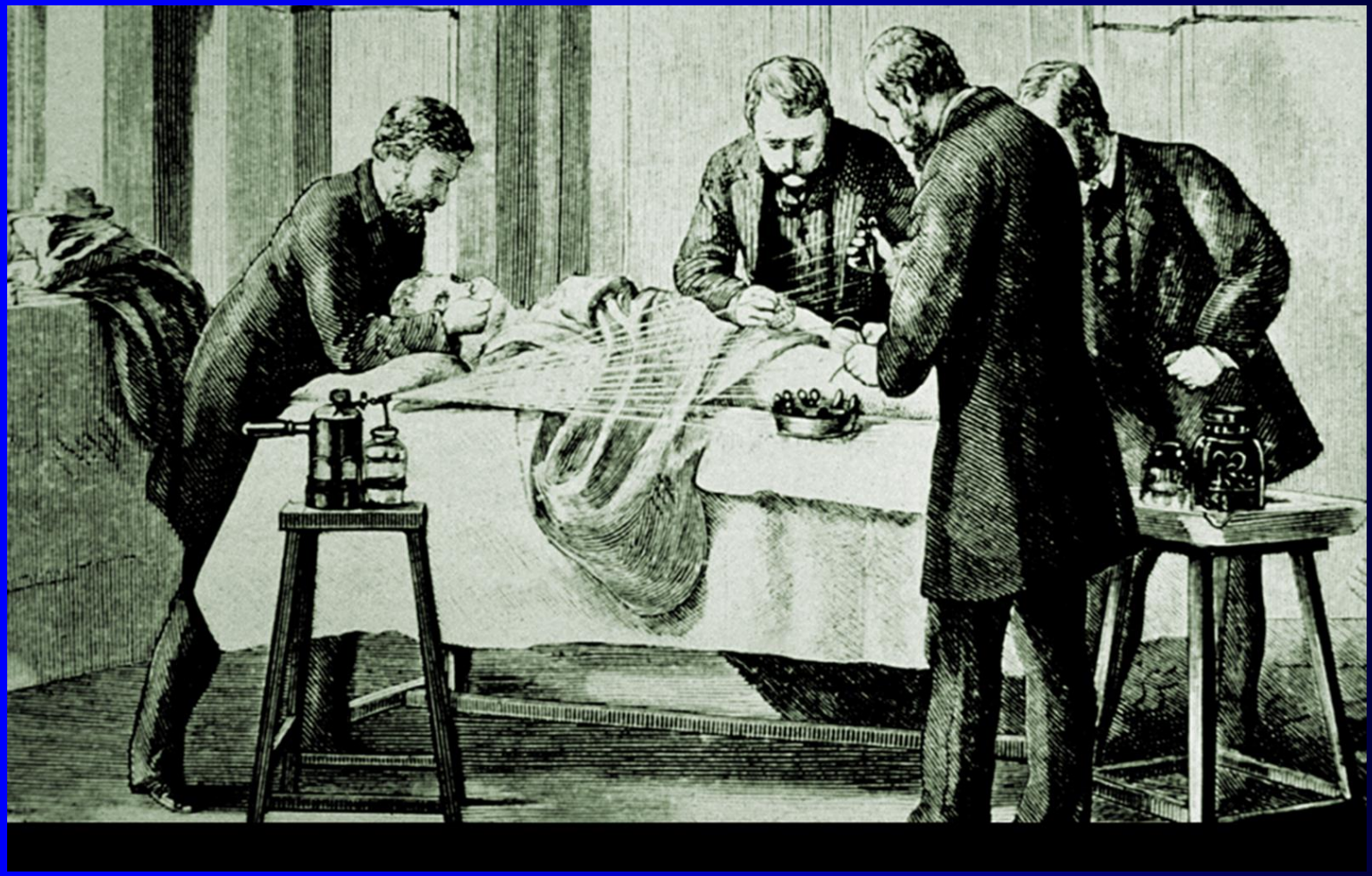
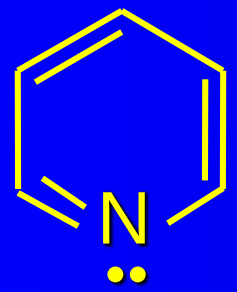
Lecture 10
More Aromatics



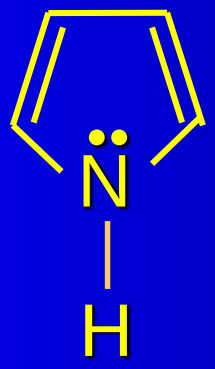
February 18, 2016

Chemistry 328N

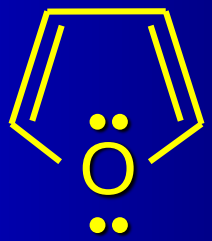
Heterocyclic Aromatic Compounds



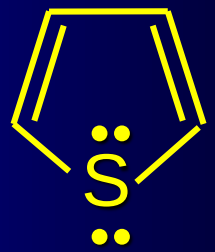
Pyridine



Pyrrole

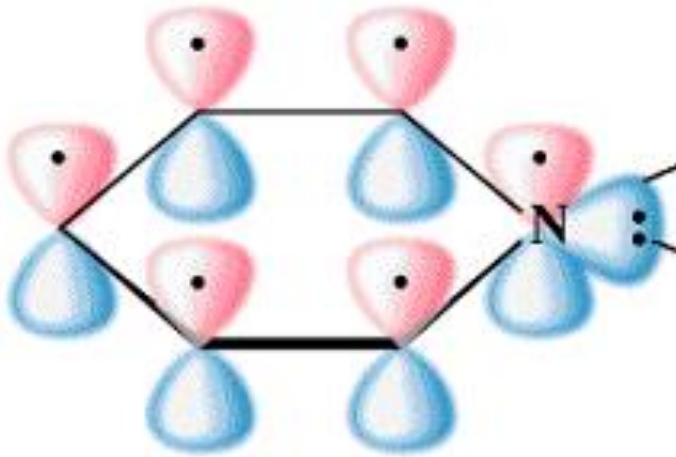


Furan



Thiophene

Hückel and Pyridine

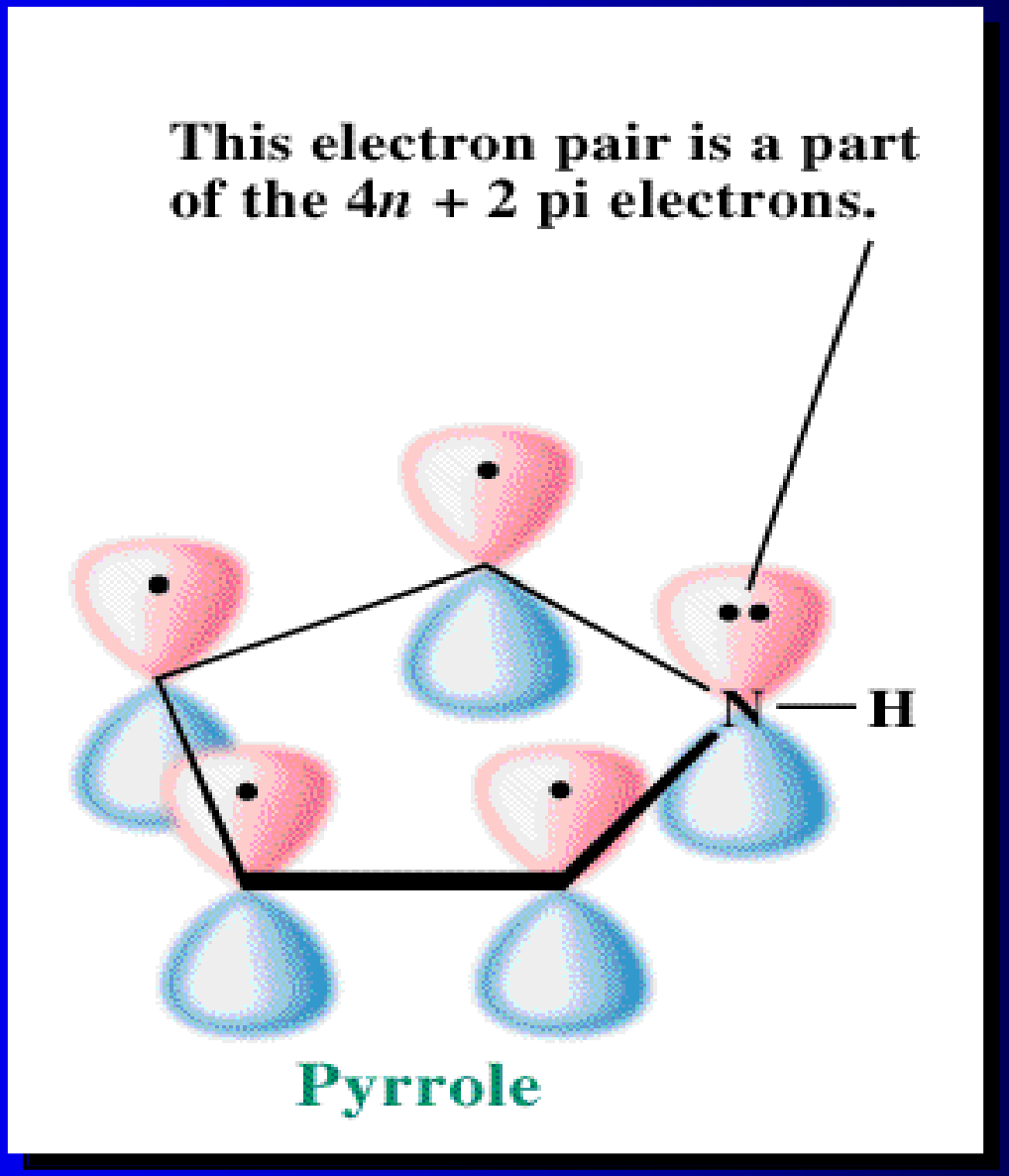


Pyridine

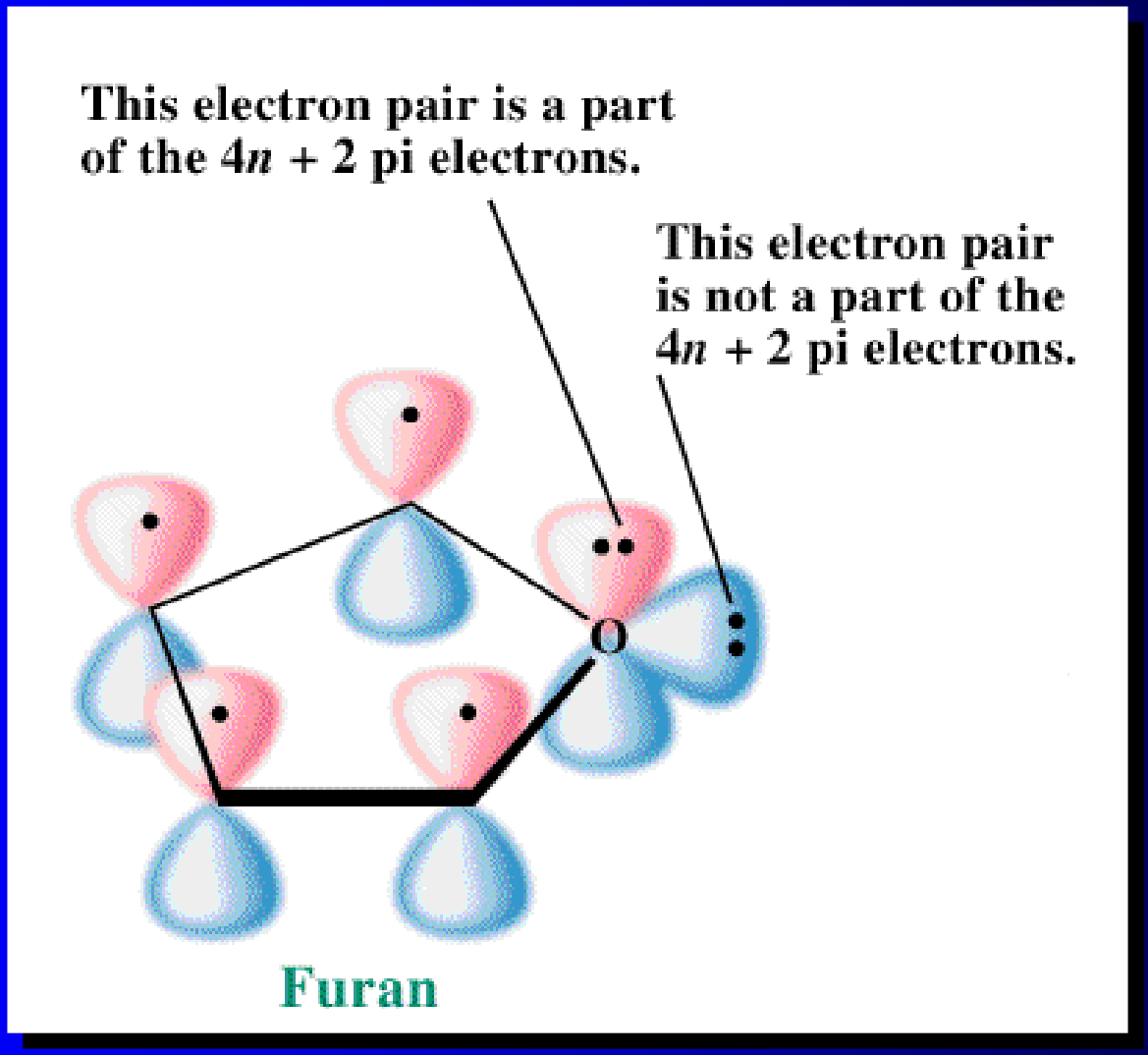
This orbital is perpendicular to the six 2*p* orbitals of the pi system.

This electron pair is not a part of the 4*n* + 2 pi electrons.

Hückel and Pyrrole

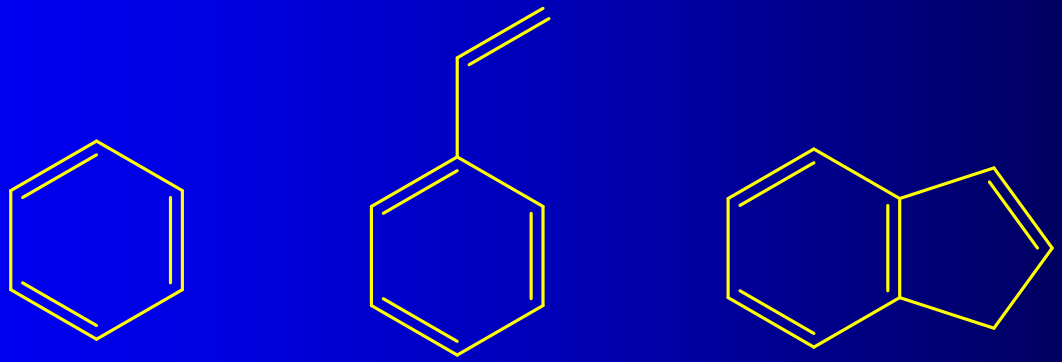


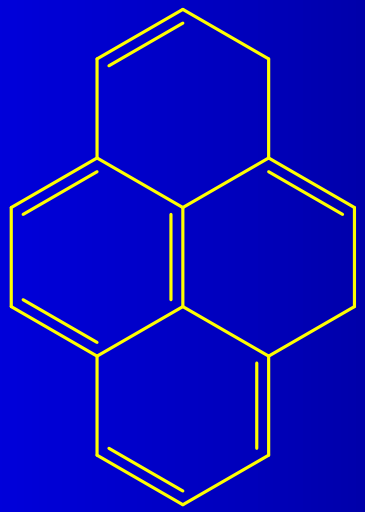
Huckel and Furan



Recognizing Aromatic Compounds

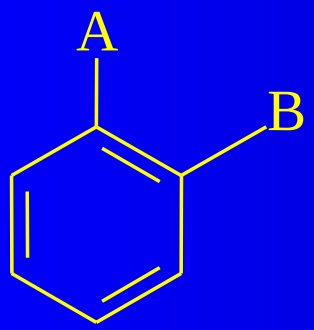
Be careful with Huckel's Rule



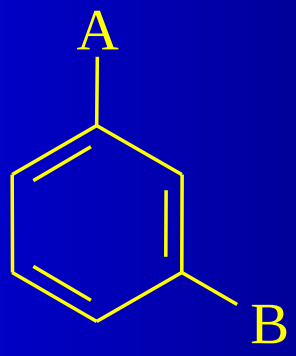


Some Nomenclature

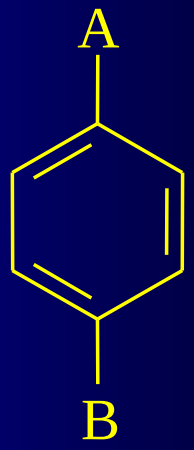
http://www.word-origins.com/definition/benzene.html



Ortho
or 1,2



Meta
or 1,3

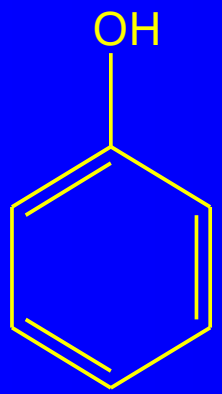


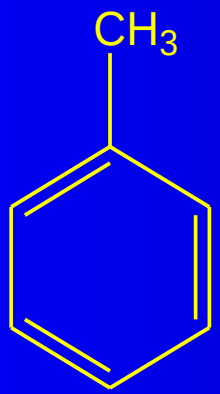
Para
or 1,4

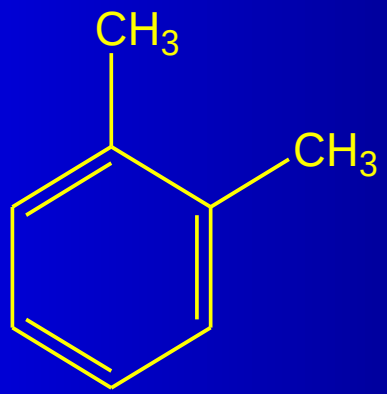
Please read about naming in Chapter 21.3!

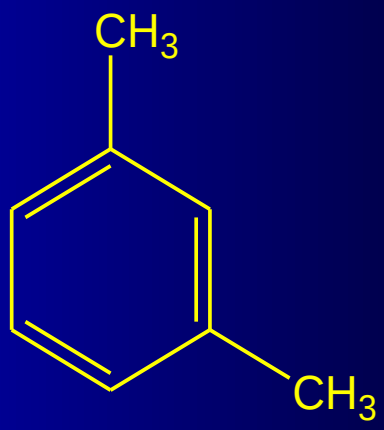
Some Nomenclature

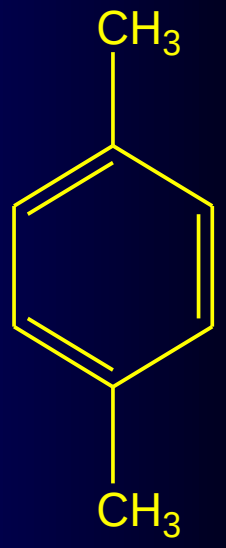
Please read about naming in Chapter 21.3. Many substituted benzenes are so old and so common that they have been given "nick" names!



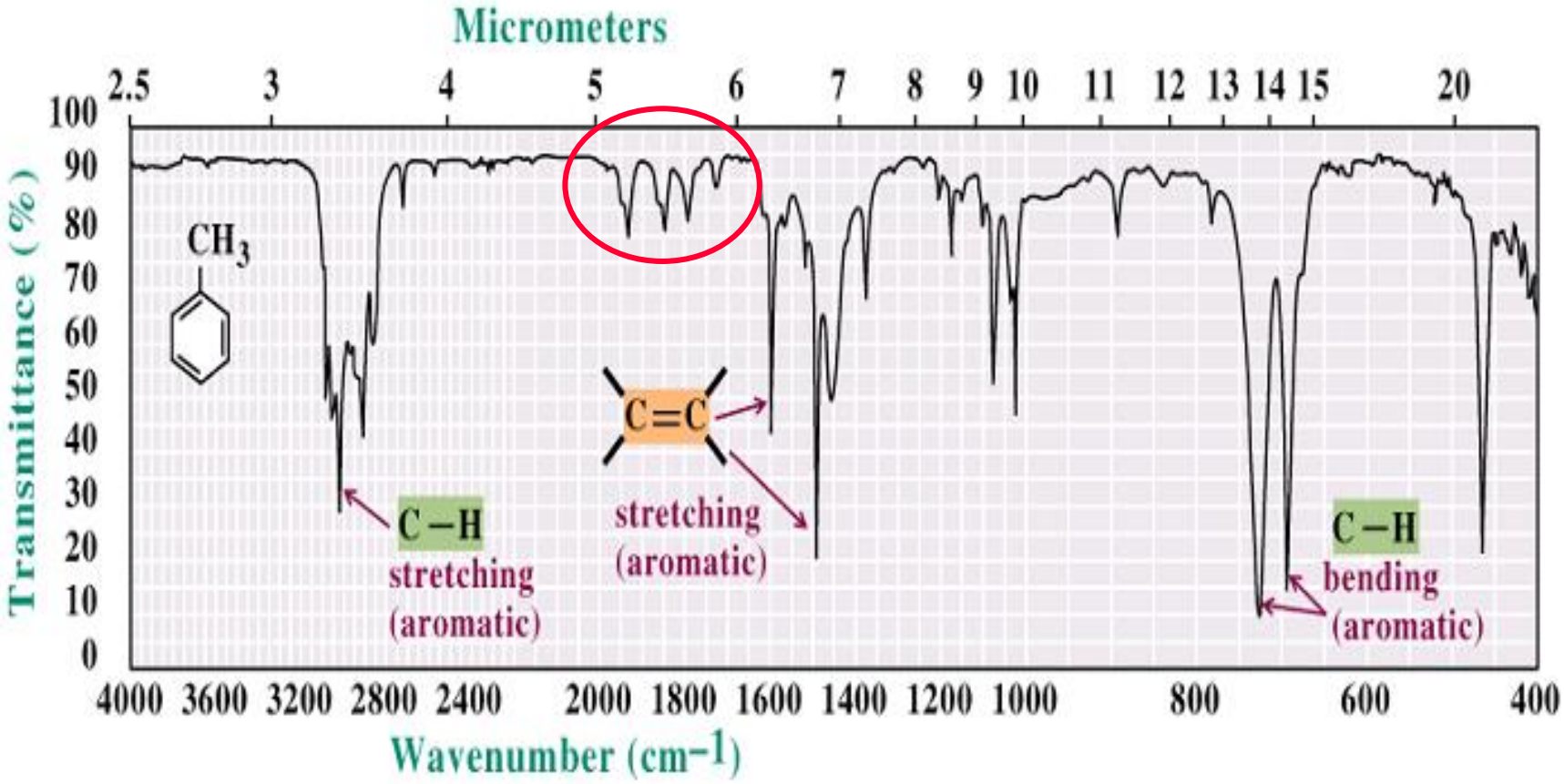




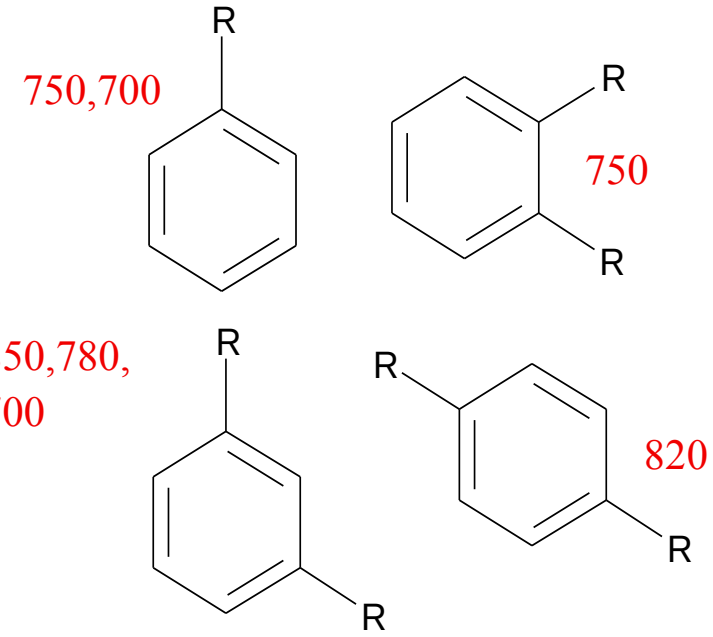




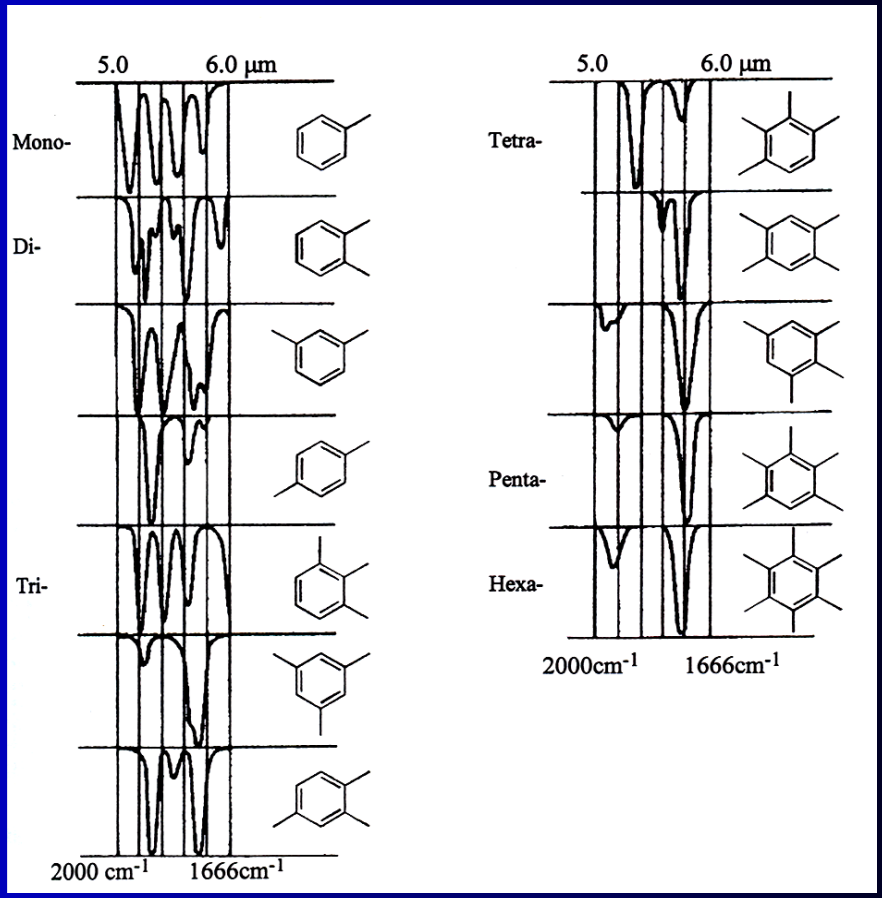
IR spectrum of toluene



Benzene rings--substitution patterns



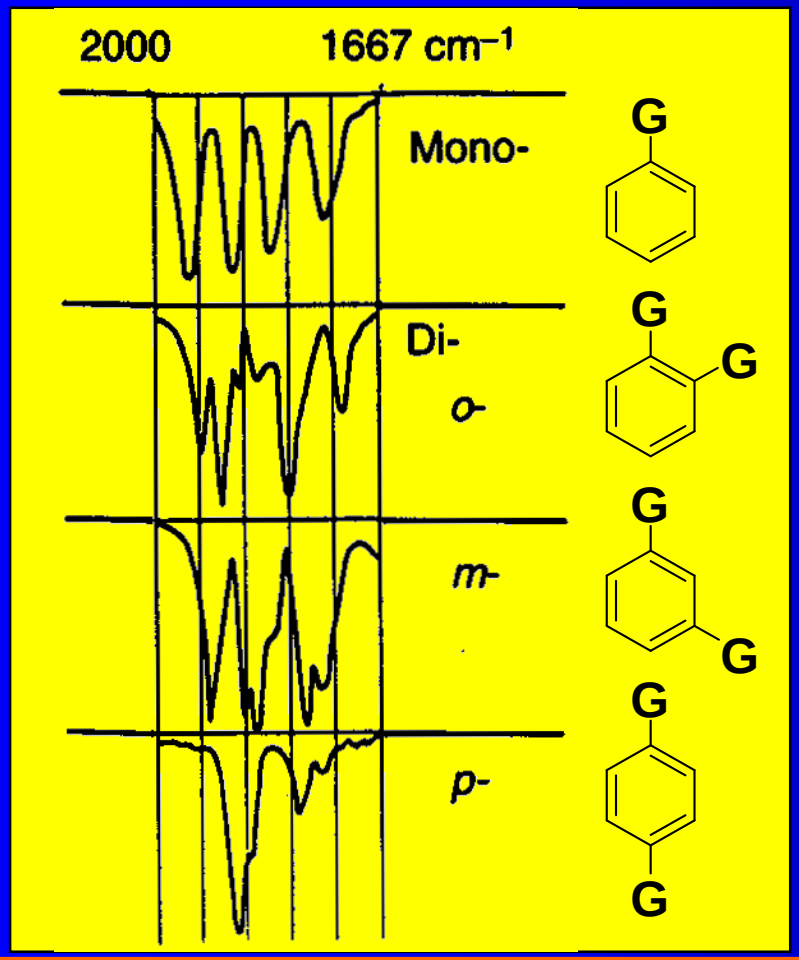
Unreliable with NO_2, CO_2H subs

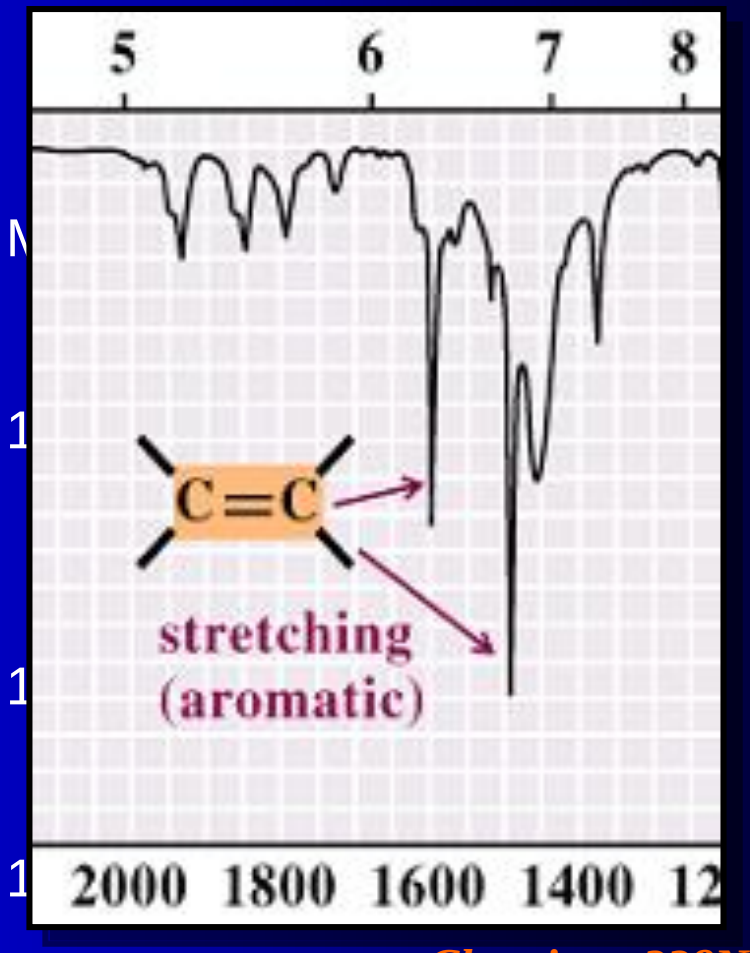


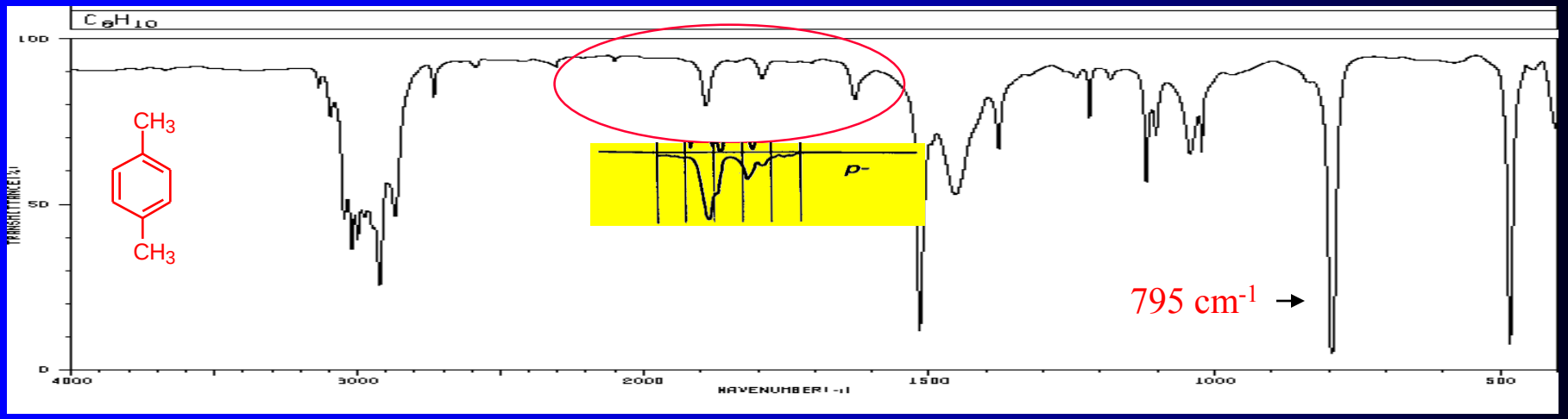
From Crewes, Rodriguez and Jaspars, ch 8

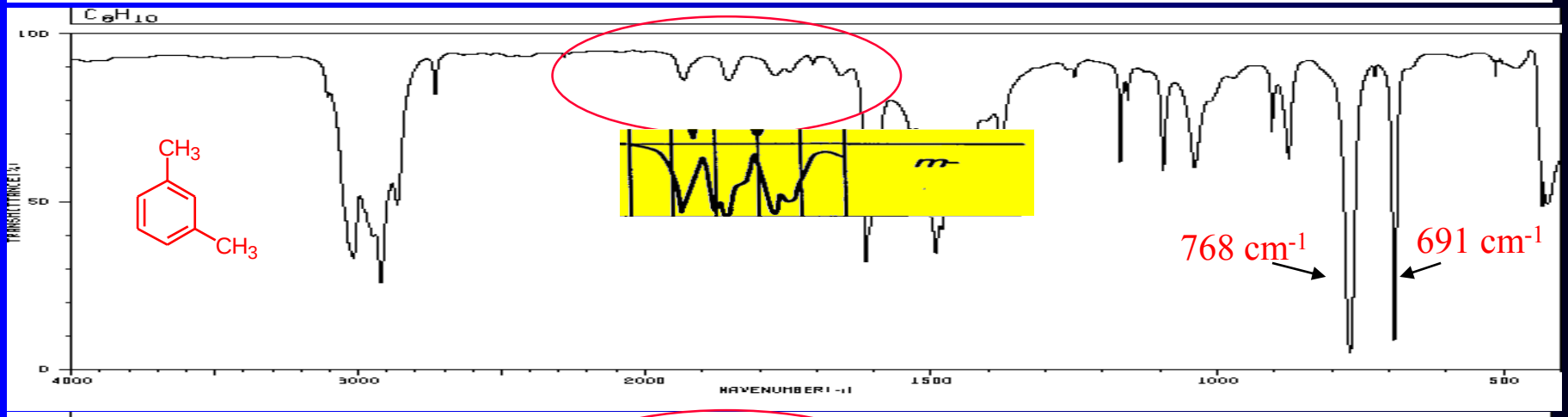
Out-of-plane bending *combinations*, quite small, but in a normally clean region of IR. Reliable even with nitro or carboxyl substitution

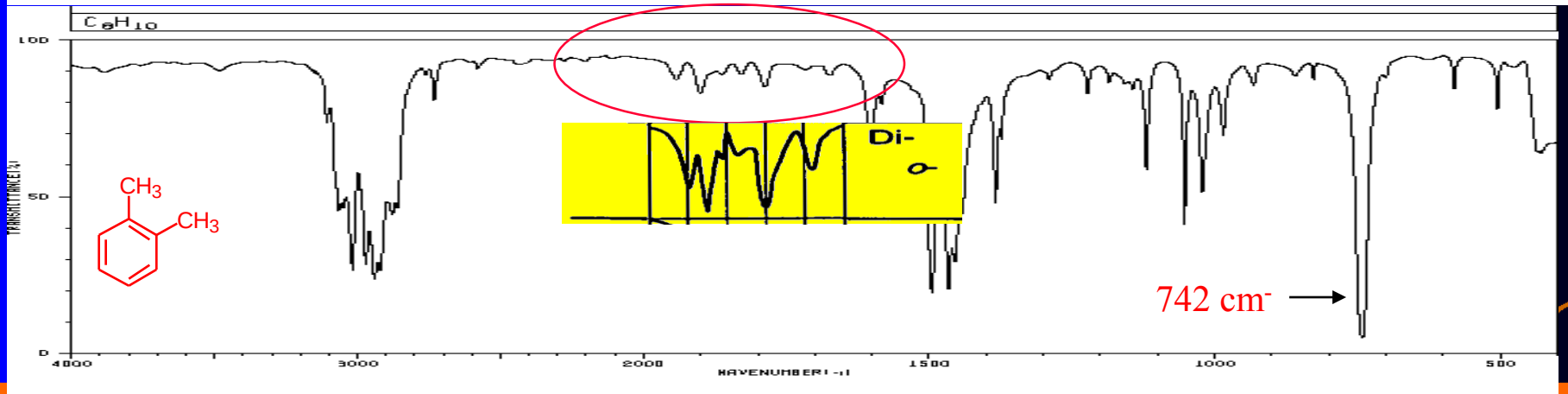
If the region between 1667-2000 cm^{-1} (w) is free of interference (C=O stretching frequency) a weak grouping of peaks is observed for aromatic systems. Analysis of this region can lead to a determination of the substitution pattern on the aromatic ring



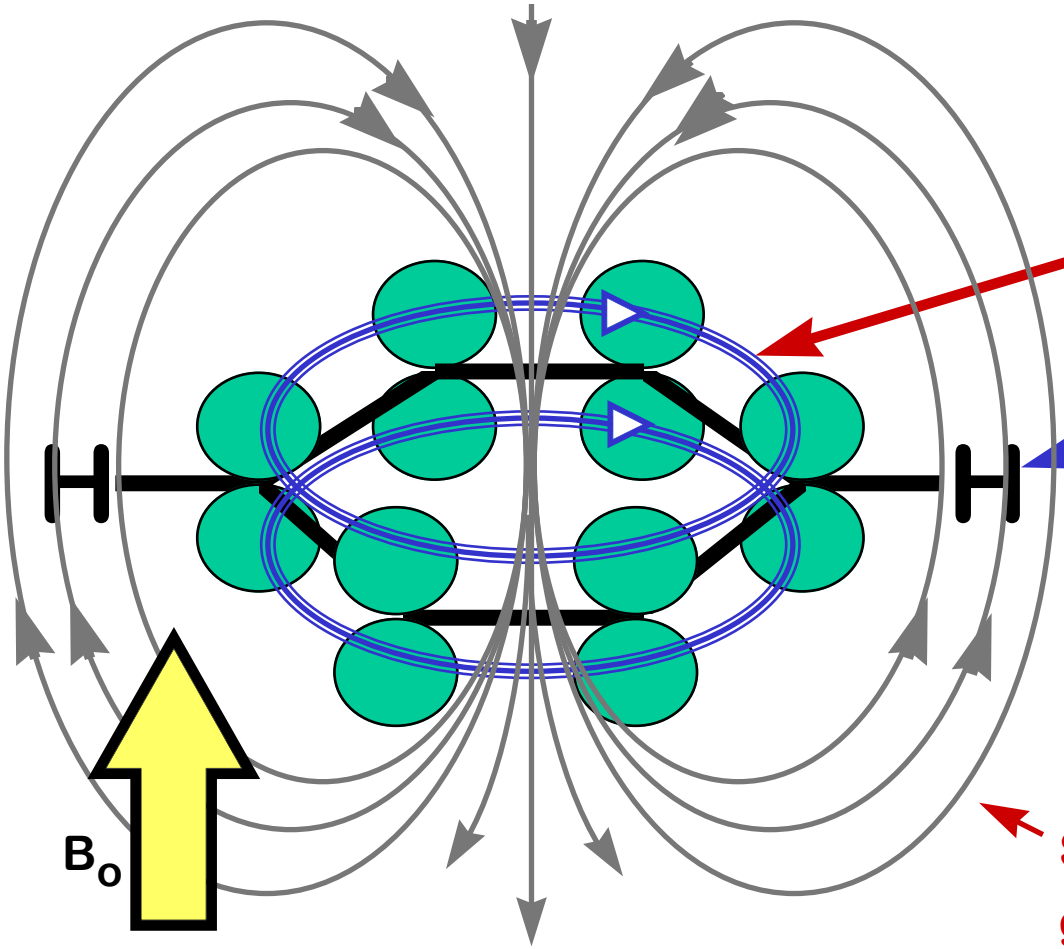



C_8H_{10}
100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
CH_3
CH_3
p-
795 cm^{-1}

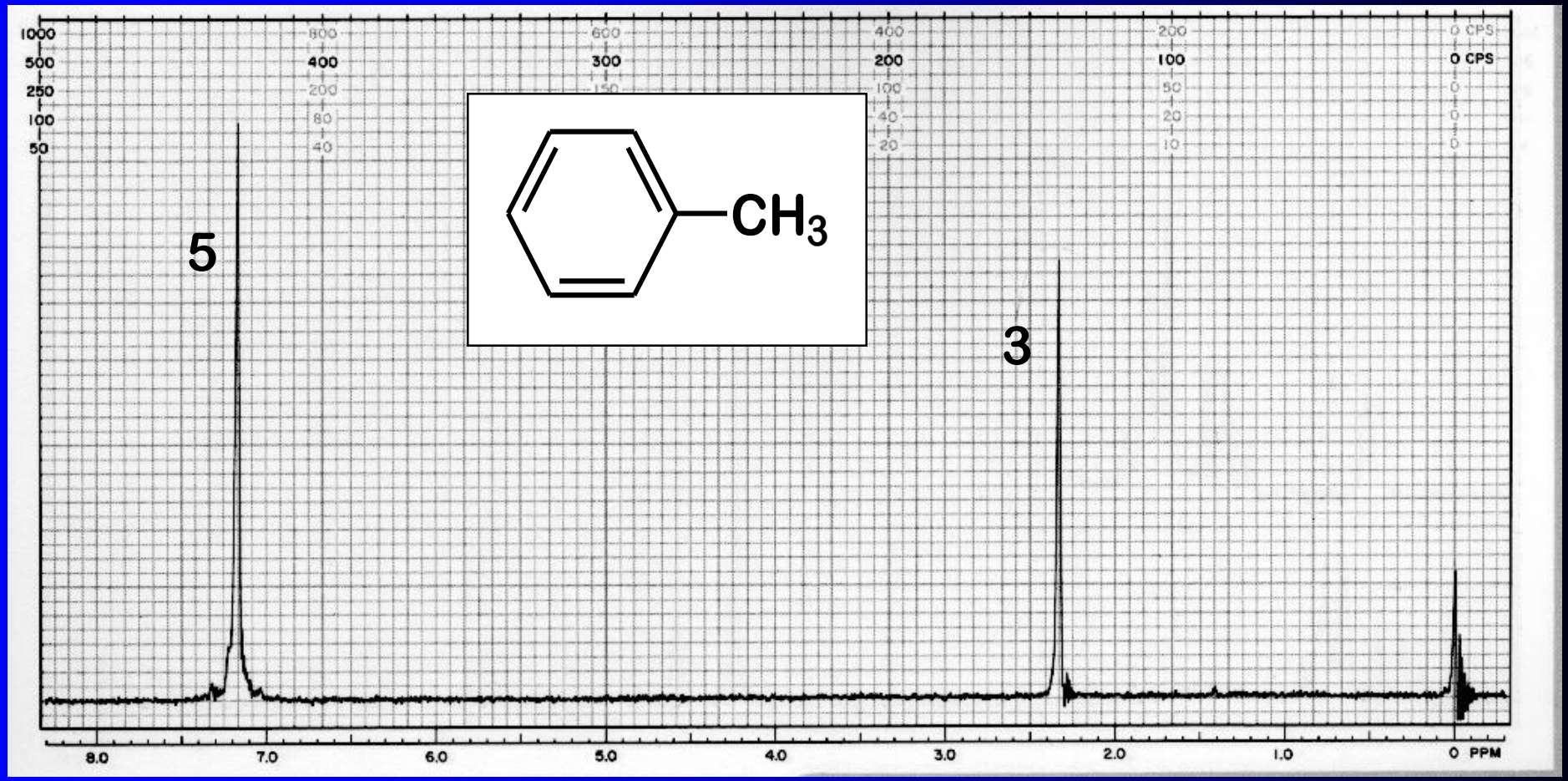

C_8H_{10}
100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
CH_3
CH_3
m-
768 cm^{-1}
691 cm^{-1}


C_8H_{10}
100
50
0
TRANSMITTANCE(%)
4000
3000
2000
1500
1000
500
WAVENUMBER(-1)
CH_3
CH_3
Di-
o-
742 cm^{-}

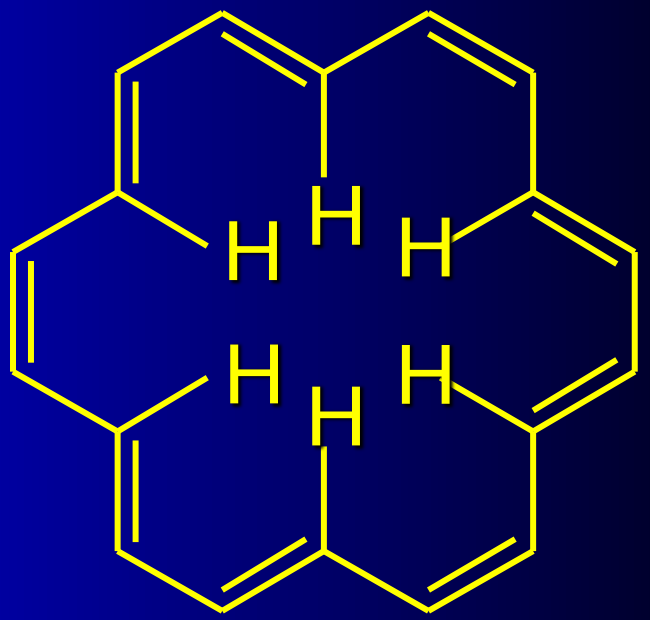
Ring Current in Benzene



NMR Spectrum of Toluene



[18]Annulene



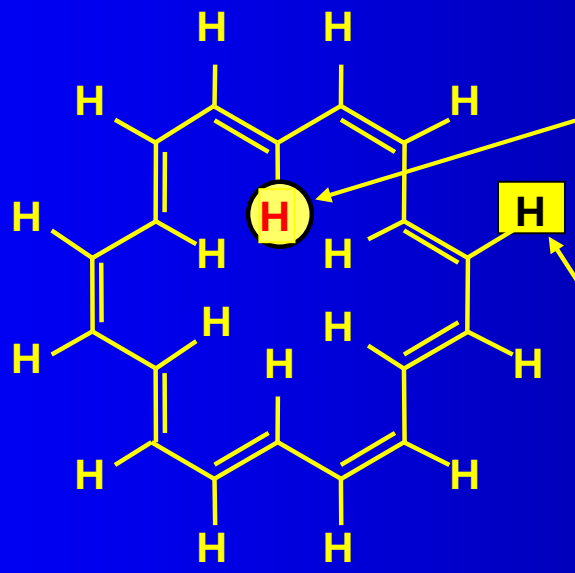
18 π electrons satisfies Hückel's rule

resonance energy = 418 kJ/mol

bond distances range between 137-143 pm

nmr Spectroscopy

- Ring Current effect is massive in the larger annulenes, for example for [18]annulene



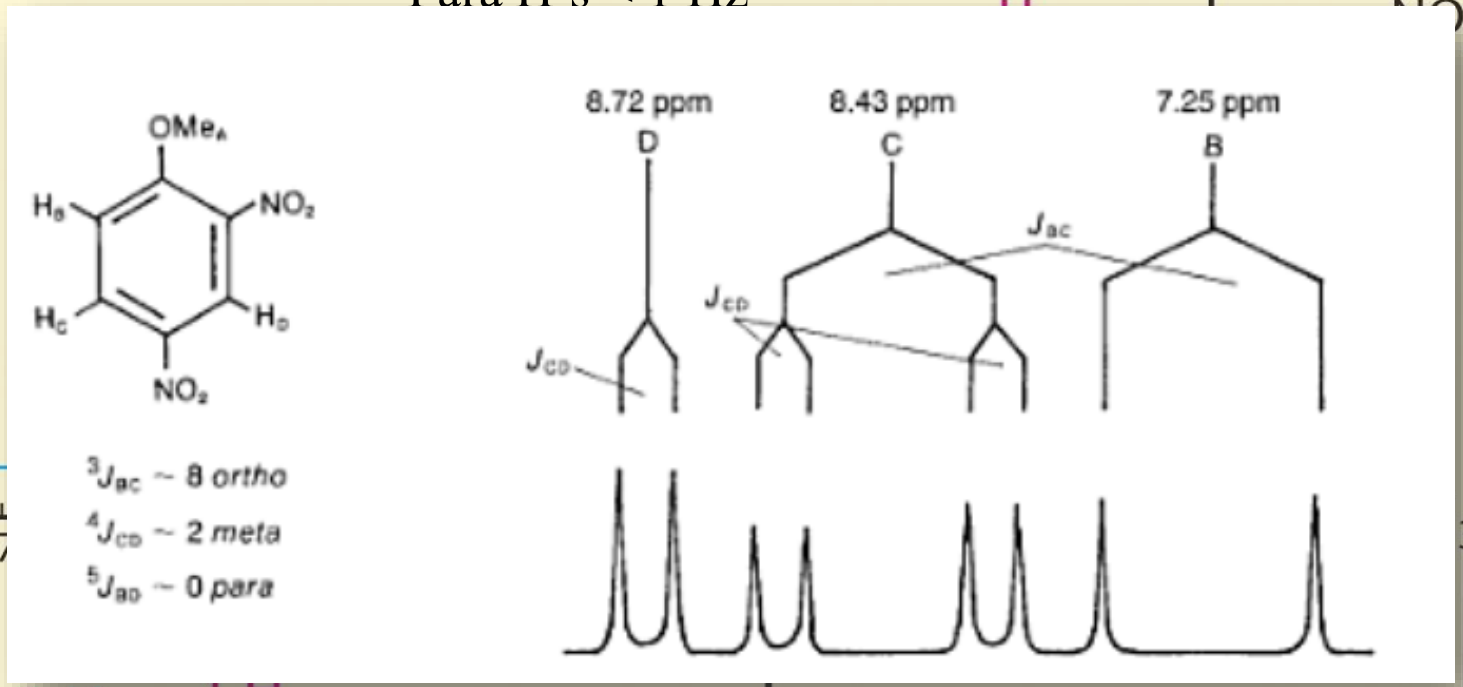
the six hydrogens on the inside of the ring resonate at δ - 3.00!!

Up field of TMS!!

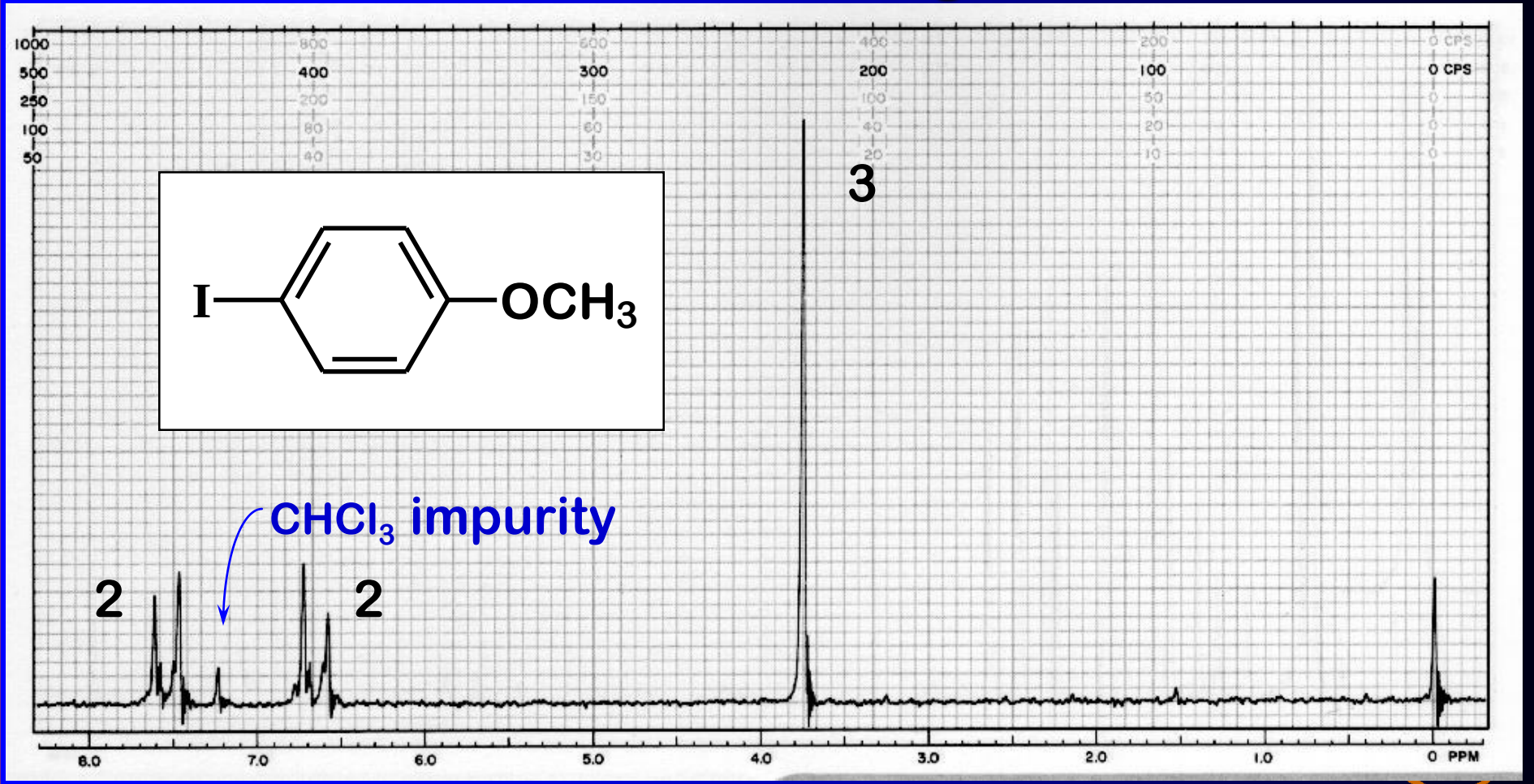
the twelve hydrogens on the outside of the ring resonate at δ 9.3

Coupling Constants - Aromatics

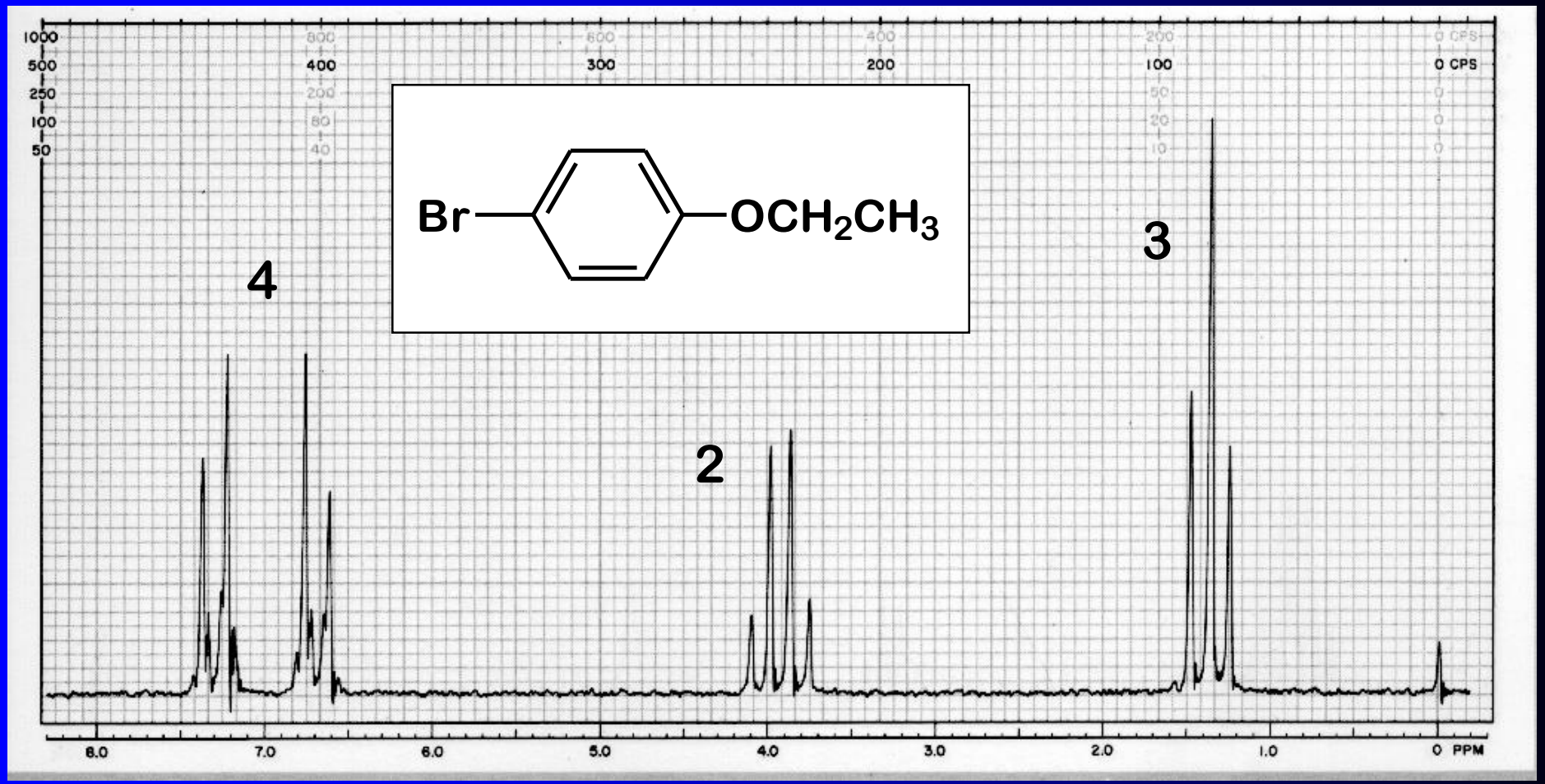
Ortho H's = 9 Hz
Meta H's = 3 Hz
Para H's < 1 Hz



NMR Spectrum of 1-iodo-4-methoxybenzene

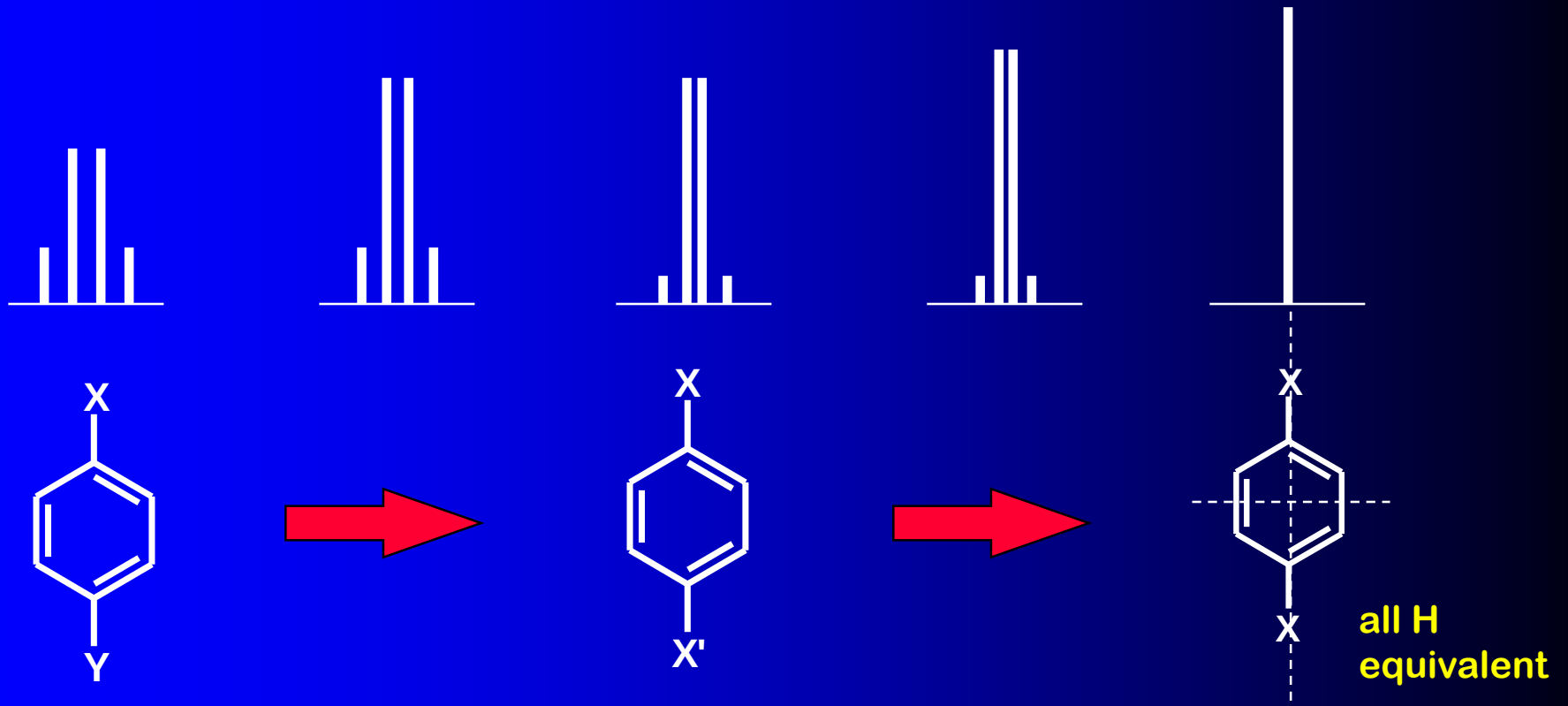


NMR Spectrum of 1-bromo-4-ethoxybenzene



THE p-DISUBSTITUTED PATTERN CHANGES AS THE TWO GROUPS BECOME MORE AND MORE SIMILAR

All peaks move closer.
Outer peaks get smaller ..... and finally disappear.
Inner peaks get taller..... and finally merge.



X ≠ Y

X ~ X'

X = X

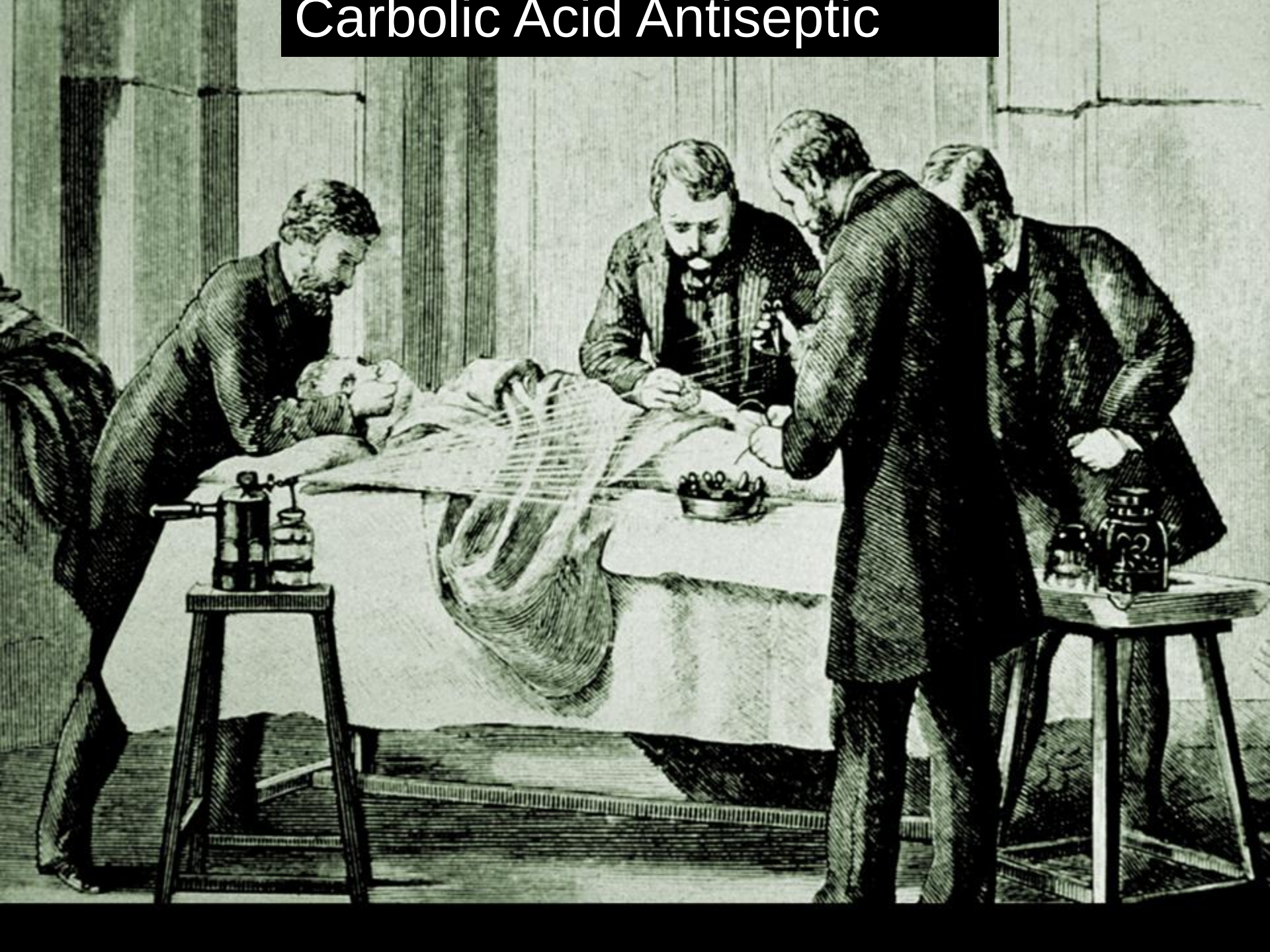
Phenol

Joseph Lister

1827 - 1909

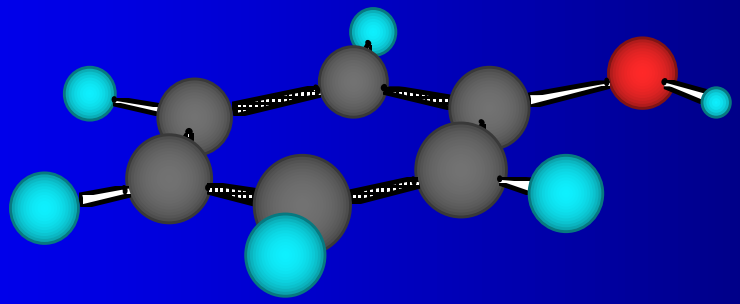
A British surgeon and a pioneer of antiseptic surgery, who successfully introduced carbolic acid (now known as phenol) to sterilize surgical instruments and to clean wounds, which led to reducing post-operative infections and made surgery safer for patients.

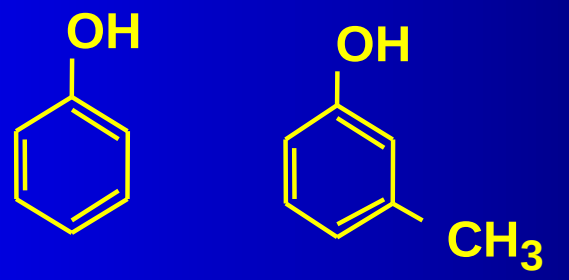
Carbolic Acid Antiseptic



Phenols

- The functional group of a phenol is an -OH group bonded to a benzene ring



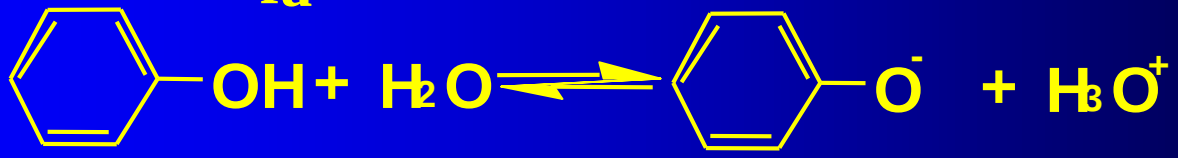


Phenol **3-Methylphenol (m-Cresol)**

Acidity of Phenols

- Phenols are much more acidic than aliphatic alcohols that also contain the -OH group

Phenol: pK_a = 9.95

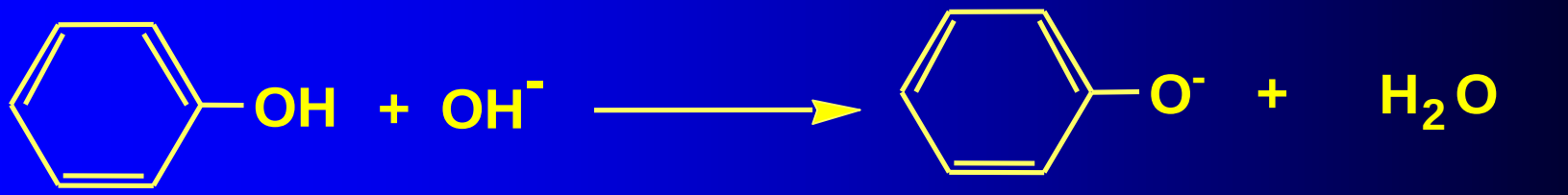


Ethanol: pK_a = 15.9

$CH_3CH_2OH + H_2O \rightleftharpoons CH_3CH_2O^- + H_3O^+$

- delocalization of the negative charge by resonance stabilizes the phenoxide ion relative to the alkoxide ion

Acidity of Phenols



pKa 9.95

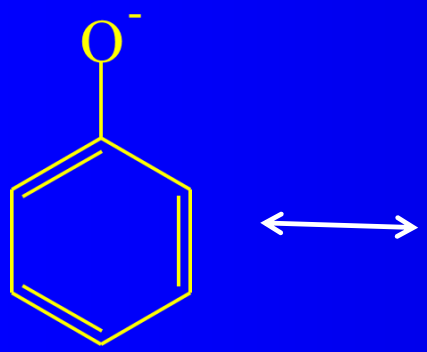
pKa 15.7

Strong acid + Strong base ⟶ Weak base + Weak acid

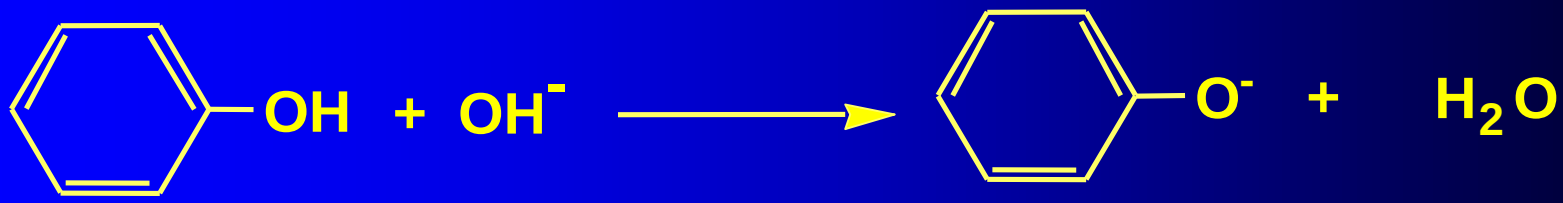
- Strong acids have weak conjugate bases
- Stabilization of anions leads to weakly conjugate bases!

Lets move electrons together!!

PLEASE FOLLOW ME STEP BY STEP



Acidity of Phenols



pKa 9.95

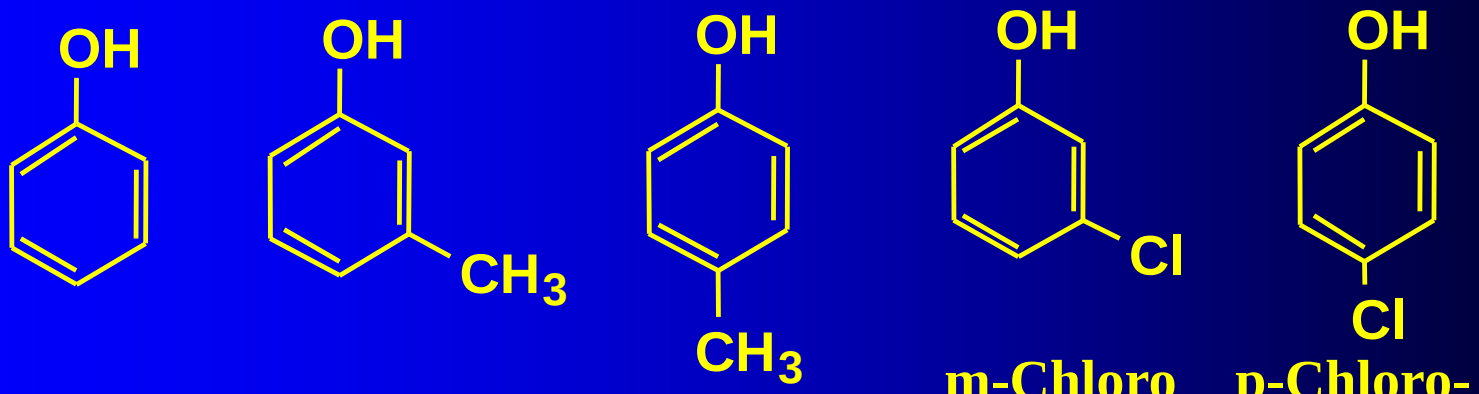
pKa 15.7

Strong acid + Strong base ⟶ Weak base + Weak acid

- Strong acids have weak conjugate bases
- Stabilization of anions leads to weak/stable conjugate bases!

Acidity of Phenols

- Alkyl and halogen substituents effect acidities by inductive effects
  - alkyl groups are electron-releasing by "induction"
  - halogens are electron-withdrawing by "induction"



Phenol pK_a 9.95

m-Cresol pK_a 10.01

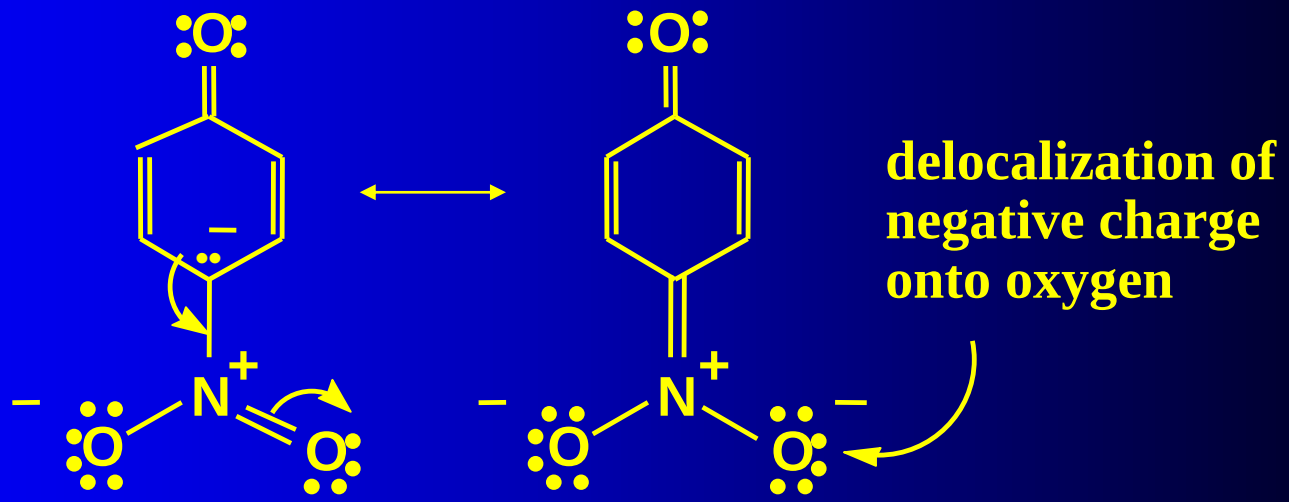
p-Cresol pK_a 10.17

m-Chloro phenol pK_a 8.85

p-Chloro-phenol pK_a 9.18

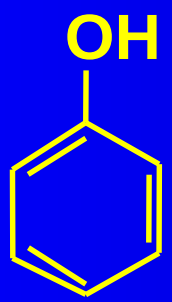
Acidities of Phenols

- Part of the acid-strengthening effect of -NO_2 is due to its electron-withdrawing inductive effect
- In addition, -NO_2 substituents in the ortho and para positions help to delocalize the negative charge by Resonance

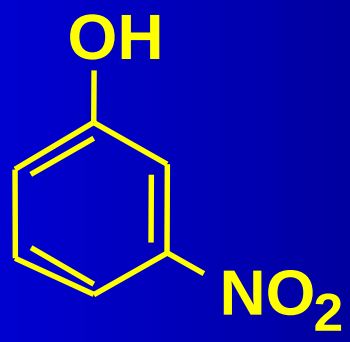


Acidities of Phenols

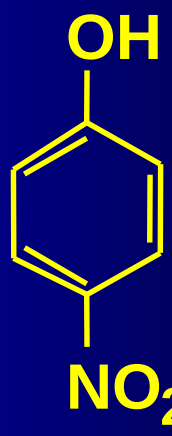
- Nitro groups increase the acidity of phenols by both an electron-withdrawing inductive effect and a resonance effect



Phenol
pK_a 9.95



m-Nitrophenol
pK_a 8.28



p-Nitrophenol
pK_a 7.15