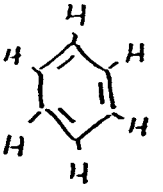
HAPTER 16 LECTURE NOTES FOR ORGANIC CHEMISTRY

AROMATIC COMPOUNDS

WHEN A NEW COMPOUND, C_6H_6 WAS DISCOVERED IN ≈ 1830 NO ONE COULD IMAGINE A STRUCTURE. MANY WERE PROPOSED, AND A GENERATION OF DEBATE FOLLOWED. IN 1858 CARBON CHAINS WERE PROPOSED IN ≈ 1860, AUGUST KEKULÉ HAD THE REVOLUTIONARY INSIGHT — A RING

KEKULÉ STRUCTURE  WAS CONSIDERED QUITE BIZARRE

SINCE BENZENE FORMS ONLY 1 1,2 DICHLORO PRODUCT, KEKULE PROPOSED THIS FAST INTERCONVERSION

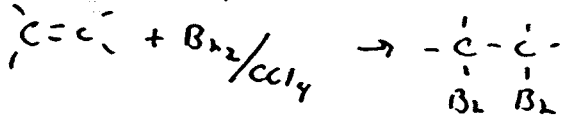
WHICH IS THE FORERUNNER OF OUR CURRENT RESONANCE STRUCTURE

 KEKULÉ STRUCTURES

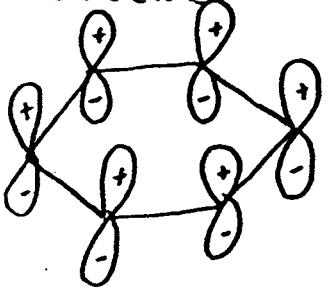
THESE ARE ONLY CONVENIENT CONSTRUCTS, A BETTER PICTURE IS

WE FIND BY HYDROGENATION THAT BENZENE HAS 36 KCAL/MOL RESONANCE STABILIZATION

THIS STABILITY MEANS THAT BENZENE DOES NOT UNDERGO ALKENE REACTION

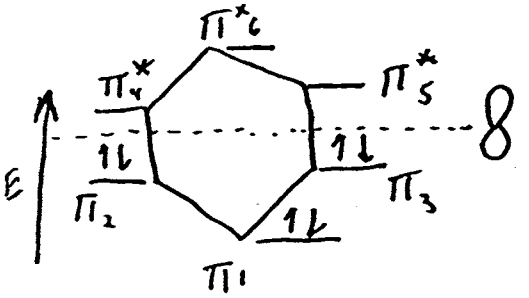


THE MOLECULAR ORBITALS OF BENZENE



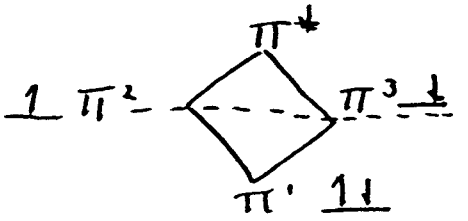
THIS IS THE LOWEST OF 6 MO's ALL BONDING

THE ENERGY DIAGRAM OF BENZENE MO's



ALL 6 π e⁻ IN BONDING MO's VERY STABLE

IN CONTRAST TO BENZENE, THE 4 π e OF CYCLOBUTADIENE OCCUPY LESS FAVORABLE MOs



THE COMPOUND HAS 2 UNPAIRED ELECTRONS IN ORBITALS OF BOND ORDER ZERO

SO, YOU CAN DRAW 2 RESONANCE STRUCTURES FOR CYCLOBUTADIENE

 BUT THE MO PICTURE SAYS NO RESONANCE STABILIZATION

AROMATIC, ANTIAROMATIC, NONAROMATIC

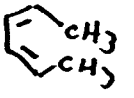
WE COMPARE MANY CYCLIC, CONJUGATED SYSTEMS

TO BE AROMATIC

1) CYCLIC, WITH CONJUGATED π BONDS
2) EACH RING ATOM MUST HAVE A P ORBITAL
3) THESE P ORBITALS MUST OVERLAP CONTINUOUSLY (USUALLY PLANAR)
4) DELOCALIZATION OF THE π ELECTRONS MUST RESULT IN LOWER ENERGY

AN <u>ANTIAROMATIC</u> COMPOUND MEETS CRITERIA 1-3 BUT π DELOCALIZATION INCREASES ENERGY  LESS STABLE THAN  OPEN CHAIN

VIOLATING CRITERIA 1-3 MEANS → <u>NONAROMATIC</u>

 → SIMILAR STABILITY ← 

TO CRITERIA 1-4 WE ADD HÜCKELS RULE

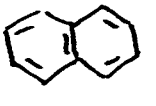
AROMATIC IF # π ELECTRONS = $4N+2$ WHERE N IS AN INTEGER

$N=1 \rightarrow 6\ \pi$ ELECTRONS
$N=0 \rightarrow 2\ \pi$ ELECTRONS
$N=2 \rightarrow 10\ \pi$ ELECTRONS

MOST LARGE RING SYSTEMS ARE NON PLANAR, THEREFORE NONAROMATIC

SOME LARGE $4N+2$ ANNULENES ARE AROMATIC

 [14]-ANNULENE AROMATIC

FUSED RING SYSTEMS CAN BE PLANAR  NAPHTHALENE AROMATIC

HE MO DERIVATION OF HÜCKELS RULE

MO's IN THESE SYSTEMS HAVE 1 LOWEST FILLED MO → THE "+2"
AND PAIRS OF HIGHER LEVEL MO's FILLED WITH 4 ELECTRONS → THE "4N"
IF THERE ARE ONLY 2 ELECTRONS FOR THESE 2 MO's THE
SHELL IS HALF FILLED, ANTI AROMATIC, LIKE CYCLOBUTADIENE

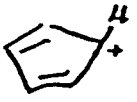
ROMATIC IONS


CYCLOPENTADIENE

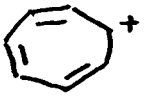
ITS UNUSUALLY ACIDIC
pK_a = 16 VS 46 FOR 

+ STRONG BASE → 
+ BH

4N+2 AROMATIC


THE CYCLOPENTADIENYL CATION HAS
4 N ELECTRONS → ANTI AROMATIC

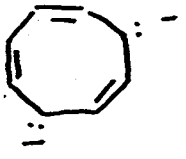
HE
CLOHEPTA CYCLOHEPTATRIENYL
ENYL CATION IS ALSO 4N+2 AROMATIC
IT THE ANION IS ANTI AROMATIC


COMMON NAME TROPYLIUM ION

REPRESENTS THE MOST STABLE CARBOCATION WE'VE SEEN

VERY UNUSUAL DIANION OF CYCLOOCTATETRAENE CAN BE MADE





NON AROMATIC
NON PLANAR

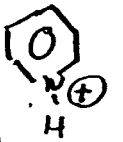
PLANAR
4N+2 AROMATIC

NEXT PAGE
SUMMARIZES AROMATIC, ANTIAROMATIC RINGS

ETEROCYCLIC AROMATIC COMPOUNDS

HETEROCYCLIC COMPOUNDS CONTAIN HETEROATOMS N, S, O

PYRIDINE IS THE AROMATIC ANALOG OF BENZENE WITH N IN THE RING


IT IS BASIC, LIKE AMMONIA →


PYRIDINIUM ION

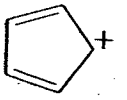
2 pi-electron systems (aromatic)

cyclopropenyl cation (cyclopropenium ion)

4 pi-electron systems (antiaromatic)

cyclobutadiene

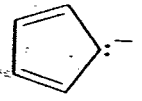
cyclopropenyl anion



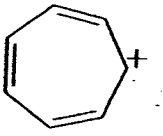
cyclopentadienyl cation

6 pi-electron systems (aromatic)

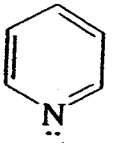
benzene



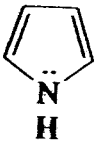
cyclopentadienyl anion (cyclopentadienide ion)



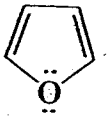
cycloheptatrienyl cation (tropylium ion)



pyridine

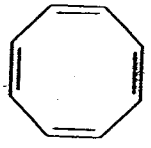


pyrrole

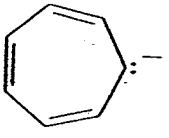


furan

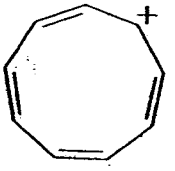
8 pi-electron systems (antiaromatic if planar)



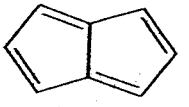
cyclooctatetraene (not planar)



cycloheptatrienyl anion

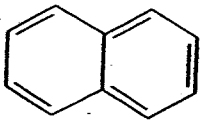


cyclononatetraenyl cation

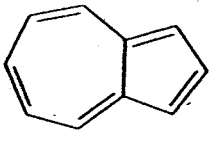


pentalene

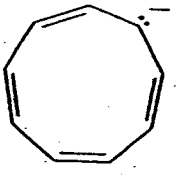
10 pi-electron systems (aromatic)



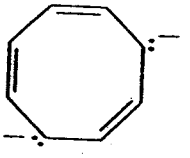
naphthalene



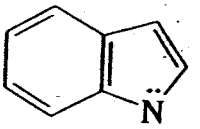
azulene



cyclononatetraenyl anion



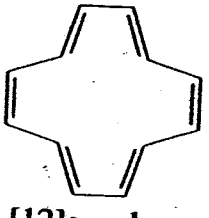
cyclooctatetraenyl dianion



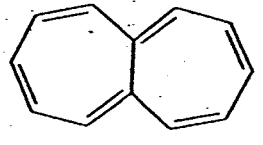
indole

(Naphthalene can also be considered as two fused benzenes.)

12 pi-electron systems (antiaromatic if planar)



[12]annulene (not planar)



heptalene

HETEROCYCLIC AROMATICS

PYRROLE

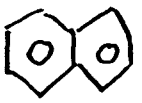
FURAN

THIOPHENE

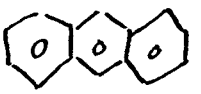
ANISOELECTRONIC SERIES WITH 6 π ELECTRONS

OLYNUCLEAR AROMATIC HYDROCARBONS (PAH)

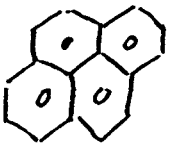
FUSED RING SYSTEMS



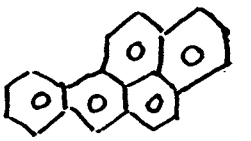
NAPHTHALENE



ANTHRACENE



PYRENE



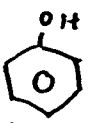
BENZO[a]PYRENE

THE HIGHER PAH ARE CARCINOGENIC SUCH AS PYRENE AND BaP

FOUND IN COMBUSTION PRODUCTS – FOREST FIRES, ENGINE EXHAUST, CIGARETTES

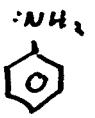
OMENCLATURE OF BENZENE DERIVATIVES

MANY COMMON NAMES

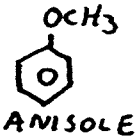


PHENOL
CARBOLIC ACID

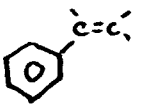
TOLUENE



ANILINE



ANISOLE



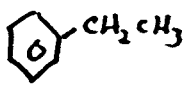
STYRENE

BENZALDEHYDE

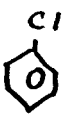
BENZOIC ACID

COMPOUNDS MAY BE NAMED AS DERIVATIVES OF BENZENE

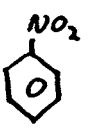
ALKYL BENZENES



HYLBENZENE

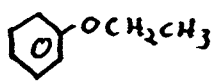


CHLOROBENZENE



NITROBENZENE

BENZENE AS A SUBSTITUENT IS CALLED PHENYL (MAY BE ABBREVIATED AS PH OR ϕ IN CONDENSED STRUCTURES)

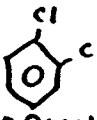


ENYLETHYL ETHER

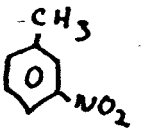
ϕ_3CH

TRIPHENYLMETHANE

SUBSTITUTED BENZENES ARE CALLED ORTHO (1,2), META (1,3), PARA (1,4)



THO DICHLOROBENZENE
-DICHLOROBENZENE

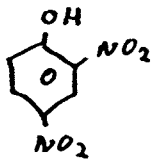


METANITROTOLUENE

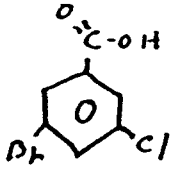
PARANITROPHENOL

ENZENES WITH 3 OR MORE SUBSTITUENTS ARE NUMBERED

1 IS ASSIGNED TO THE CARBON BEARING THE FUNCTIONAL GROUP THAT DEFINES HE BASE NAME

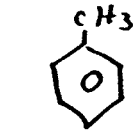


2,4-DINITROPHENOL

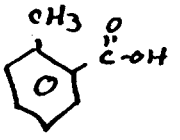


3-BROMO-5-CHLORO BENZOIC ACID

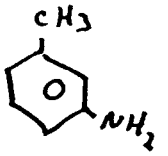
OME MORE COMMON NAMES



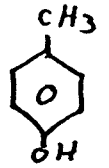
TOLUENE



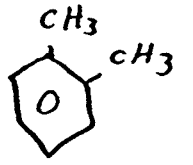
O-TOLUIC ACID



M-TOLUIDINE

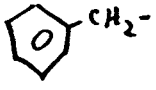


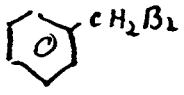
P-CRESOL



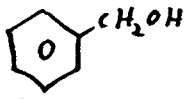
O-XYLENE

IE 7 CARBON UNIT IS CALLED BENZYL





BENZYL BROMIDE



BENZYL ALCOHOL

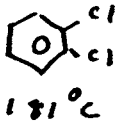
INALLY, AROMATIC COMPOUNDS ARE SOMETIMES CALLED ARENES

AR- FOR SHORT AR-O-R AR-NH$_2$

RYL AS SUBSTITUENT ARYL ALKYL ETHER ARYL AMINE

HYSICAL PROPERTIES

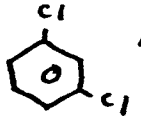
HIGH SYMMETRY MEANS LOW POLARITY IN THIS SERIES



ODCB

BP 181°C

MP -17°C



MDCB

173°C

-25°C

PDCB

170°C

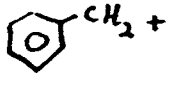
54°C

IGH SYMMETRY GIVES GOOD CRYSTAL PACKING

ECTROSCOPY OF AROMATIC COMPOUNDS

IR C=C STRETCH 1600 LOWEST OF THE C=C STRETCHES

MASS BENZYLIC COMPOUNDS CLEAVE TO STABLE BENZYLIC CATIONS



$C_7H_7 = 91$

NMR AR-H 6.5-8.2 PPM HIGHER SHIFTS FROM e^- WITHDRAWING SUBSTITUENTS, $-C\equiv N$, $-\overset{O}{\overset{\|}{C}}-$, $-NO_2$

LOWER SHIFTS FROM e^- DONATING $-OH$, $-OR$, $-NH_2$

CHAPTER 16

SKILLS

CHOOSE AROMATIC, NONAROMATIC OR ANTIAROMATIC	15, 19, 20, 23, 29
NOMENCLATURE	SEC 12.1-12.2
KNOW THE ANNULENES AND THEIR IONS (SEE SKILL 1)	16, 17, 18, 21
UNDERSTAND THE ISOMER NUMBER PROOF OF STRUCTURE	PG 469 FF

CHAPTER 17

UNDERSTAND THE MECHANISM OF ELECTROPHILIC AROMATIC SUBSTITUTION	45-48
SHOW THE PRODUCTS/REAGENTS FOR VARIOUS SUBSTITUTIONS	31-35, 39
PREDICT THE EFFECTS OF SUBSTITUENTS ON RATE AND REGIOCHEMISTRY	31-37, 40-42
USE THESE REACTIONS IN SYNTHESIS	38, 43, 44