REACTIONS AND PROPERTIES OF AROMATIC HETEROCYLCES

خصائص وتفاعلات الحلقات aromaticity

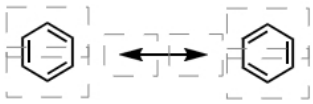
Dr. Solomon Derese

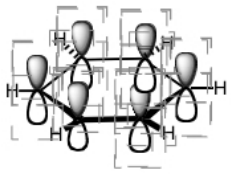
Aromaticity

Hückel

4n + 2

Benzene





All C sp^2

الحلقات aromaticity هي حلقات تشبه حلقة البنزين لكن تختلف بإنه إستبدلنا كربونة بذرة heteroatom(N.,O,S)

تذكير بكيفية تحديد الحلقة aromatic:-

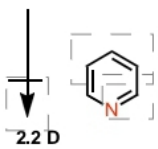
1-حلقي .... 2- conjugated (تبادل روابط أحادية و ثنائية)

٣-Huckle role :-(4n+2=πe)

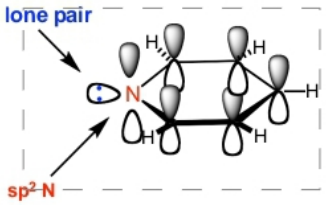
6-Membered heterocyclic rings

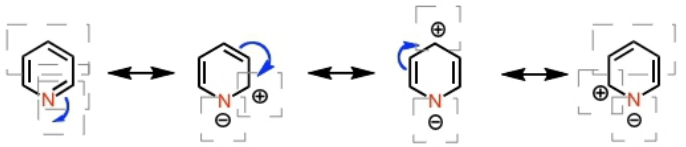
Heteroatom: N (or O)

Pyridine



N more electroneg. than C



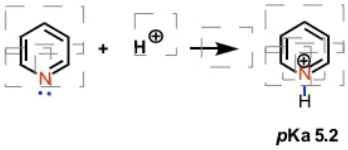


C-2, C-4 and C-6
Electron defficient

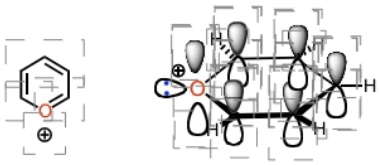
6-Membered heterocyclic rings

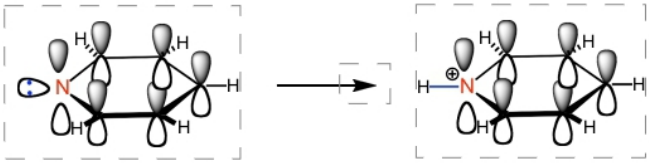
Heteroatom: N (or O)

Pyridine as a base



Pyrylium cation





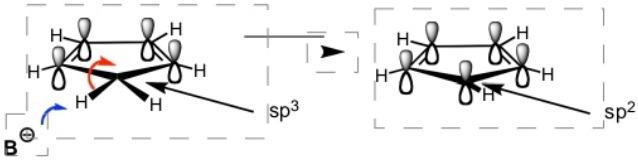
Still aromatic!

5-Membered heterocyclic rings

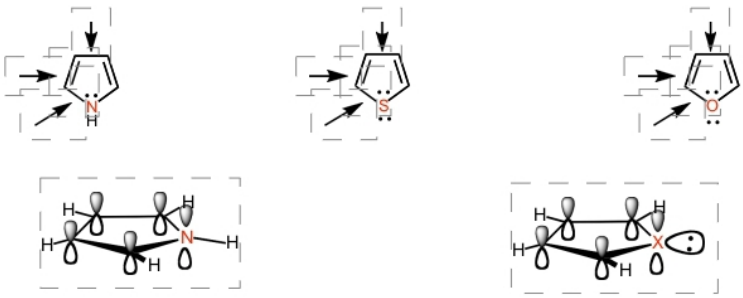
Heteroatom: N, O, S

Cyclopentadiene

Cyclopentadienyl
6 π–electrons



Pyrrole **Thiophene** **Furan**



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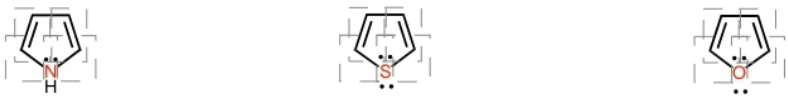
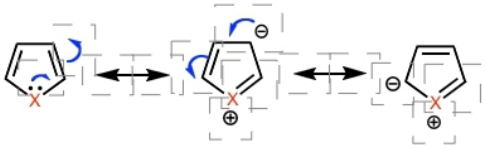
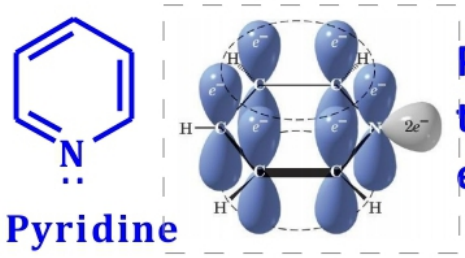




All C electron rich

SIX MEMBERED AROMATIC HETEROCYCLES

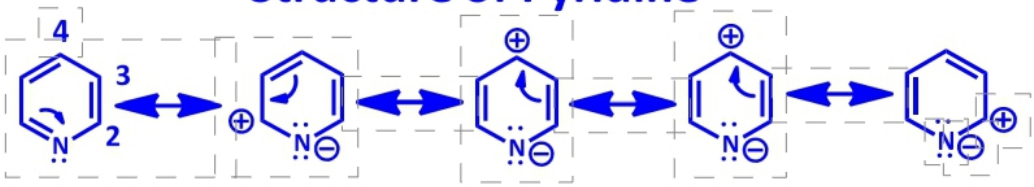


Pyridine

Pyridine is aromatic as there are six delocalized electrons in the ring.

Six-membered heterocycles are more closely related to benzene as they are aromatic on the basis of their π-electron systems without the need for delocalization of heteroatom lone pairs. The empirical resonance energy for pyridine is about 28 Kcal/mol, only slightly lower than that for benzene.

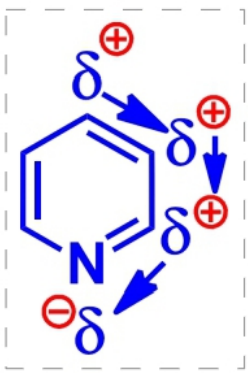
Structure of Pyridine

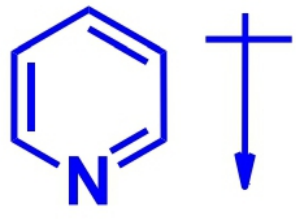


Pyridine has divalent negatively charged N, which is a stable condition for N. The positive charge is dispersed to carbons around the ring, specifically to C-2 and C-4.

The net effect is to reduce the π-electron density in the ring relative to benzene, and as result pyridine is electron deficient compared to benzene.

As a result, unlike benzene pyridine is polar molecule due to the electronegative nitrogen.





μ = 2.2 D

$Z = O^+, S^+, N$

Six membered heterocycles with an electronegative heteroatom are generally electron deficient compared to benzene. Such compounds are classified as π-deficient.

Electron-withdrawing heteroatoms decrease the π-electron density at the carbon atoms and are thus π-deficient relative to benzene.

Six memberd ring:

Heteroatom تمتلك electorongativity اكبر من c
لذلك تقوم بسحب الإلكترونات ويصبح عليها شحنة سالبة(-)

والكربونة شحنة موجبة (+) /// تهجين sp2 ما بتشارك إلكترونات

مما يعمل على تقليل π density لل aromaticity ring

وتصبح أقل من benzene بقليل ..... Reactivity لل six memberd ring أيضا تصبح أقل من benzene

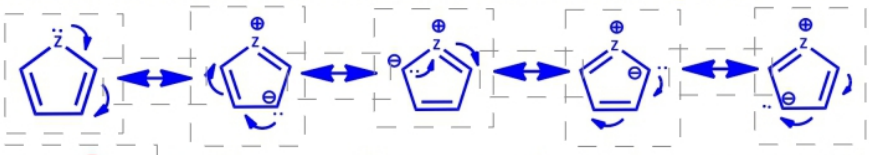
Resonance energy تتكون على الكربونة ortho(C2)
او c4(para)

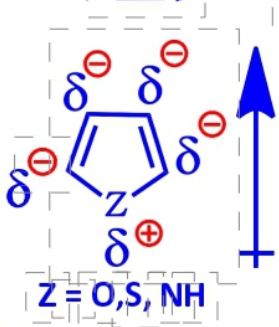
Meta (c2) لا يتكون عليها resonance energy

All six memberd ring π difecent

بسبب إنه lone pair الموجودات على heteroatom ما بتتشارك فيهم وأيضا بتعمل على سحب إلكترونات
فبتعطيها خصائص (week) bases وتتفاعل مع الحموض لتكون salt
نتيجة resonance energy يصبح للكربونة التي سُحب منها إلكترونات شحنة موجبة وبنعتبرها (electrophile) وتتفاعل معnucleophile
يعني كل الحلقات السداسيه تعمل على تكوين تفاعل nucleophile substance

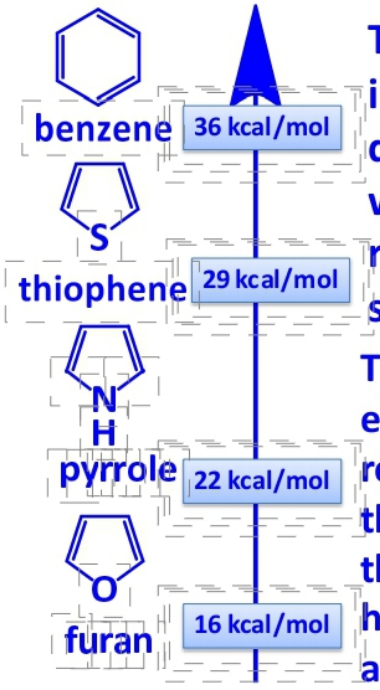
Structure of five membered heterocycles





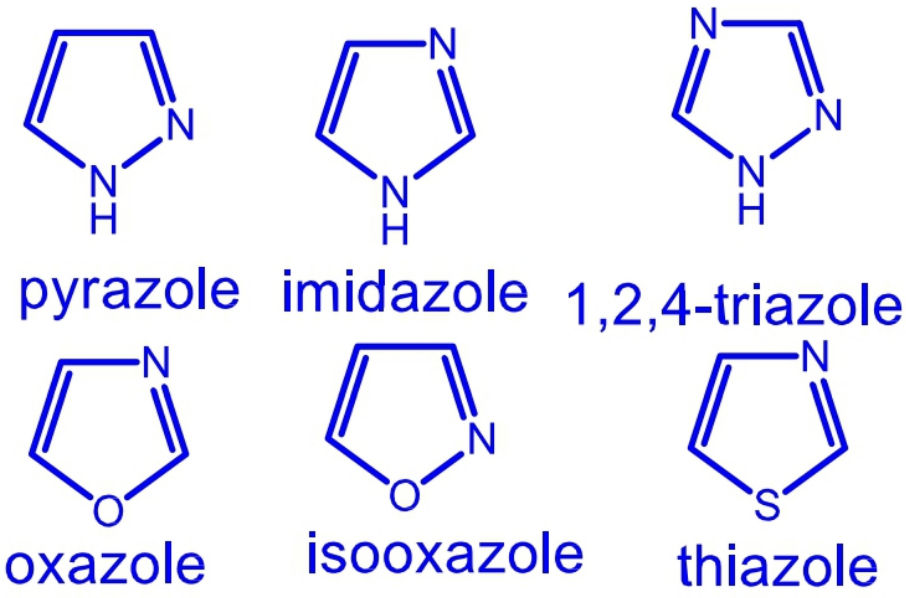
The five-membered aromatic heterocycle ring has a π-electron excess (six on five atoms), while in benzene, the π-electron density is one on each ring atom.

Five membered heterocycles with an electronegative heteroatom are generally electron rich compared to benzene (six electrons for five carbons). Such compounds are classified as π-excessive.



The degree of aromatic character in a five membered ring is determined by the ease with which the lone pair may be released into the delocalized system.

The ease with which the lone pair electron is released is directly related to the electronegativity of the heteroatom. Thus the lower the electronegativity of the heteroatom, the higher the aromaticity.



اما تركيب aromaticity five ring

هي على عكس الحلقة السداسية

1- التهجين sp3 تشارك lone pair مع الكربونات c2 او c3

Mostly c2 لكن إذا صار blocked لل C2 بتتشارك مع C3

تصبح heteroatom ذات شحنة موجبة والكربونة شحنة سالبة فبتشكل تفاعل electrophile substitution

Five memberd ring:-6πe and 5C

عشان هيك بتكون π excessive

Reactivity:- جميع الحلقات الخماسية (aromaticity) أكثر reactivity من benzene

The degree of aromatic

Benzene>thiophene>pyrrole>furan

اعتمدنا بالترتيب على عاملين :- ١- سهولة تشارك lone pair directly

electorongativity:- indirectly -2