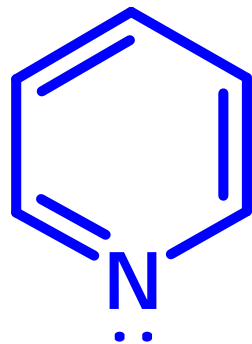
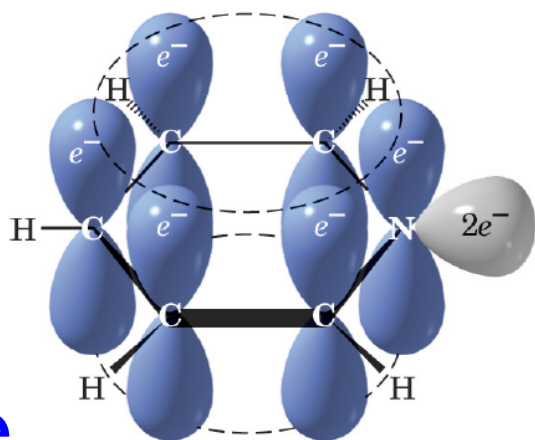


SIX MEMBERED AROMATIC HETEROCYCLES



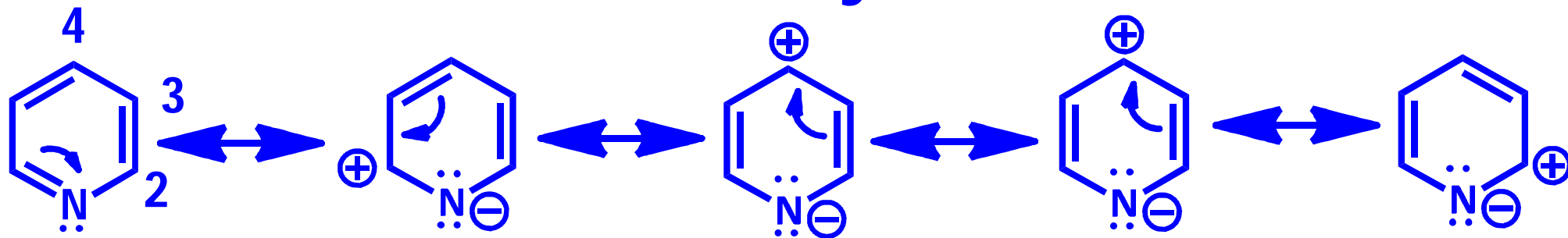
Pyridine



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.

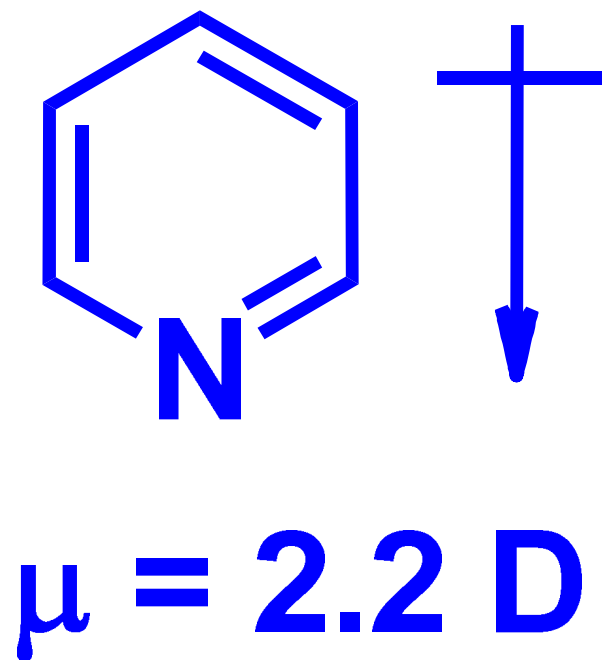
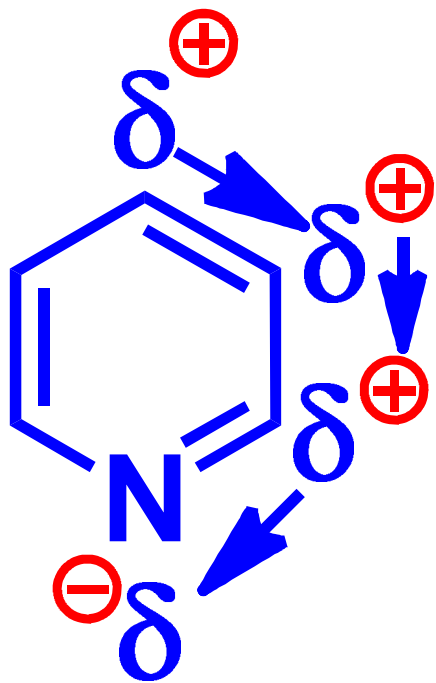
Structure of Pyridine

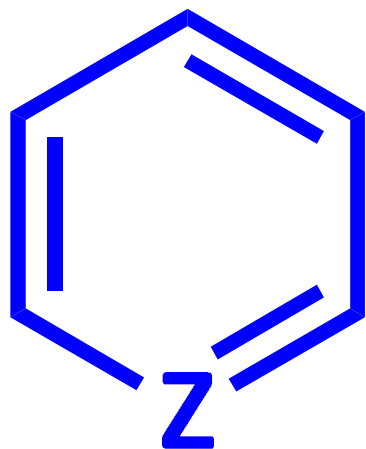


Pyridine has divalent negatively charged N, which is a stable condition for N. The positive charge is dispersed to carbons around the ring, specifically to C-2 and C-4.

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.



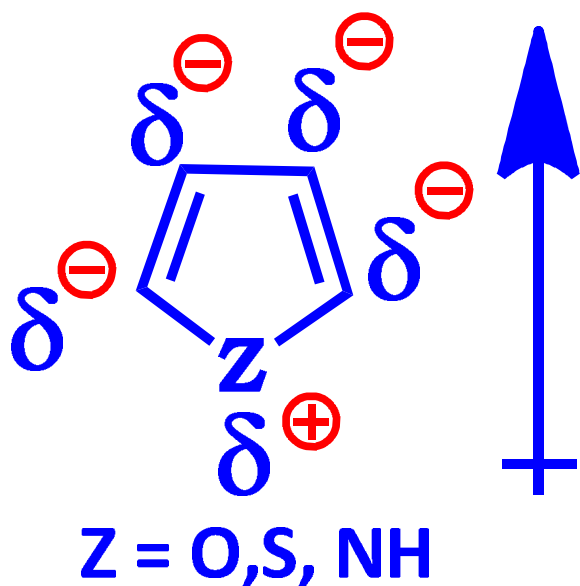
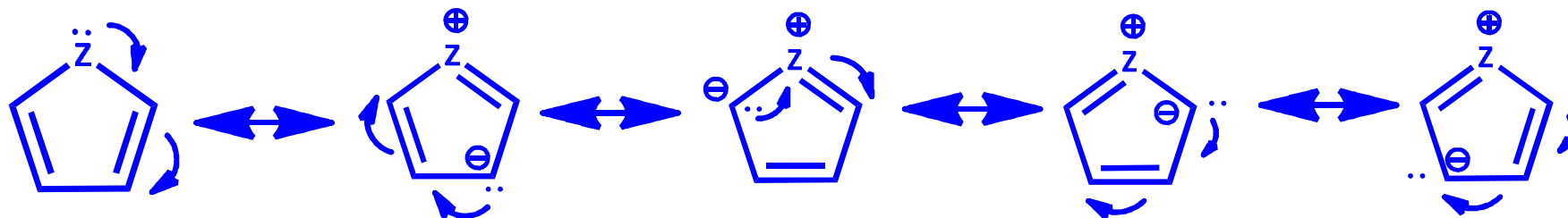


$Z = O^+, S^+, N$

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

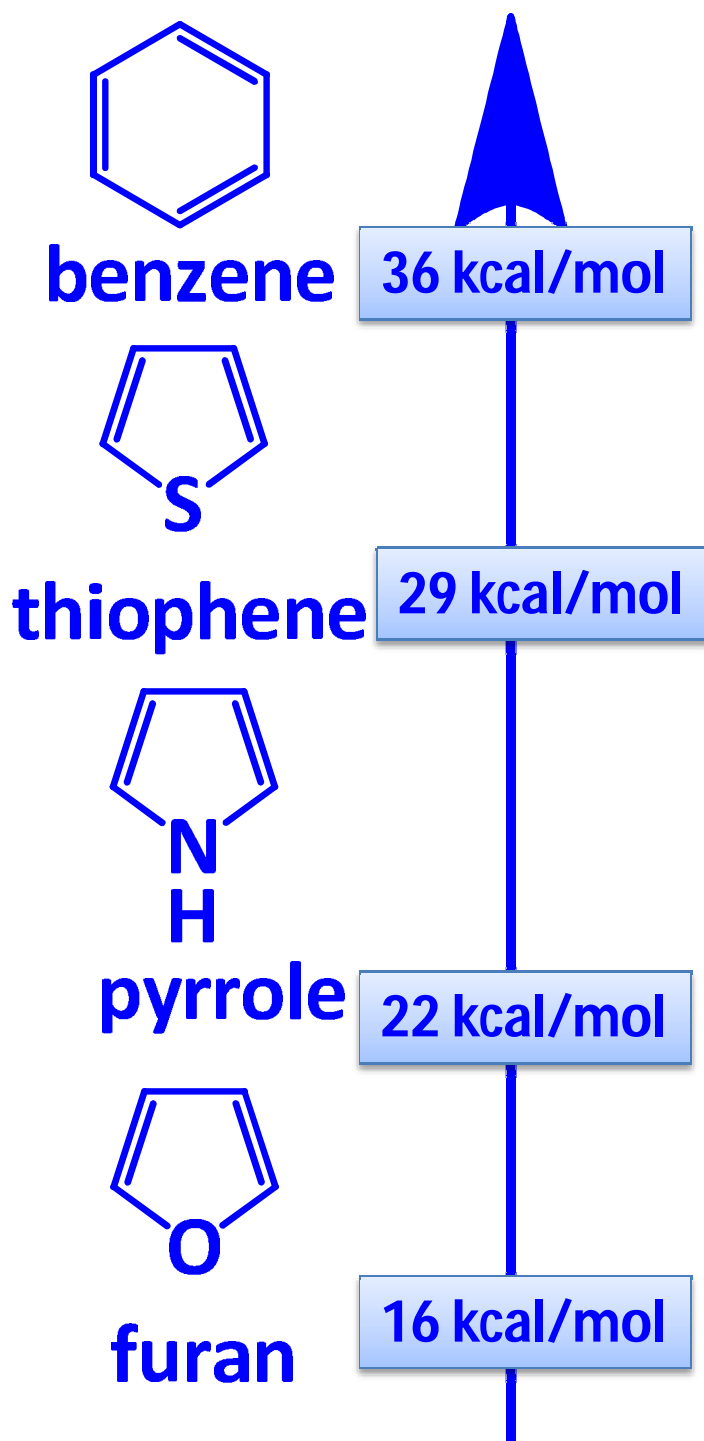
Electron-withdrawing heteroatoms decrease the π -electron density at the carbon atoms and are thus π -deficient relative to benzene.

Structure of five membered heterocycles



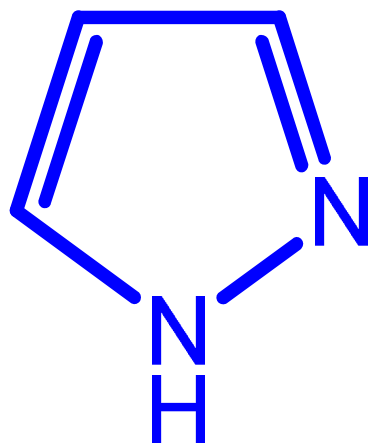
The five-membered aromatic heterocycle ring has a π -electron excess (six on five atoms), while in benzene, the π -electron density is one on each ring atom.

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.

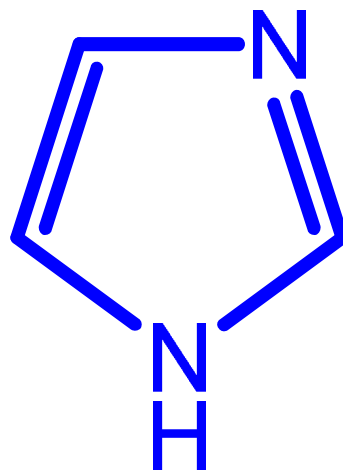


The degree of aromatic character in a five membered ring is determined by the ease with which the lone pair may be released into the delocalized system.

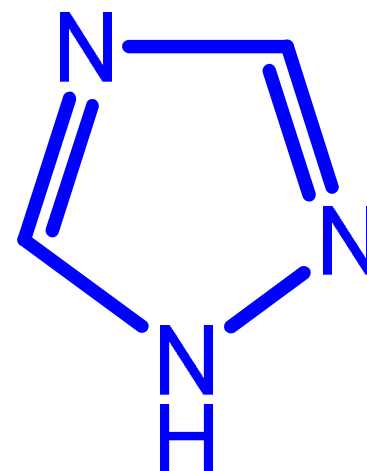
The ease with which the lone pair electron is released is directly related to the electronegativity of the heteroatom. Thus the lower the electronegativity of the heteroatom, the higher the aromaticity.



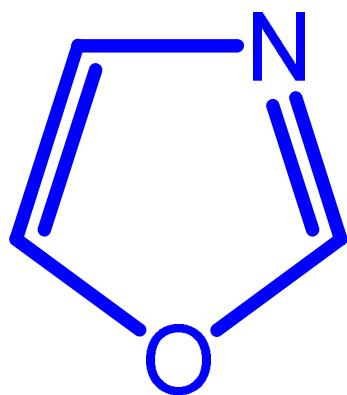
pyrazole



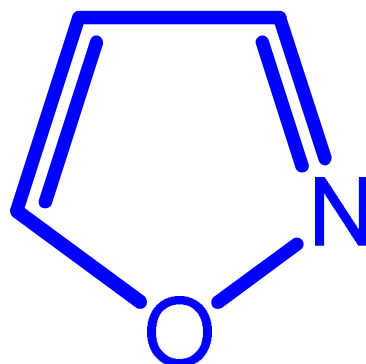
imidazole



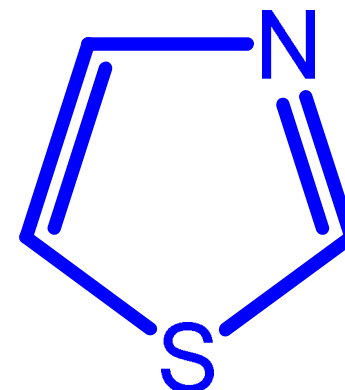
1,2,4-triazole



oxazole



isooxazole



thiazole

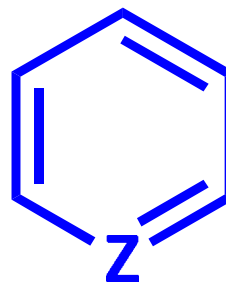
Aromatic Heterocycles

π - Excessive



Z = O, S, NH

π - Deficient



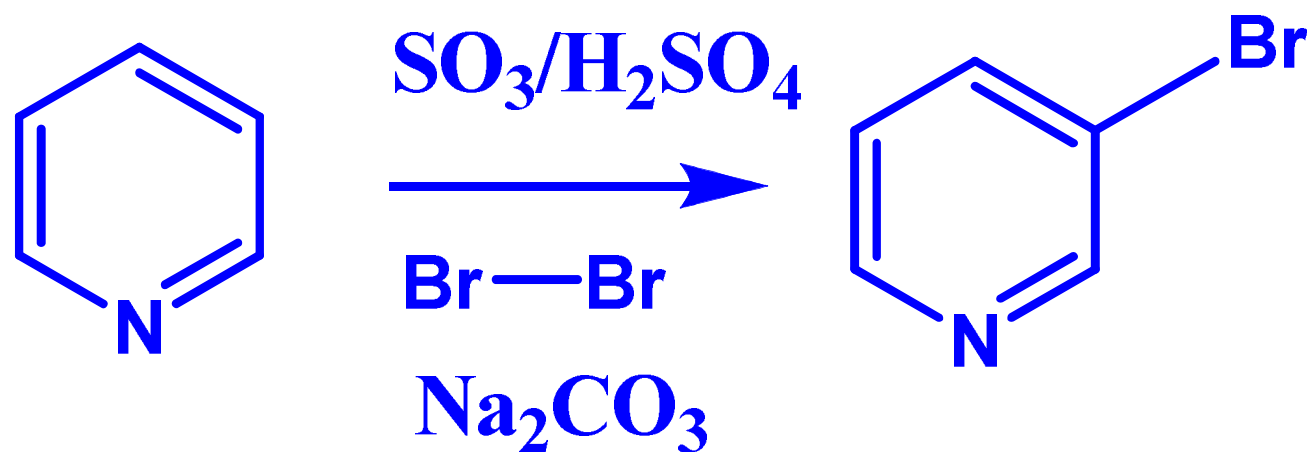
Z = O⁺, S⁺, N

This classification is not trivial; there is a vast difference between the properties of the two types of aromatic compounds.

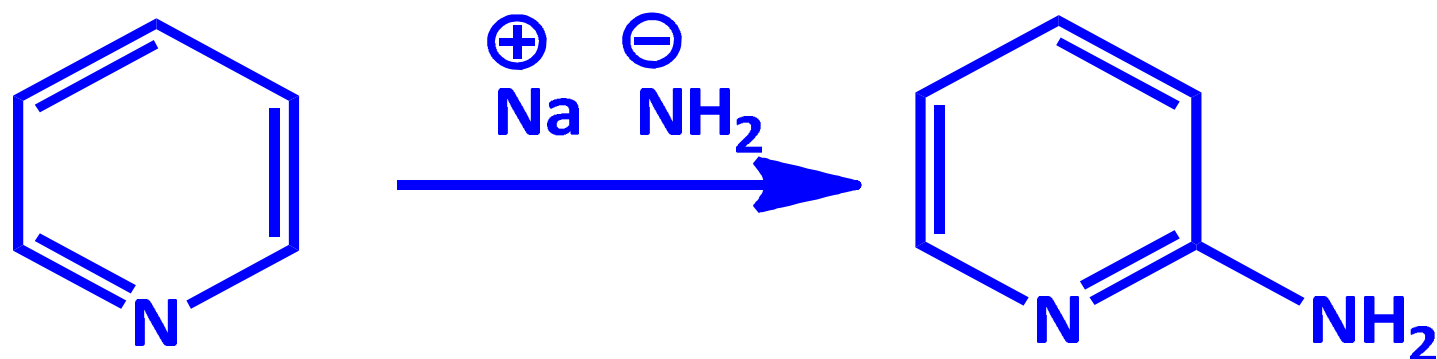
Reactions of π -deficient heterocyclic aromatic compounds

A hallmark of π -deficient heterocyclic systems is their low reactivity with electrophilic agents, **slower than benzene**. For example, pyridine is less reactive than benzene by a factor of 10^6 when subjected to conditions of nitration. The reactivity is on the order of that of nitrobenzene, which is well known to require much more drastic conditions than those for benzene itself.

For example, 3-bromopyridine is formed when pyridine is reacted with bromine in the presence of oleum (sulfur trioxide in conc. sulfuric acid) at 130°C.



Conversely pyridines are susceptible to nucleophilic attack.



Reactions of π -excessive heterocyclic aromatic compounds

A significant feature of the π -excessive ring systems is that they undergo electrophilic aromatic reactions **faster than benzene**.

The reactivity is greater than that of benzene and is in roughly the same range as found for benzenes bearing electron releasing groups such as in aniline. The greater electron density in these rings accounts for this higher reactivity.

These heterocycles undergo electrophilic aromatic substitution reactions much faster than benzene under similar conditions. The reasons for this are:

- I. The resonance energy of the heterocycles is less than that of benzene, i.e. less aromatic than benzene.
- II. The five-membered aromatic heterocycle ring has a π -electron excess (six on five atoms), while in benzene, the p-electron density is one on each ring atom.

Reaction with bromine requires no Lewis acid and leads to substitution at all four free positions.

