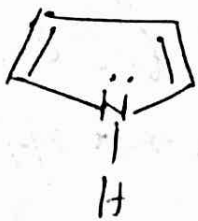
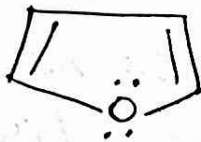


Pyrrrole, Furan, Thiophene



Pyrrrole



Furan



Thiophene

Structures

Resonance Theory

In case of pyrrrole, furan and thiophene, only four π electrons are contributed by the carbon atoms of the each heterocycle. In order to achieve aromatic sextet each heteroatom must contribute two non-bonding electrons to the ring for delocalization.

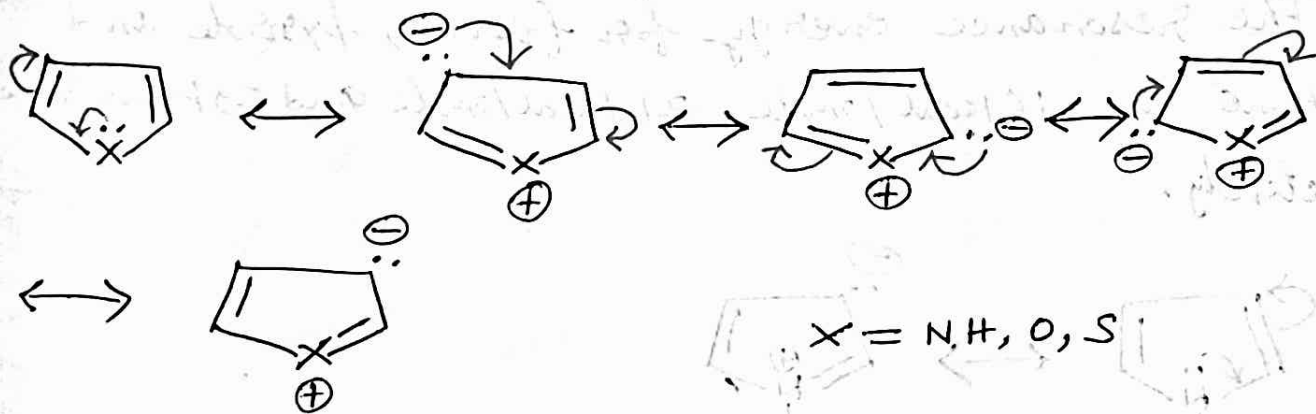
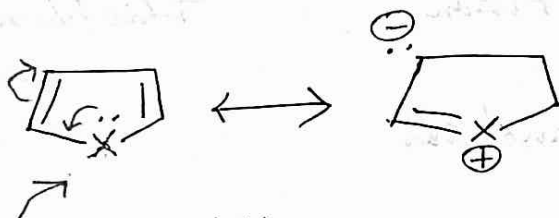


Fig. Resonance structures of five membered heterocycles

Basic Properties

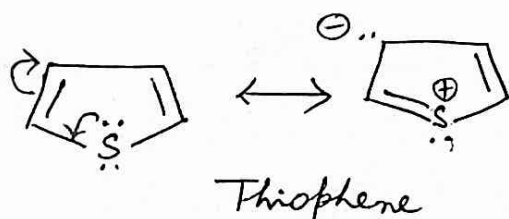
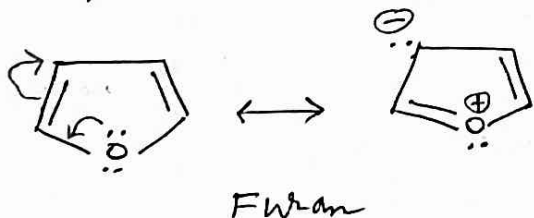
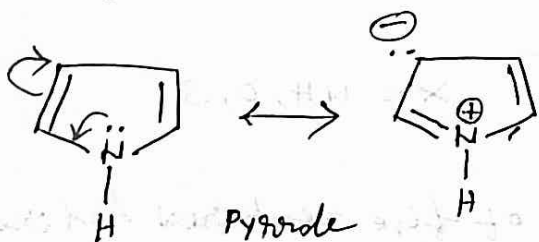
Since the non-bonding electron pair of heteroatom in each heterocycle is contributed to the ring to get aromatic sextet, they are not available for donation to a proton — thus these heterocycles are not appreciably basic.



Lone pairs not available for protonation

Resonance Energies

The resonance energy for furan, pyrrole and thiophene are 16 kcal/mole, 21 kcal/mole and 29 kcal/mole respectively.



Since, the electronegativities for furan, pyrrole, and thiophene heteroatoms are in the order $O > N > S$,

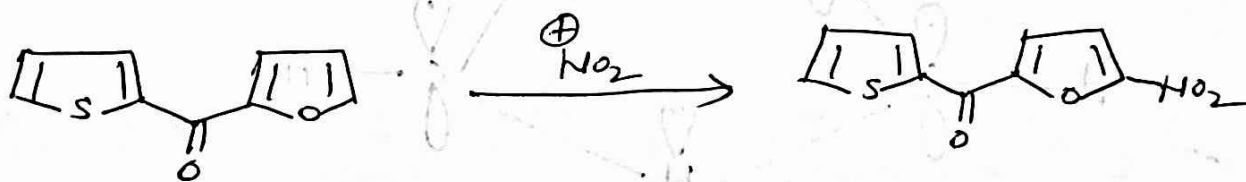
it is evident the least electronegative atom sulfur with positive charge is more stable than positive charge on 'N' or 'O' atoms in the resonating structures.

Therefore thiophene is the most stable and furan is least stable, pyrrole is in between them in terms of stability.

Therefore, aromaticity order: thiophene > pyrrole > furan — which is reflected in their resonance energies values.

Hence, furan being least aromatic is more reactive than pyrrole and thiophene.

An illustrative example is:



Molecular Orbital Theory

According to molecular orbital theory, each of the heterocyclic ring is planar pentagon containing four sp^2 hybridized carbon atoms and one sp^2 hybridized heteroatom. Each carbon atom contains singly occupied unhybridized p -orbital and the heteroatom contains doubly occupied unhybridized p -orbital. These p -orbitals are at right angles to the molecular plane. Overlap of p -orbitals of carbons and heteroatom form a π -electron cloud above and below the ring plane. Since, there are 6π electrons in each ring they follow Huckel's rule $(4n+2)\pi$, where $n=2$ and therefore, they are aromatic.

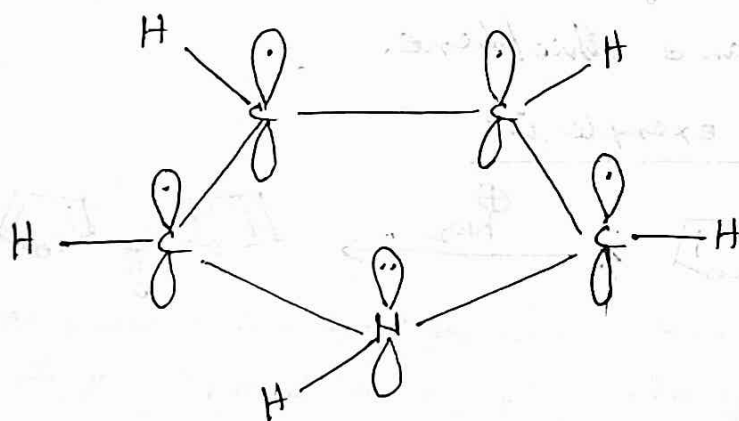
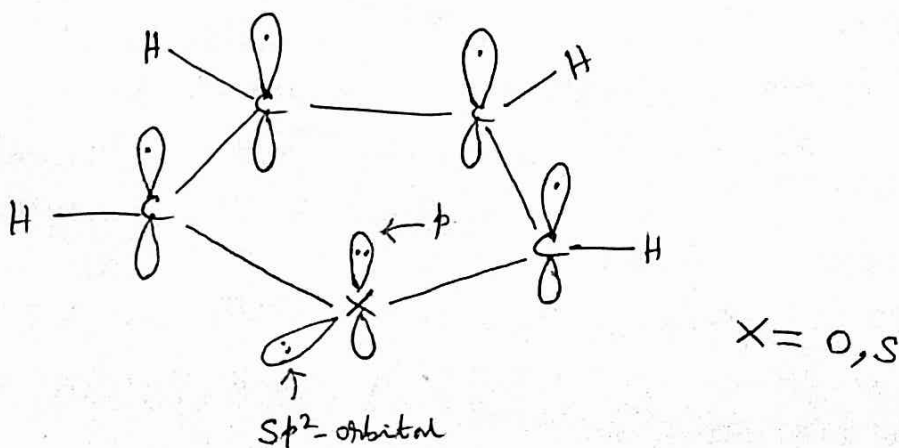


Fig: Overlap of p -orbitals in pyrrole

In furan and thiophene, the oxygen and sulfur atoms carry an unshared pair of electrons in an sp^2 orbital.



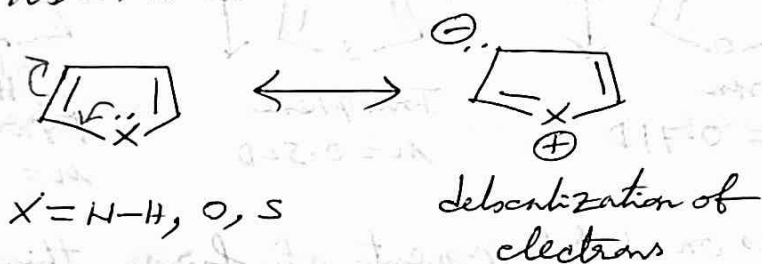
Five-membered aromatic heterocycles undergo electrophilic substitution reactions much faster than benzene — Why?

The reactivity of pyrrole, furan and thiophene towards electrophilic substitution reaction resembles that of phenol and aniline.

This is because of the fact that the lone pair of electrons from the heteroatom ^{is contributed} towards the ring for delocalization.

This makes the ring electron rich and thus activated.

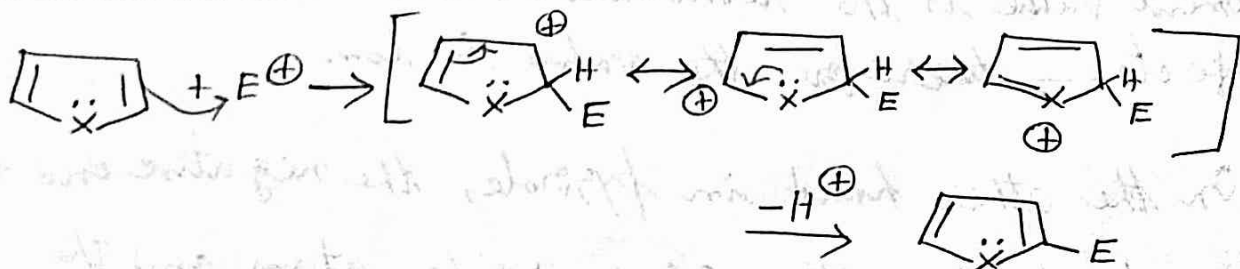
Therefore substitution occurs faster than in benzene.



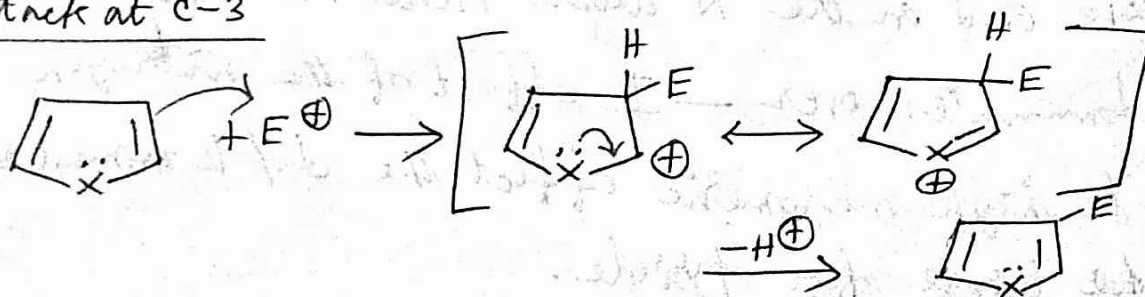
Position of the electrophilic substitution reaction

Electrophilic substitution occurs at C-2 position of pyrrole, furan and thiophene. This can be explained by considering the attack of an electrophile at C-2 and C-3 positions of pyrrole, furan and thiophene.

Attack at C-2



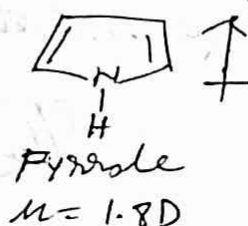
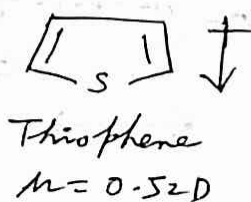
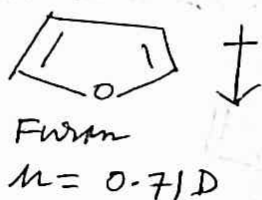
Attack at C-3



Intermediate carbocation formed by the attack at c-2 position can have three resonating structures whereas, the intermediate carbocation formed by the attack at c-3 position can have only two such resonating structures.

Therefore attack at c-2 by the electrophile would be preferred.

Dipole moments of Furan, Thiophene and Pyrrole



Studies on dipole moments of furan, thiophene and pyrrole reveal interesting facts.

In Furan and Thiophene, the negative end of the dipole is towards the heteroatom and the values are quite low.

This suggests that inductive effect ($-I$) of oxygen and sulphur are predominant than the mesomeric delocalisation ($+M$ effect) of lone pair of electrons of oxygen and sulfur atom. The observed dipole moment value is the resultant of these two opposite effects — therefore the value is low.

On the other hand, in pyrrole, the negative end of the dipole is on the ring carbon atoms and the positive end on the N atom. Here $+M$ effect predominates over $-I$ effect of the nitrogen. Due to high mesomeric effect the dipole moment value is ~~the~~ large for pyrrole.