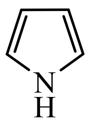
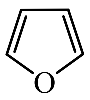
## 3 ) Five – membered rings:

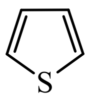
The simplest five – membered heterocyclic compounds are pyrrole, furan and thiophene, each of which contains a single hetero atom.



Pyrrole



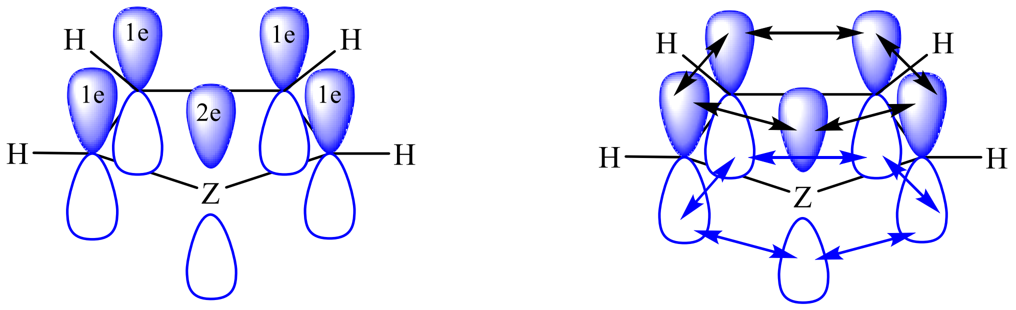
Furan



Thiophene

If we examine the structure for these compounds we can find that they consist of five membered planar aromatic ring system, since the ( *p* ) orbital of each of oxygen, nitrogen or sulfur possess an unshared pair of electrons that overlap with the ( π ) orbital's resulting in the formation of two electronic clouds ( π clouds ) one above and one below the plane of the ring as in benzene figure ( 1 ).

**<u>Note</u>**: the π clouds contain a total six electrons, the aromatic sextet.



( a ) ( b )

Z= NH, O or S

Figure ( 1 ): five membered heterocyclic molecule. ( a ) Two electrons in *p* orbital of hetero atom; one electron in *p* orbital of each carbon. ( b ) overlap of *p* orbitals to form π bonds.

Delocalization of the π electrons stabilizes the ring, thus the resonance energy for furan is 23 Kcal/mole while thiophene and pyrrole 31 kcal/mole. Thus the resonance energy will follow the sequence:

Benzene 36 > Pyrrole and Thiophene 31 > Furan 23

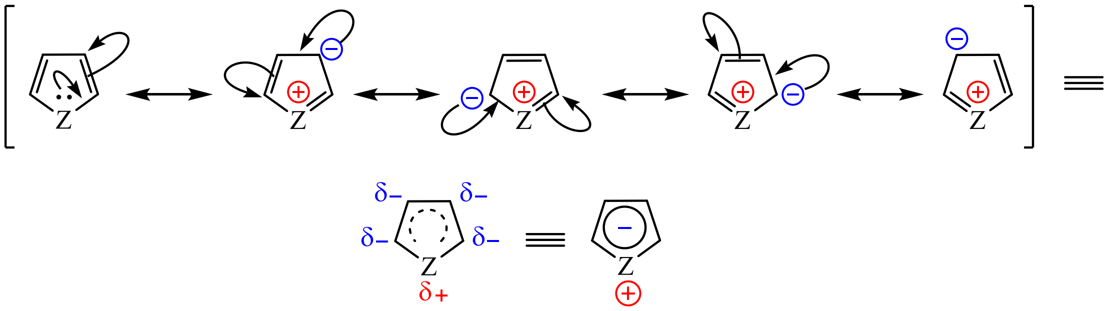
Aromatic properties for these compounds compared with benzene will be as the following:

Benzene > Thiophene > Pyrrole > Furan

Since benzene is a homocyclic compound and there is no differences in electronegativity between ring atoms, as in hetero aromatic systems.
Thus as the electronegativity of the hetero atom increase, the contribution of the unshared pair of electrons will decrease, hence the aromaticity (aromatic character) will decrease. So thiophene has more aromatic properties than pyrrole and furan respectively.

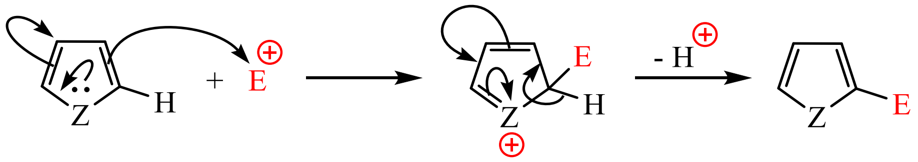
Electronegativity: O (3.44) > N (3.04) > S (2.58)

Delocalization will produce a resonance hybrid structures as the following:



Z= NH, O or S

These compounds are reactive toward electrophilic reagents ( like aromatic compounds ) and this due to the contribution of the lone pair of electrons at the hetero atom ( O, S or N ) by mesomeric effect as the following:



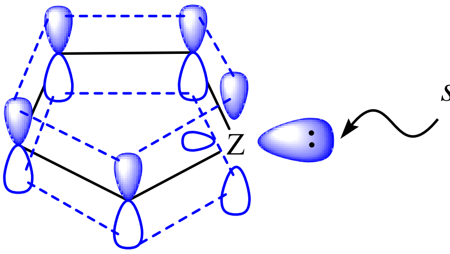
( Electrophilic Substitution )

The reactivity sequence will be as following:

Pyrrole > Furan > Thiophene > Benzene

**Notes**:

a) Pyrrole is more reactive than furan since the resonance energy is higher.
b) Thiophene is less reactive than furan towards electrophilic substitution due to the *p* electrons of sulfur are in *3p* orbital which overlap less effectively than the *2p* orbital of N or O atoms with the *2p* orbital of carbon.
c) The nitrogen atom has only one lone pair of electros, while both of oxygen and sulfur have two lone pair of electrons.
d) As the number of lone pair increase the donation is decreased.
e) The second lone pair of electrons is placed in the $sp^2$ hybrid orbital in plane with no chance to overlap as the following:



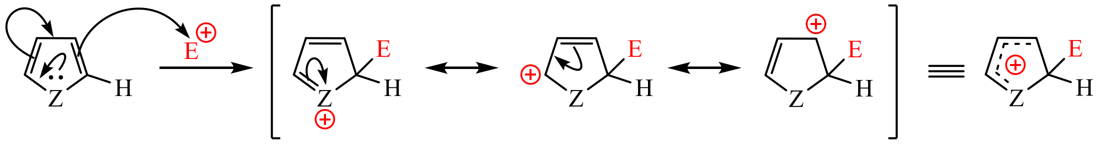
*$sp^2$ orbital doesent overlap*
( *in plane* )

## 4 ) Relative reactivity of α- and β- positions:

As we learned from our previous study that ( electron donating groups EDGs ) on benzene ring direct the incoming electrophile to ( *o* – *p* ) positions, while ( electron withdrawing groups EWGs ) direct to ( *m* ).

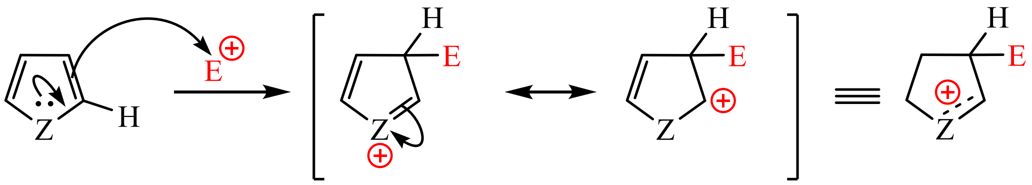
In heterocyclic system the hetero atom play a role in the direction of the incoming electrophile in the electrophilic substitution reactions as the following:

1 ) Attack at C2 or α:



more stable
( I )

2 ) Attack at C3 or β:



less stable
( II )

Attack at position 2 yields a carbocation that have a three hybrid structures, while attack at position 3 yields a carbocation with two hybrid structures only, thus attack at position 2 is preferable than that at position 3, since the developing positive ( +ve ) charge is accommodate by three atoms of the ring instead of by only two.