### Five-Membered Heterocycles Containing Single Hetero Atom



orbital structure of pyrrole





The aromaticity order in these heterocycles depends on the electronegativity of the heteroatom : 0 > N > S and, therefore, the aromaticity follows the order as

Thiophene > Pyrrole > Furan

## **Resonance Stabilization:**



X = O, NH or S

Note-Two uncharged resonance structures can be written for benzene, whereas only one structure without involving charge separation is possible for these heterocycles

Evidences-

1. Bonds of these compounds are intermediate in length between the normal single and double bonds for C-C, C-N, C-S and C-O bonds

2. The dipole moment of tetrahydrofuran is 1.73 D, due to the greater electronegativity of oxygen than carbon. The dipole moment of furan is smaller than THF (0.70 D) and in opposite direction due to electron pair delocalization into the ring. Pyrrole and thiophene can be explained in a similar manner



General mechanism of electrophilic substitution in the five-membered heterocycles



A look at the above resonance forms makes it clear that attack at position 2 will be preferred due to extra stabilization caused by the contribution of an additional structure.

# **Furan**

#### Preperation

### 1. Paal-Knorr Furan Synthesis

The acid-catalyzed cyclization of 1,4-dicarbonyl compounds known as the Paal-Knorr synthesis



#### Mechanism



2. By the decarboxylation of furoic acid



3. Commercially it is prepared from agricultural waste (rice-bran and oat-hulls) containing pentosans





Electrophilic substitution reaction of Furan