FIVE MEMBERED RING

Pyrrole

BSc. Part III (Hons.)

Organic chemistry

Paper : VII

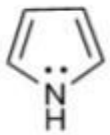
By

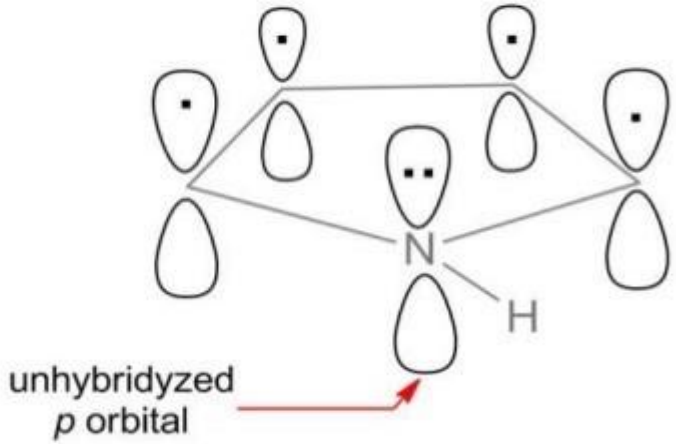
Dr. Manju Kumari

The pyrrole ring system is important as it is found in many natural products including hemoglobin, chlorophyll and alkaloids.

Structure of pyrrole :

1. Aromaticity





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Aromaticity

Pyrrole have 4 C and 1 N , all are sp^2 hybridized

sp^2 hybridization is planar, it makes a planar pyrrole ring structure

Each ring atom also contains unhybridized p orbital that perpendicular to the plane of σ bonds (plane of ring).

Here p orbitals are parallel to each other, so overlapping btw orbitals is possible.

The total nu of non bonding e- are 6 (4 of four C, 2 from one N)

The resonance of 6 e- follows the Hückel's rule

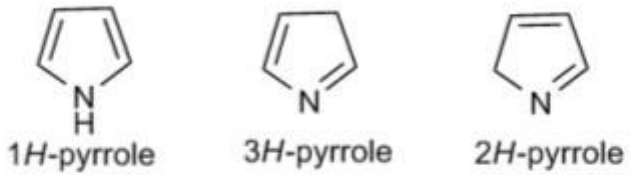
So the pyrrole is aromatic .

Pyrrole and thiophene are found in small amounts in coal tar.

The pyrrole ring is the basic unit of the porphyrin system, which occurs in chlorophyll and in hemoglobin.

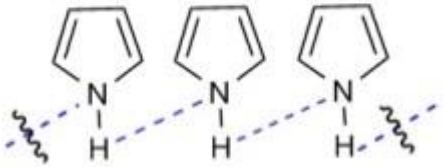
2. Tautomerism

- Rapid migration of hydrogen from N to the C.

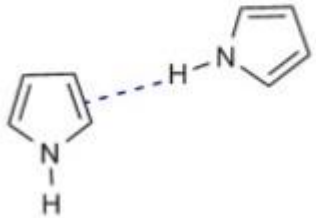


1*H*-pyrrole 3*H*-pyrrole 2*H*-pyrrole

3. Hydrogen bonding



Intramolecular H-bonding
(rise b.p.)

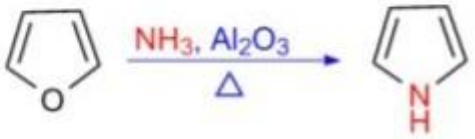


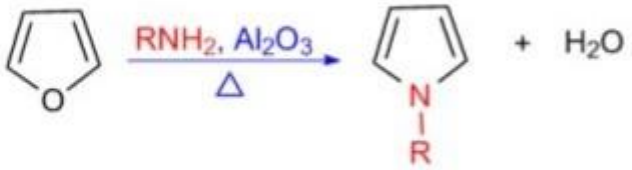
Intramolecular H-bonding
btwn N-H & π- e- system

Preparation :

1. From Furans

- Industrial process
- Passing furan over ammonia in presence of alumina as catalyst at high temp.

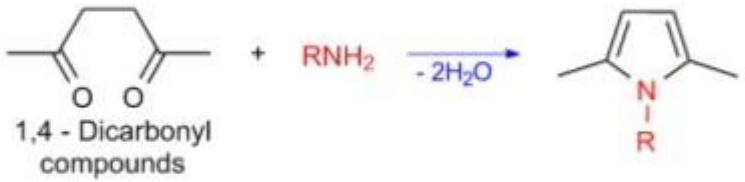




Synthesis

2. Paal-Knorr synthesis

- 1,4 - Dicarbonyl compounds react with ammonia *or* primary amines to give pyrroles.



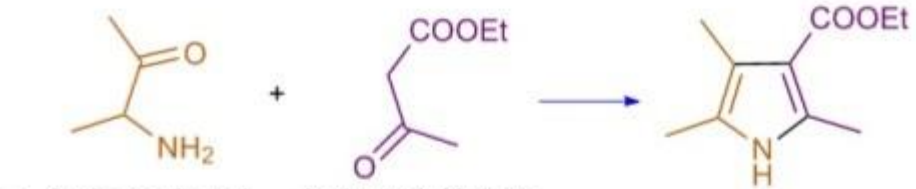
Mechanism

- Successive nucleophilic additions of the amine nitrogen to each of the two carbonyl carbon atoms, imine formation and the dehydration represent the net course of the synthesis.

ynthesis

. Knorr synthesis

Condensation of α- aminocarbonyl component with 2nd component containing an electron-withdrawing group (e.g. an ester) α to a carbonyl group



α- Aminocarbonyl compounds Activated Ketone

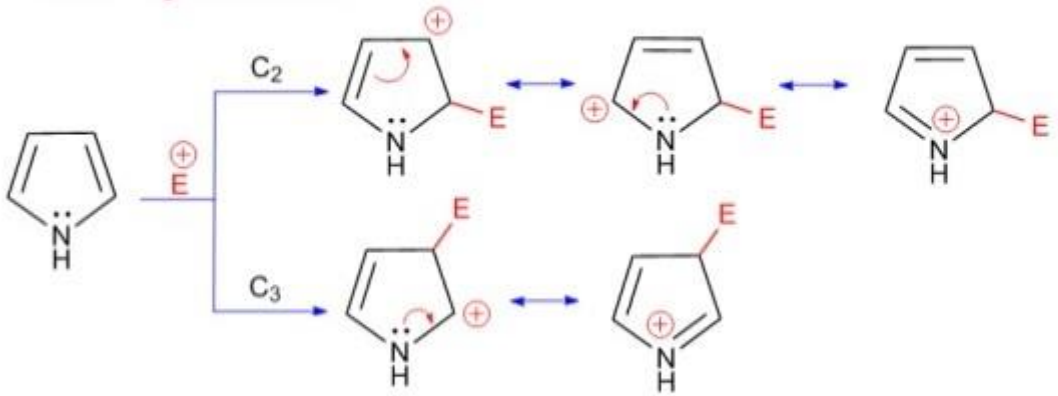
Physical properties : Pyrrole is a colourless liquid. It is slightly soluble in water but totally miscible with ether.

Chemical Properties :

Reactions

1. Electrophilic substitution

Pyrrole undergoes electrophilic substitution reaction at 2nd position



2 reasons…

- C2 attack gives more resonance contributing structures than C3.
- Extra stable contributing structure generates upon C2 attack

2. Reduction

Uses : (1) as a commercial solvent;
(2) for pharmaceuticals .