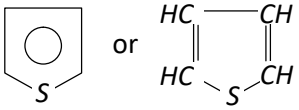
Heterocyclic compounds.

These are cyclic compounds in which the ring includes in addition to carbon atoms at least one atom of another element (Hetero = other, different). The common hetero atoms present in the carbon rings are O,N and S.

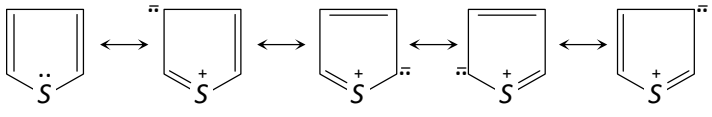
(1) **Thiophene**

It is found in the benzene fraction of coal-tar and petroleum. The benzene fraction is shaken with cold concentrated sulphuric acid. Thiophene present in the fraction combines with sulphuric acid more readily than benzene to form thiophene sulphonic acid which is separated with water being soluble. Thiophene sulphonic acid is treated with super-heated steam to recover thiophene.

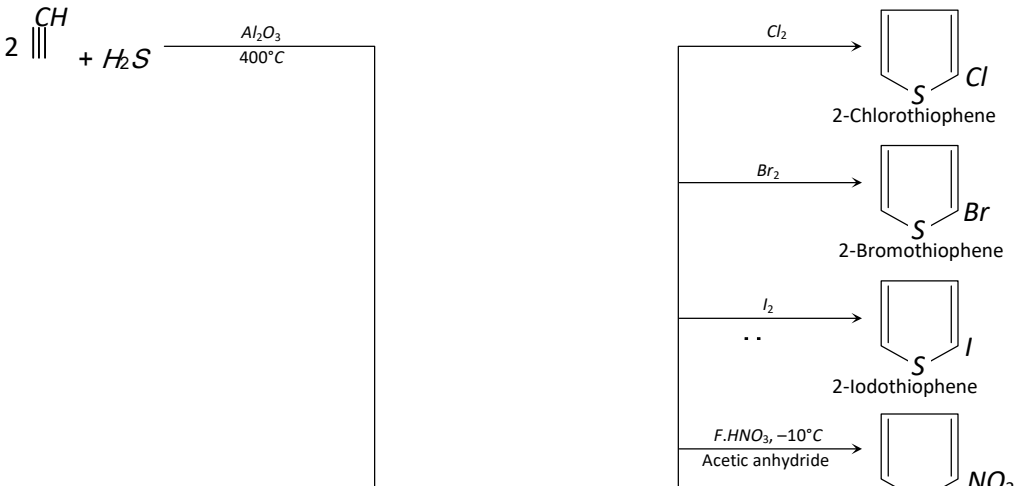


Properties: It is a colourless liquid. Its boiling point is 84°C. Its odour is similar to that of benzene. It is insoluble in water but soluble in organic solvents. It is flammable and toxic in nature.

Its resonance energy is $31\ k\,cal\,mol^{-1}$. Hence, it is more stable and resembles benzene more closely than furan $(23\ k\,cal\,mol^{-1})$ and pyrrole $(25\ k\,cal\,mol^{-1})$. It does not show basic properties and does not undergo **Diels-Alder reaction.**



Thiophene as a resonance hybrid (Resonance energy is 31 *k cal /mol*



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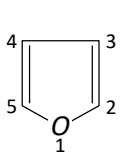
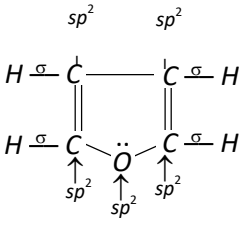
(2) Furan

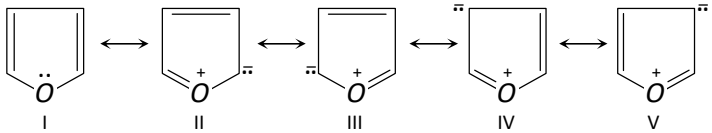




Furan derives its name from furfur meaning bran in Greek which is the source of its aldehyde, furfural. It is present in pine-wood tar and may be extracted from it.

Furan shows aromatic behavior because resulting · -molecular orbital satisfies the Huckel rule $((4n+2)\pi$ where, $n=1$.

Furan is also considered as a resonance hybrid of the canonical forms. Out of which the first three are the main contributing structures.



Canonical forms of furan

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Furan has resonance energy about $23\ k\ cal\ mol^{-1}$ which is less than benzene. However it is less aromatic and more reactive than benzene.

Properties: Furan is a colorless liquid. Its boiling point is 32°C. It is insoluble in water but soluble in organic solvents. It is a reactive compound. It is a weak base. In Furan electrophilic substitution reactions take place preferably at 2 and 5 position where electron density is high. If these positions are occupied, substitution occurs at 3 and 4 positions. It undergo **Diels-Alder reaction.**

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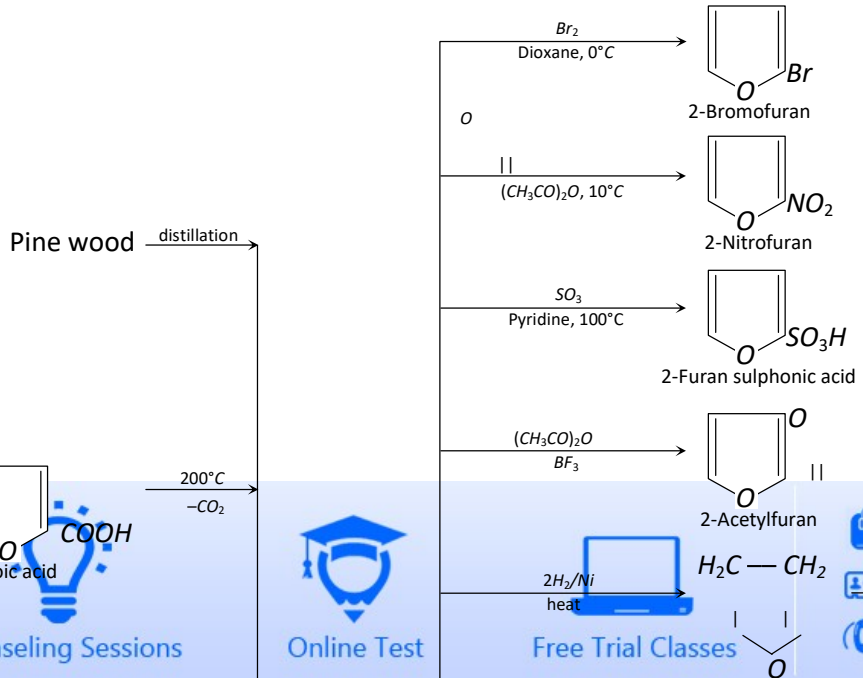

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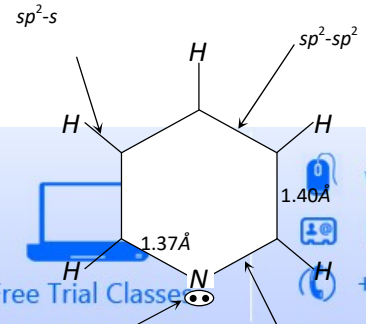
(3) **Pyridine**

Pyridine is a six membered aromatic heterocycle with one nitrogen atom in the ring. It may be supposed to have been derived by replacement of $= CH -$ group of benzene by $= N -$. Hence, it is isoster of benzene. Its systematic name is **azabenzene.** (Prefix aza stands for nitrogen). The hybrid structure of pyridine is represented as:



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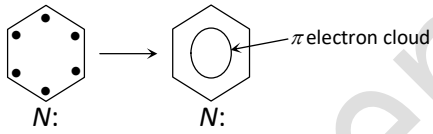
(i)**Properties:**It is a colourless liquid having an unpleasant odour. It boils at 115°C. It is miscible with water and is hygroscopic. It is a good solvent for many organic compounds and inorganic salts.

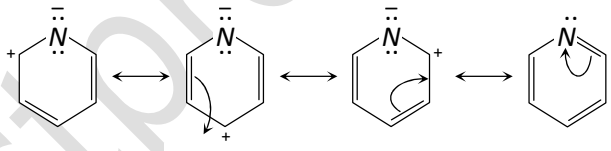
(ii) **Aromatic character:**Each carbon atom and nitrogen atom in the ring have sp^2 hybridized and one unhybrid p-orbital containing one electron. These orbitals overlap to form π molecular orbital consisting six electrons. The π molecular orbital satisfies Huckel's rule $(4n+2)$ and thus aromatic properties are observed in pyridine.

The resonance energy is 43 k cal/mol and bond length of $C-C$ bond is 1.40 Å and $C-N$ 1.39 Å.



$4n+2=6\,;\ n=1$

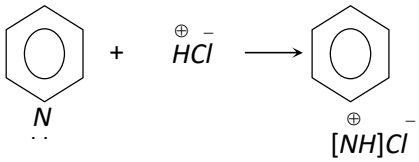
(iii) **Resonance structure:**



Canonical form of pyridine

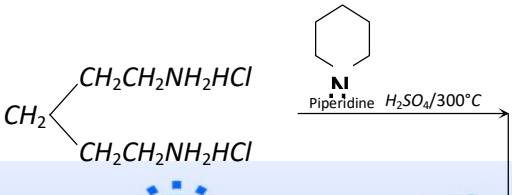
(iv) **Basicnature:**Pyridine is basic in nature due to presence of lone pair nitrogen atom. It is more and more basic than pyrrole and less basic than aliphatic amine.

Example:

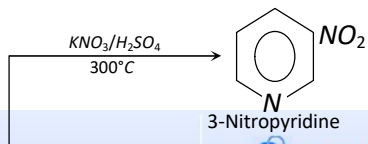


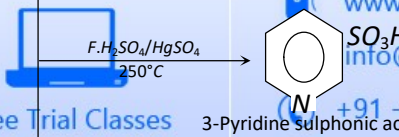
Pyridinium hydrochloride

(v) Chemical properties:



Penta methylene diamine dihydrochloride





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(vi) **Uses**

(a) To denature alcohol.

(b) As a basic solvent in organic reactions.

(c) For preparing sulpha-pyridine and vitamin B_6.

(d) As a catalyst in many reactions, e.g., in the formation of Grignard reagent, in Perkin and Knoevenagel reactions.

(4) **Pyrrole**

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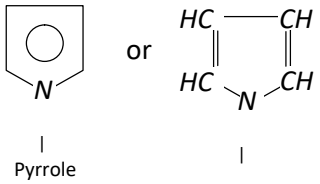
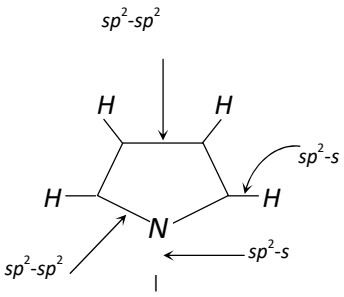
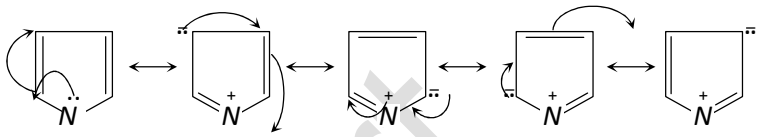
It occurs in coal-tar and bone oil and is found in many natural products including chlorophyll, haemoglobin and alkaloids.

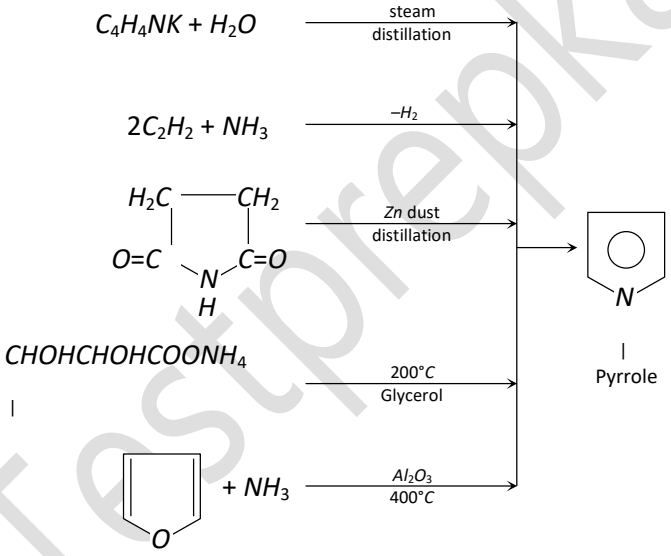


Pyrrole





(i)**Preparation:**



Note: Furan needed for the process is obtained from agricultural waste materials which are rich in pentosans. The pantosans on acid hydrolysis yields furfural which is decarbonylated.

(ii)**Properties:** Pyrrole is a colorless liquid. Its boiling point is 131°C. It is slightly soluble in water but highly soluble in alcohol and ether. Its odour is similar to chloroform. It rapidly becomes brown when exposed to air. Vapours of pyrrole turn a pine splint moistened with HCl red. Pyrrole derives its name from this property.

Chemical properties:

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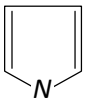

Pyrrole

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(iii)**Uses:**Itis used as a commercial solvent, as an intermediate in the production of nylon and for making pharmaceuticals.

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