Quadrant II – Notes

Programme: Bachelor of Science (Third Year)

Subject: Chemistry

Paper Code: CHC107

Paper Title: Organic Chemistry

Unit: Unit 4 – Section B- Chemistry of Heterocyclic compounds

Module Name: Structure, Resonance, Stability & Industrial source of Furan

Module No: 19

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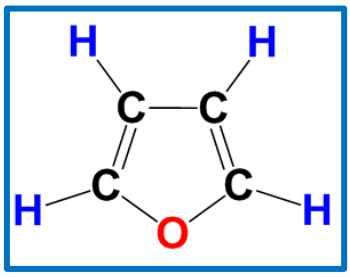
Notes:

Furan- a brief introduction

- Furan is a five membered heterocycle with four carbon atoms and one oxygen as heteroatom.
- Compounds containing such heterocyclic ring are also referred to as furans.

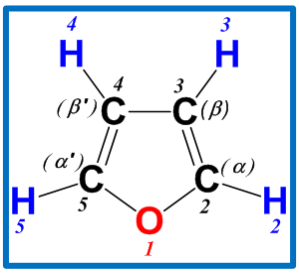


Nomenclature

- *Preferred IUPAC Name* : Furan
- *Systematic IUPAC Name*: 1,4-Epoxybuta-1,3-diene
  1-Oxacyclopenta-2,4-diene
- *Other names* : Furfuran, Oxole, Divinylene oxide.

Numbering in Furan

- The numbering begins from the heteroatom.

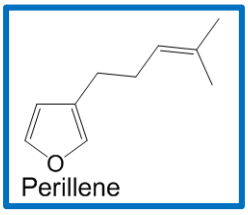


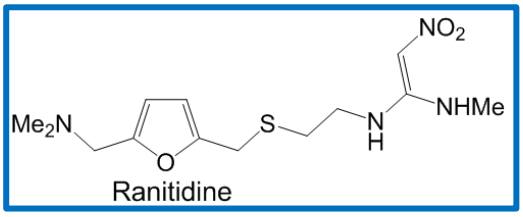
Properties

- A colourless, volatile liquid with strong ethereal odour
- Boiling point: 31.4°C; Density: 0.936 g/mL
- Solubility: soluble in alcohol, ether, acetone, slightly soluble in water.
- Flammable and can form explosive peroxides on exposure to air.
- Toxic and may be carcinogenic.

Applications

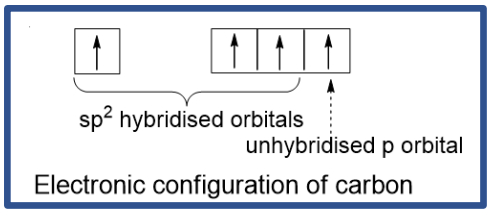
- Furan is a precursor for solvent THF & pharmaceutical & agrochemical compounds.
- Furan ring system is found in some of the natural products & medicinal compounds, for eg.
- Perillene (a plant metabolite)
- Ranitidine (medicine used for treatment of stomach ulcers)

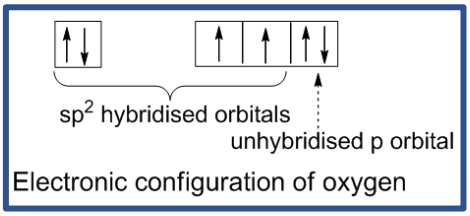


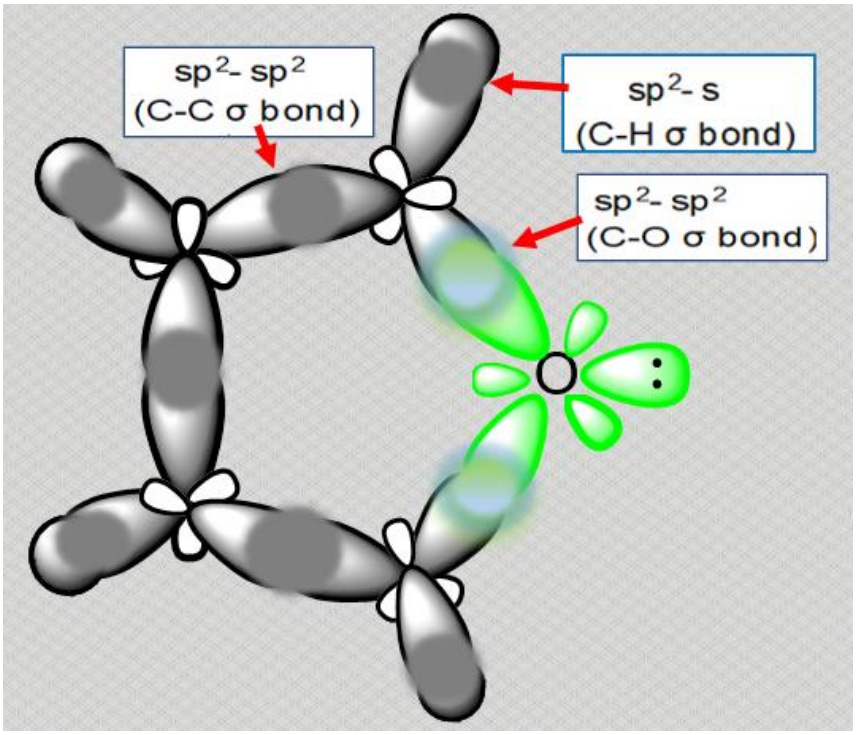


Structure

- Molecular Formula: **C_4H_4O.**
- Furan is Cyclic, pentagonal, planar, with four sp^2 hybridised carbon atoms & one sp^2 hybridised oxygen atom.
- Each Carbon is attached to 1 hydrogen atom.





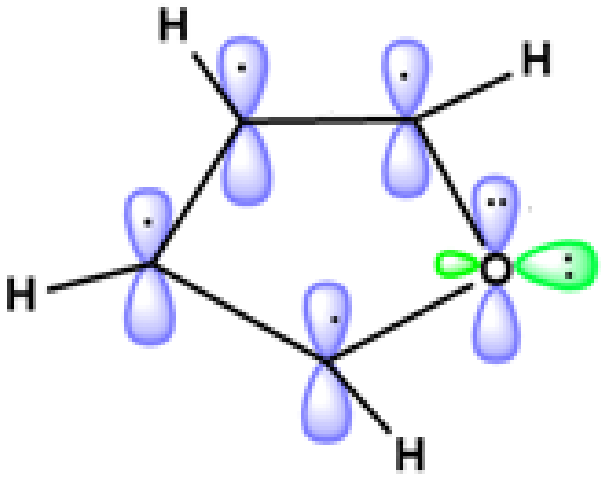


Each of the two α carbon atoms have three sp^2 hybrid orbitals, one of which is utilized for C-C σ bond formation by overlap with one of the three sp^2 hybrid orbitals of the adjacent β carbon atom. The second sp^2 hybrid orbital overlaps with 1s orbital of hydrogen to form C-H σ bond. The third sp^2 hybrid orbital is utilized for C-O σ bond formation by overlap with one of the three sp^2 hybrid orbitals of oxygen.

We have already seen that the β carbon atom utilises one of its sp^2 hybrid orbitals for C-C σ bond formation with one of the sp^2 hybrid orbitals of adjacent α Carbon atom. The second sp^2 hybrid orbital overlaps with 1s orbital of hydrogen to form C-H σ bond. The third sp^2 hybrid orbital is utilized for C-C σ bond formation by overlap with one of the three sp^2 hybrid orbitals of adjacent β' carbon atom.

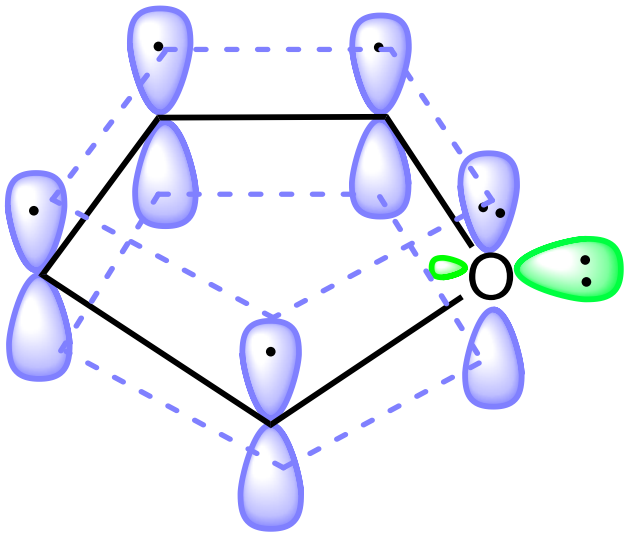
The geometry at both the α carbon atoms and at both β carbon atoms is same (there is a mirror plane bisecting the molecule passing through centre of oxygen atom). The oxygen atom has three sp^2 hybrid orbitals, two of which having one electron each are utilised for C-O σ bond formation by overlap with sp^2 hybrid orbitals of α and α' carbon atoms. The third sp^2 hybrid orbital

contains a lone pair of electrons which is unshared. Besides this oxygen atom has a p orbital with a pair of electrons. This p orbital is perpendicular to the sp^2 orbital containing unshared pair of electrons and to the plane of the ring as well.
Each carbon atom also has a p orbital containing single electron.



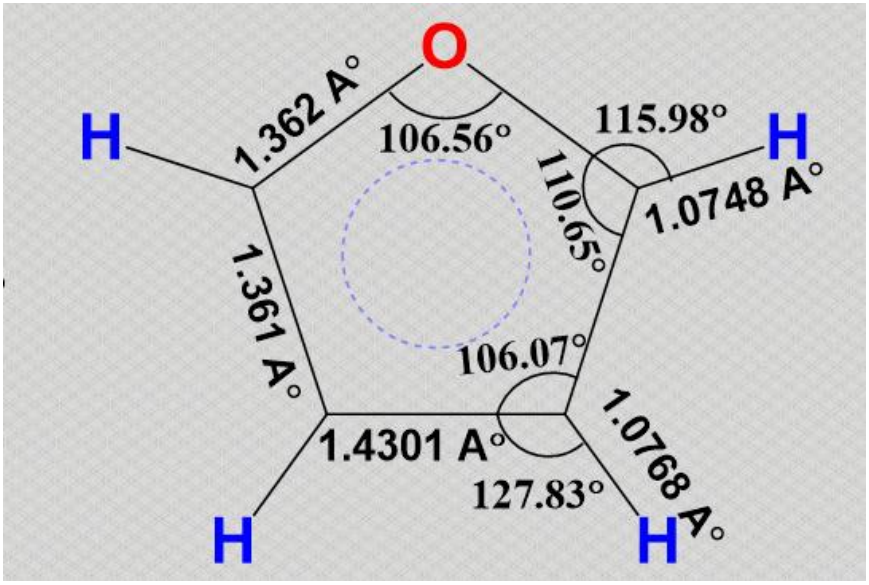
Orbital structure of furan

- p orbital of O with 2 electrons & p orbital with 1 electron on each C overlap to form **cyclic π electron cloud** above & below the plane of ring.
- The electron pair in p orbital of O constitute aromatic sextet.
- (no. of π e^- **= 6** π e^- **:Hückel's no)**
- The 6 p orbitals are mutually parallel & perpendicular to the plane of ring. sp^2 orbital of oxygen containing the lone pair is perpendicular to the p orbitals & this lone pair of electrons does not participate in delocalisation.



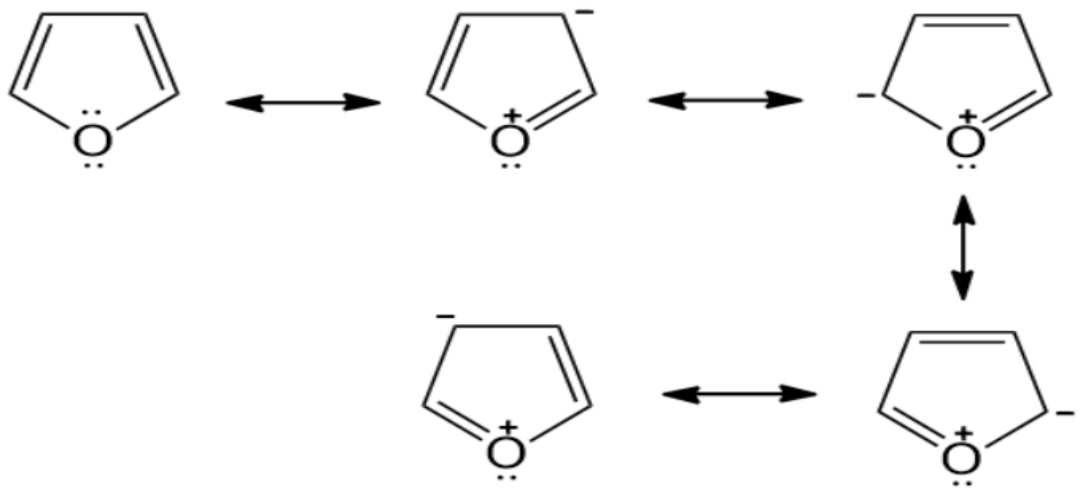
Thus furan is cyclic, planar, conjugated and has Hückel's no of pi electrons. (4n + 2)π e^- **= 6** π e^-

Furan is 5-membered **aromatic** heterocycle.



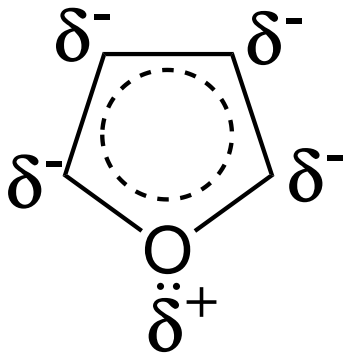
Equilibrium geometries of Furan

Resonance: The aromaticity in furan can be represented by the following resonance contributors.



- The Resonance hybrid structure of furan is confirmed by measurement of bond length by X ray analysis
- It is important to note that C-O bond length in furan (1.362 A^0) < normal C-O single bond length (1.43 A^0)

- C-O bond : has significant double bond character.



Resonance hybrid of Furan

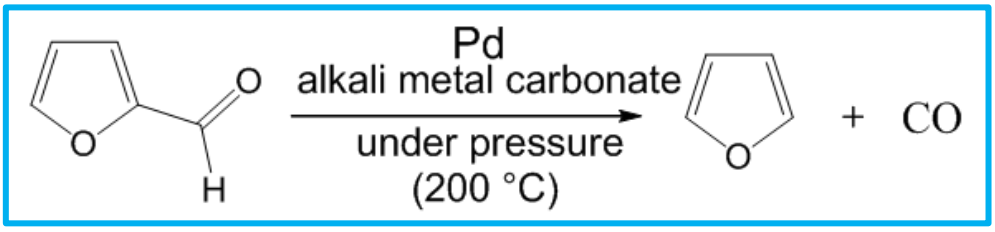
Stability

- Delocalization of the π electrons stabilizes the ring.
- Heats of combustion indicate resonance stabilization for furan to be 16 k cal/mol (resonance energy) which is more than most conjugated dienes (about 3 kcal/mol). Hence it tends to undergo reactions such as electrophilic substitution in which the stabilized ring is retained. However resonance energy for benzene (36 k cal/mole) > resonance energy for furan.

  Benzene is more aromatic and stable than furan.

Industrial source: on industrial scale, typically Furan is prepared by 2 methods

1. **The Pd-catalyzed decarbonylation of furfural**



- In a typical procedure, furfural is refluxed under pressure at 200° C in presence of supported Pd catalyst and alkali metal carbonate.
- Furfural decomposes on Pd surface to furan & CO
- Furan and CO thus formed are continuously removed from the reaction mixture by distillation.
- A typical productivity of 4–10 kg of furan /g of Pd is obtained.

2. **Partial Oxidation of 1,3-Butadiene**

- Another method involves a low-temperature (90–120 ° C) **copper catalyzed** partial oxidation of 1,3-butadiene, with maximum butadiene conversion of 20 %