Welcome to this module on structure, resonance, stability and industrial source of furan. In this module, after a brief introduction on furan, we will focus on the structure of furan, resonance in furan, stability of furan and industrial source of furan. At the end of this module you will be able to explain the structure of furan. Explain the resonance phenomenon in furan. Explain the stability of furan and describe the industrial source of furan. Furan is a 5- membered heterocycle with four carbon atoms and one oxygen atom as the heteroatom. Compounds containing such heterocyclic ring are also referred to as furans.
Furan is also known as furfuran, oxole or divinylene oxide. The numbering in Furan begins from the heteroatom, that is, oxygen and the positions adjacent to the heteroatom are indicated as alpha, and alpha dash and the positions away from the heteroatom are indicated as beta and beta dash. Furan is a colorless volatile liquid which is soluble in alcohol, ether, acetone, and slightly soluble in water. It is flammable and can form explosive peroxides on exposure to air. Furan is a precursor for solvent Tetrahydrofuran and a number of pharmaceutical and agrochemical compounds. Furan ring system is found in some of the natural products and medicinal compounds, for example perillene, which is a secondary plant metabolite and ranitidine which is medicine used for treatment of stomach ulcers.

Now, let us understand the structure of Furan which has molecular formula C4H4O. Can we consider furan to be an ether? or a conjugated diene? if we consider furan to be just a conjugated diene, then it is expected to undergo addition reactions. However, along with certain tendency to undergo addition reactions, furan preferably undergoes electrophilic substitution reaction such as nitration, sulfonation, halogenation, etc. So is furan aromatic? Does it satisfy all the criteria for aromaticity? let's see.

Furan is cyclic, pentagonal, planar with four sp2 hybridized carbon atoms and one sp2 hybridized oxygen atom. Each carbon is attached to one hydrogen. Each of the 2 alpha carbon atoms of the Furan have three sp2 hybrid orbitals, one of which is utilized for carbon carbon Sigma Bond formation by overlap with one of the three sp2 hybrid orbitals of the adjacent Beta carbon atom. The second sp2 hybrid orbital is used for carbon hydrogen Sigma bond formation by overlap with 1S orbital of hydrogen and the third sp2 hybrid orbital is used for carbon oxygen Sigma bond formation by overlap with one of the three sp2 hybrid orbitals of oxygen. Now we have already seen that the beta carbon Atom has three sp2 hybrid orbitals, one of which it has utilized for carbon carbon Sigma bond formation. The second sp2 hybrid orbital is used for carbon hydrogen Sigma bond formation and the third sp2 hybrid orbital is utilized for carbon carbonSigma bond formation by overlap with one of the three sp2 hybrid orbitals of the adjacent beta dash carbon atom. This molecule has a mirror plane. there's a mirror plane bisecting the molecule passing through the oxygen Atom.

So the geometry around both the Alpha carbon atoms is same. Similarly, the geometry around both the beta carbon atoms is same. It is important to note here that the oxygen Atom has three sp2 hybrid orbitals, two of which having single electron each are utilized for carbon-oxygen Sigma bond formation by overlap with the sp2 orbitals of the adjacent Alpha carbon atoms. The third sp2 hybrid orbital contains a pair of electrons which is unshared. Besides this, oxygen atom also has a p orbital which contains a pair of electrons. This p orbital is perpendicular to the plane of the ring as well as to the sp2 Orbital containing the unshared pair of electrons, each of the four carbon atoms also have a p orbital with a single

electron. The p orbital of oxygen with two electrons and the p orbital with one electron on each carbon overlap to form cyclic pi electron cloud above and below the plane of ring. The electron pair in the p orbital of oxygen constitute aromatic sextet. It is apart of conjugation, so the total number of π electrons in furan is 6. And six pi electrons is a Huckel's number. The six p orbitals are mutually parallel and perpendicular to the plane of ring accounting for effective overlap, which is required for aromaticity. The sp2 orbital of oxygen containing the lone pair is perpendicular to the p orbitals and thus this lone pair of electrons does not participate in delocalization, so furan is cyclic, planar, conjugated and satisfies Huckel's rule. So we can say that Furan is a 5-membered aromatic heterocycle. The C-O bond length in Furan is 1.362 armstrong and the COC bond angle is106.56 degree as calculated experimentally.

Now these are the resonance contributors for furan which represent aromaticity in furan. Now with the help of curved arrows I will show you how we're getting these different resonance contributors. So first I'll push this lone pair of electrons onto this carbon oxygen bond, and this pi electron density towards this carbon. So the oxygen is now trivalent and positively charged and the carbon becomes negatively charged. Then I will push this negative charge towards this point and. So I will use this curved arrow to show this delocalization of electrons. So basically these resonating contributors are depicting the delocalization of electrons. Delocalization of π electrons.

Now we can draw an average of all these resonance contributors, which is the resonance hybrid. We can see that oxygen atom is having partial positive charge and all the four carbon atoms have partial negative charge. This structure of resonance hybrid in furan was confirmed by measurement of bond length by X Ray analysis. In particular, the C-O bond length in Furan was found to be less than the normal C-O single bond length.
So the C-O bond in Furan has significant double bond character. Delocalization of πelectrons stabilizes the ring. Heats of combustion indicate resonance stabilization for furan to be 16 kilocalories per mole, which is more than most of the conjugated dienes, hence furan tends to undergo reactions such as electrophilic substitution, in which the stabilized ring is retained.

However, the resonance energy for benzene is more than that for furan, and thus benzene is more aromatic and stable than furan.
Typically on industrial scale, furan is prepared by two methods, one of which involves Palladium catalyzed decarbonylation of furfural. In a typical procedure furfural is refluxed under pressure at 200 degrees Celsius in presence of supported Palladium catalysts and alkali metal carbonate. Furan and carbon monoxide thus formed are removed from the reaction mixture continuously by distillation.
A typical productivity of 4 to10 kilogram of furan per gram of Palladium is obtained. Another method involves partial oxidation of 1, 3-butadiene by a relatively low temperature copper catalyzed oxidation, with the maximum butadiene conversion of 20%.

These are my references. Thank you.