Hello students

In this session I'll be covering Unit IV, that is Chemistry of Heterocyclic Compounds.
Module name is Structure, Resonance, Stability and Industrial source of Thiophene and Module number is 21.

Outline of the module:
In this module we will be discussing the structure of thiophene, resonating structures of thiophene, stability of thiophene, aromaticity of thiophene, industrial source of thiophene and lastly summary and references.

Learning outcomes:
At the end of this module, students will be able to:
Understand and explain the structure of thiophene
Discuss the aromaticity of thiophene
Explain various resonating structures of thiophene
Analyze the stability and aromaticity of thiophene and discuss the industrial source of thiophene.

In the beginning, we will see the structure of thiophene. So it's a 5-membered ring with sulfur heteroatom as a part of the ring. The other four atoms of the ring are carbons and each carbon is attached to one hydrogen atom. Thiophene is a colourless liquid with a mildly pleasant odour similar to benzene. It has boiling point of 84 degree centigrade.
Thiophene was first discovered in 1882 in coal tar benzene as an impurity. It was named from theion (a Greek word for sulfur) and phaino (a Greek word which means shining).

Now, let us see the numbering in type of in thiophene. In thiophene, the sulfur heteroatom is given first preference and hence is number 1 and the remaining carbons are numbered from 2 to 5 in either clockwise fashion or in anti-clockwise fashion.The two carbons which are directly attached to sulfur are alpha carbons whereas the other two carbons which are attached to alpha carbons are called as beta carbons. Thus we have two alpha carbons and two beta carbons in thiophene. Thiophene is an aromatic compound and its structure is analogous to structure of pyrrole and furan. Thiophene is aromatic because it is cyclic and planar in nature; it has closed conjugation of π electrons delocalizing over the ring; and it obeys Huckel's rule of $4n+2\pi$ electrons. These are the six electrons which are responsible for making this thiophene aromatic. So the two electrons comes from the lone pair of sulfur and the remaining 4 electrons comes from 4 carbons, that is, 1 carbon gives one π electron and thus a total of 6 electrons are revolving over these 5 atoms. So out of two lone pairs of sulphur, 1 lone pair of electron is a part of aromatic sextet, whereas the second lone pair of electrons is not a part of the aromatic sextet. Thiophene is an electron rich heteroatom and since 6 electrons are revolving over 5 atoms, thiophene is sometimes called as π-excessive compound.

Then dipole moment of thiophene:

It is having a dipole moment of 0.52 Debye and the dipole moment is directed towards the sulfur heteroatom in thiophene. Here the inductive effect is more significant than the mesomeric effect. Also, I have shown here the different bond lengths of different bonds in thiophene.

Now the very important part, that is, resonating structures of thiophene:
This resonating structure I is one of the resonating structure of thiophene, that is the neutral structure, there is no charge in this structure. However, when one of the lone pair is delocalized towards the adjacent side, these electrons can further shift and as a result we can get resonating structure II, in which there is plus charge on sulfur and negative charge on carbon 3. Further this negative charge can be delocalized and now the negative charge comes on carbon 5 and thus we get another resonating structure III. This negative charge I can further delocalize on the other side and carbon 2 gets negative charge and we can write resonating structure IV. This carbon 2 the negative charge can further delocalize and now carbon 4 gets negative charge and we can have structure V. And finally this negative charge from carbon 4 can be delocalized further and we get back the resonating structure of thiophene which is neutral and it is resonating structure I. So this is how we can get different resonating structures I-V for thiophene.
Here, if you look at the structure carefully, structure I is neutral without any charge, whereas structure II to structure V, all these four structures are having + charge on sulfur, whereas negative charge is there on different carbons. So all these four resonating structures are charged structures. Coming to the contribution of these resonating structures through the resonance hybrid, all these structures do not equally contribute to the resonance hybrid. This is because of the difference in the stability of these resonating structures. The structure I of thiophene is more stable, as a result it will contribute maximum to the resonance hybrid, followed by structures III and IV, which are more stable than structures II and V. Structures III and IV are more stable because the + and - charge are on adjacent atoms whereas in structures II and structures V, the negative charge is away from the positively charged sulfur atom. As a result, they are less stable and hence will contribute minimum to the resonance hybrid. So as a result the order is like this: Structure I will contribute maximum to the resonance hybrid followed by structures III and IV and least contribution will be from structure II and structure V.

Stability of thiophene:
Thiophene is comparatively more stable than pyrrole or furan. This is because, larger the bonding radius of sulfur, the bonding angles are larger. The angle strain is somewhat relieved and there is a contribution to the stabilization involving sulfur d-orbital participation. Thiophene is more aromatic than pyrrole or furan. This is because the canonical structure participation to the resonance hybrid is more in thiophene, because the sulfur is less electronegative. There is also better stabilization of the positive charge in the canonical structures of thiophene. Hence canonical structures of thiophene contribute more to the resonance hybrid, making it more aromatic.

Lastly, we will see some industrial source of thiophene.
Here is the one reaction wherein thiophene is obtained from n-butane and sulfur at high temperature. Secondly, by passing a mixture of acetylene and hydrogen sulfide through a tube containing alumina at

400 degree centigrade, we can get thiophene. Thiophene can also be obtained by heating sodium succinate with phosphorus trisulfide.

So in summary, we have seen that thiophene is a 5-membered aromatic heterocyclic compound. Thiophene heteroatom has 2 lone pairs of which only one lone pair of electron is a part of the aromatic sextet. The dipole moment in thiophene is directed towards sulfur atom Thiophene is a resonance hybrid of five non-equivalent resonating structures I to V; which we have already seen; and they contribute unequally to the resonance hybrid. Thiophene is comparatively more stable and more aromatic than pyrrole and furan. And lastly, we have seen different industrial sources of thiophene.

These are the different references which are to be referred for this module.

Thank you.