Supramolecular Chemistry-I

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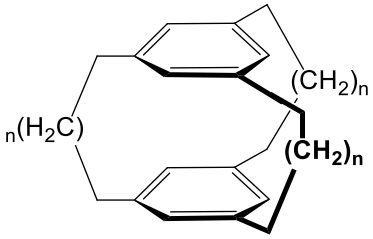
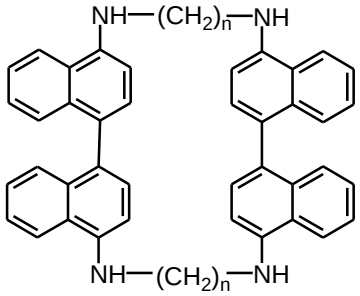
Week - 03

Lecture - 12

Good morning, we have been discussing macrobicyclic cryptands. So, today we will discuss another type of compounds, where you have bridged aromatic hydrocarbons. They are called cyclophanes. The cyclophanes have bridged aromatics and so their cavity is hydrophobic in nature.

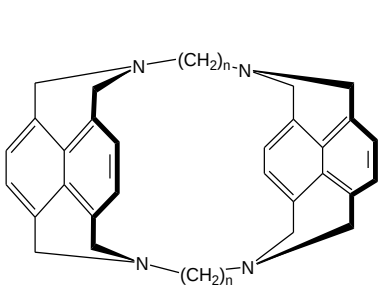


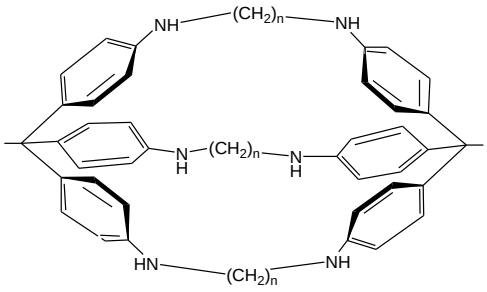


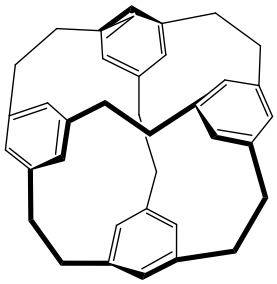
n= 5,7

Here, cavity is completely hydrophobic. When we discussed cryptands, I told you that in cryptands cavity can be hydrophobic as well as hydrophilic. So, we can play around. One side of the cavity can be hydrophobic, another side could be completely hydrophilic and all that and it has donor atoms and all that.

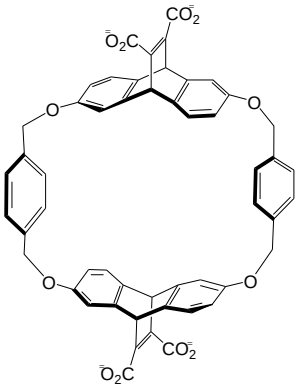
And in cyclophanes, you have completely hydrophobic and because it is aromatic bridged, so the cavity is very self persistent. That means, shape of the cavity will not change and it can discriminate non-polar guests depending upon the size of the guest and size of the cavity. So, there is an oil spill. You have to remove that oil spill. So, that time we can use cyclophanes. Therefore, cyclophanes are also very important macrocyclic and macro- bicyclic compounds. I will not discuss synthesis of these cyclophanes. They are similar to when we discuss synthesis of macrocycles or macrobicyclic compounds. So, these are also similar. Let me draw some more structures, representative cyclophanes. For example, these are interesting looking structures, but the architecture is very similar to your cryptands like it has also a cavity and it is also bicyclic and so on. Let me draw this and show these beautiful structures.



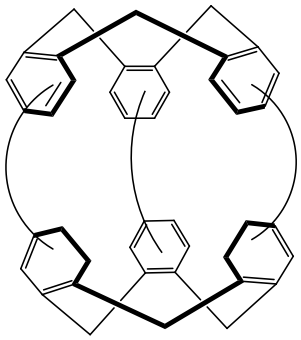




So, these are typical cyclophanes and as you can see the cavity is hydrophobic. This one is not absolutely hydrophobic and if we protonate this compound, this compound is not totally insoluble in aqueous medium, but soluble in organic non-polar solvents. This compound is similar, but if I protonate that suppose I protonate that with an acid, then it will become NH2 and then it will become positively charged. In that case, it will be soluble in aqueous solvents. In that case, if some organic compounds, non-polar compound is dissolved within aqueous solvents, this cyclophane can extract that depending upon as I told you cavity size and the guest size matching must be there.



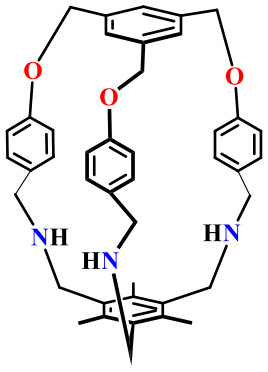
These can be water soluble cyclophanes like the figure above. Here is one interesting cyclophane.



This structure I will write completely. It cannot form any protonated form because there is no nitrogen to protonate. However, it has a three dimensional cavity and almost circular. This particular cyclophane can accept metal ions depending upon its size matching. Because it can form metal-π interactions.

Finally, once I get out of this cryptands and related compounds, I will discuss about another very important series of compounds which have seen an explosive growth in the last 5-10 years. They are called self persistent organic cages. There is a subtle difference between cryptands and self-persistent organic cages. I have drawn only one here.

I will not try anymore. What happens is you have aromatic bridgeheads and you have three arms or three bridges attached to the aromatic bridgehead. Because it is aromatic bridgehead and the three bridges, they also contain aromatics. As a result, the particular compound although it is like a cryptand architecture, it is non-flexible.That is why whether you put a metal ion in or not, it is always keeping its shape unaltered. That is why it is called self persistent organic cages. What is the difference between self persistent organic cages and cryptands? In a cryptand, when a metal ion goes inside, then some of these donor atoms present in the bridge. They can move around little bit, not much little bit and so that these donor atoms can wrap around a metal ion nicely.



But in this case, that is not possible. When you put a metal ion or leave it empty, the shape is not going to change. That is why it is known as self persistent organic cages. I will take it from here from next class. Thank you.