Supramolecular Chemistry-I

Prof. Parimal Kanti Bharadwaj

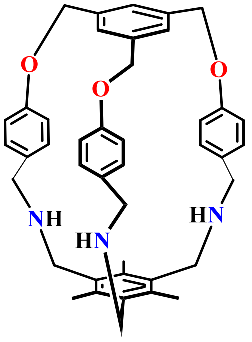
Department of Chemistry

IIT Kanpur

Week - 03

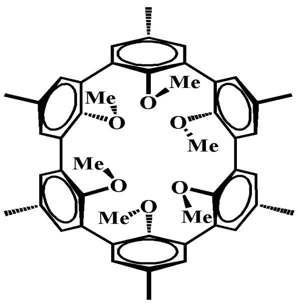
Lecture - 13

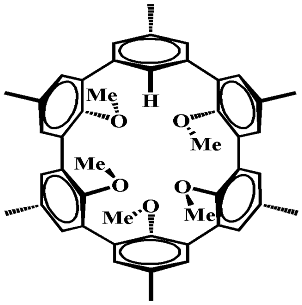
So, we have been discussing cryptands and its different variations. In my last class, I touched upon self-persistent organic cages. You can see that this particular organic cage is quite rigid. This binding site is very rigid. It has some flexibility on the side, but the two ends are very rigid.



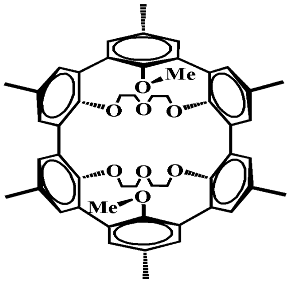
So, this is the difference between self-persistent organic cages and cryptands. Cryptands are flexible. They can wrap around a metal ion well, but this particular molecule looks like a cryptand but it cannot wrap around a metal ion. You will say why you call it a different name. These structures came into prominence very lately, say 10 years back and they are also extremely important. Self-persistent organic cages can be really big with very large cavity. The rigidity comes from aromatic bridgehead.

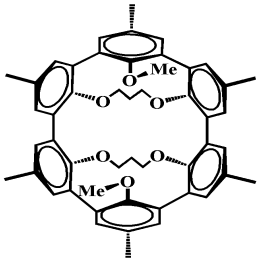
So, now I will come to another type of molecule known as spherands. As the figures below suggest it is a very rigid structure and looks like a sphere.





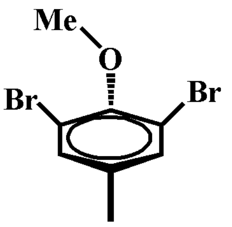
The oxygen donors present here are not coplanar but alternately up and down as the methyl groups indicate. For six-membered, where we have all OMEs then it will be a three OMEs are up, oxygens are up and three are down in a trigonal anti prismatic fashion. So they can easily form octahedral metal complexes. This means a six-membered spherand will have six oxygen that will make perfectly octahedrally transposed. So, when a metal ion that likes to bind ethereal oxygens goes inside, it can make a very facile complex. Also, sperands are not solvated. In addition to the simple sperands, some other derivatives are also there.

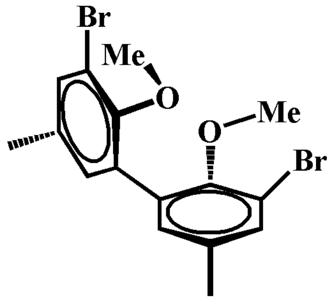


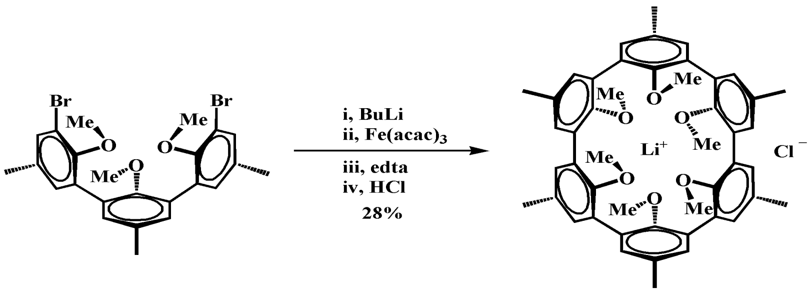


How to synthesize them? That is kind of difficult, but still let us see. The critical ring-closures in the syntheses require converting aryl bromides to biaryls. The aryl bromide is lithiated, and the resulting aryllithium is oxidized with Fe(acac)$_3$ to produce aryl radicals which couple.

$$\text{Ar-Br} \xrightarrow{\text{BuLi}} \text{Ar-Li} \xrightarrow{\text{Fe(acac)}_3} \text{Ar-Ar}$$





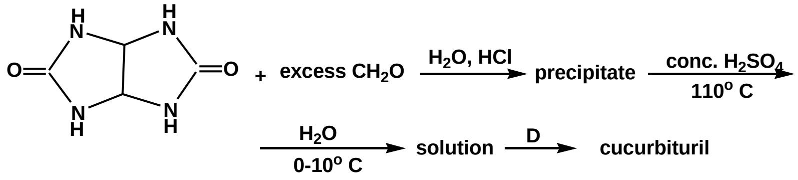


So, this is the way we synthesize spherands.

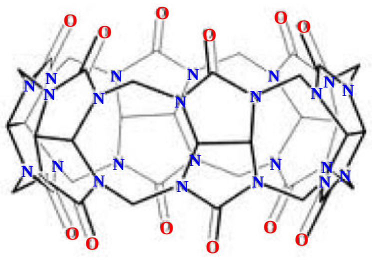
Now let us start something else. Now we will show you another structure. You might be wondering why I am trying to give you different kinds of structures in this class. The reason is these supramolecular synthons will be later useful. We will use them later to have interesting systems to tackle a phenomenon. We need different types of molecules and these molecules are that is why these supramolecular synthons can be made to form supramolecular species. That does not mean non-cyclic compounds aliphatic or aromatic they are useless not that they will be in addition to these cyclic structures. So all these things will be obvious as we go along.

So now another type of compound we will discuss, called cucurbiturils. These compounds were synthesized serendipitously not that they were designed and synthesized. We saw in one previous lecture that phenol and formaldehyde can lead to the polymer Bakelite when the phenol is unsubstituted. But when phenol is substituted in the para position with tertiary butyl group then we can get calixarenes. A quite similar situation here.

When glyoxal reacts with urea it form a compound named glycouril. So if you react glycouril with excess glyoxal in aqueous HCl, a precipitate forms. That precipitate upon treatment with concentrated sulfuric acid, heat it up to 110°C gives a clear solution. You should be very very careful when you make this kind of material. And then if you add so you have a solution now a sulfuric acid solution of a clear solution you dilute it with lots of water you put and cool it to 0 to 10°C.



Upon slow evaporation, a mixture of cucurbiturils is obtained as a white solid. So, synthesis of cucurbituril is very interesting and it was done first in 1905. This synthesis was achieved serendipitously but even then it was revisited in 1980s. But even now this is synthesized as above. Now how does it look? I have copied it from elsewhere as it is impossible to draw.



Important characteristics are that all the nitrogens are in tertiary amide form and tertiary amides called aminal linkage are insoluble in water. The molecular structure is such that it has a bulging middle portion that is hydrophobic in nature with two open ends that are hydrophilic.

So not only in water but in most organic solvents cucurbiturils are insoluble; they are soluble only in concentrated sulfuric acid and then when you add water they will be precipitating out. The name cucurbituril comes from its similarity with pumpkin. Here, all valences of carbon and nitrogen are satisfied and so the middle part is hydrophobic. While at the entry on both sides are hydrophilic due to the presence of carbonyl groups.

The depth of the middle hydrophobic part is equal to that of 4 carbon chain carbon length and it can it can go inside easily into the hydrophobic pocket. So, I have completed this next time I am going to do something known as cyclodextrins and almost we are coming almost at the end of describing these materials their structural features and then we will use them one after another as we progress then you will know why I am taking so many lectures describing this kind of compounds. So, today I will stop. Thank you.