Supramolecular Chemistry-I

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Week - 01

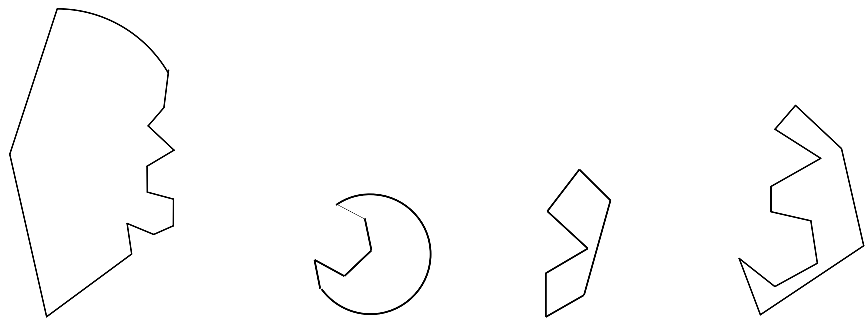
Lecture - 03

Hello again, I will be discussing an important concept today that is called molecular recognition.

Molecular recognition can be defined as the readout of information stored in the host by the guest. So, a guest can read the information stored in the host and I am sure by now you know host and guest. Host is usually the bigger partner and a guest is the smaller partner. Host and guest will form a complex, called supramolecular complex. So, let me emphasize that the definition of molecular recognition is important to memorize. How any information can be coded in the host? The information in the host is in terms of its architecture that should be complimentary to the guest molecule in terms of geometry, charge distribution, nature of the interacting surface, and so on. The interaction between the host and the guest is specific and the interaction energy can be as high as several kcal per mole. This understanding is absolutely important to understand supra- molecular chemistry.

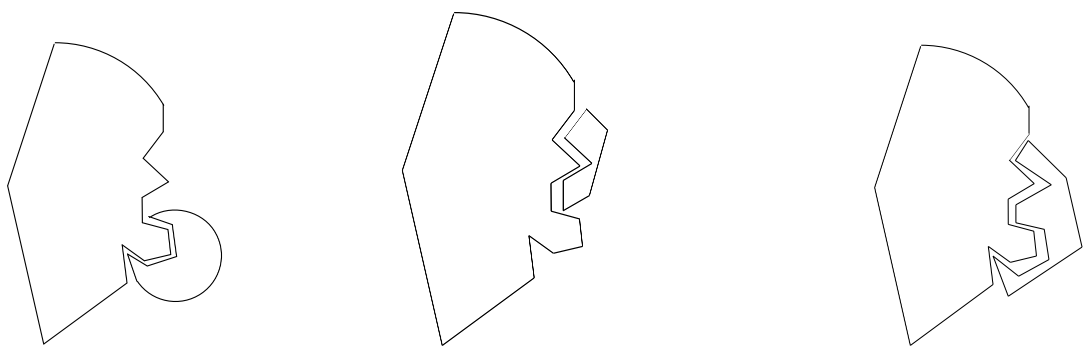
One very important point: if there are many guests, guest 1, guest 2, guest 3, guest **n** then the best Guest will be the one forming most stable complex. It is important to realize that for stable complex formation, the Host and the Guest should be in close to each other over a large surface area. Because then there will be more intermolecular forces operating between the two making a very stable complex. Chemists have appreciated that molecular recognition between two partners lead to manifestation of interesting properties. It is, therefore, important to realize that mere recognition is not desirable unless it is accompanied by changes in properties of the whole system. So, remember the principle: more contacts more stable is the complex.

Let me draw cartoons and then through that I will explain molecular recognition. So, this is my host and these are the guests.



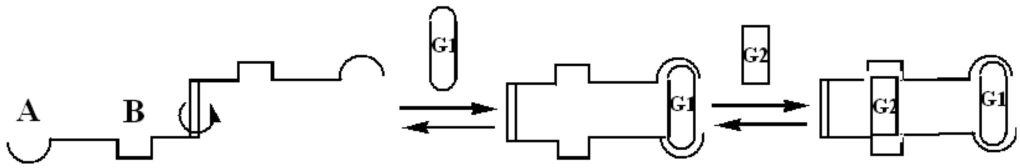
Host Guest 1 Guest 2 Guest 3

Now, what do you think? Which one will form very stable host guest complex? If you mix all three you find that guest 3 and the Host have shapes that are quite similar such that over a large surface area the Host and the Guest3 will be in contact. Now, let us see how the other complexes are formed. My drawing is not perfect, but hopefully you understand what I mean.

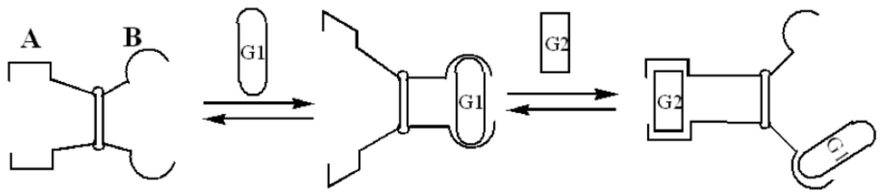


Complex 1 Complex 2 Complex 3

So, we can give a large number of guests in the system against this Host and it will be found that guest 3 will preferentially bind because it will be in close contact over a large surface area with the Host. Because of that, large number of van der Waals interactions, dipolar interactions, hydrogen bonding, etc., that are additive in nature in this case will lead to large drop of free energy (i.e., ΔG will be very negative) making a stable host-guest complex. Molecular recognition is a fundamental concept of supraumolecular chemistry, all right. I will tell you two more systems about cooperativity let us see.



A: Positive cooperativity



B: Negative cooperativity

I will give you some real-life examples in future, but right now I am discussing only the principles. For system **A**, it can rotate upon binding a guest as shown so that binding of the second guest will be much easier. In case of **B** if a guest (G1) comes and binds as shown, binding of the second guest will be difficult. That is negative cooperativity. This cooperativity is also known as the allosteric effect. So, when you have several guest then when the binding of one helps binding of the other then we call it positive allosteric effect (positive cooperativity). The second one where binding of the first guest hinders the second is known as negative allosteric effect.

So, in addition to molecular recognition, the energetics must be kept in mind. and the Gibbs free energy is less negative. When Gibbs free energy is less negative compared to the summation of individual effects then that is called negative allosterism or negative cooperativity. When the Gibbs free energy is more negative than summation of binding of then it is called a positive cooperativity. So, the Gibbs free energy is less negative in negative cooperativity and Gibbs free energy is more negative in positive cooperativity alright. So, when we discussed about molecular recognition, these 2 things are very important. Now it will be interesting to know how can we deal thermodynamically the this host guest complexation reactions.

So, I will stop here now. Thank you.