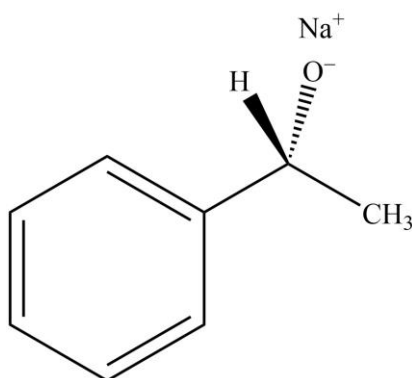


## ❖ Bonds Weaker Than Covalent

The bonds we have studied so far in this chapter possess bond dissociation energy in the range of 200–400 kJ mol<sup>-1</sup> i.e., covalent bonds. However, there are some bonds with very low bond dissociation energies as well (10–40 kJ mol<sup>-1</sup>). Therefore, in this section, we will discuss different types of bonds that are weaker than the typical covalent bond and results in supramolecular systems.

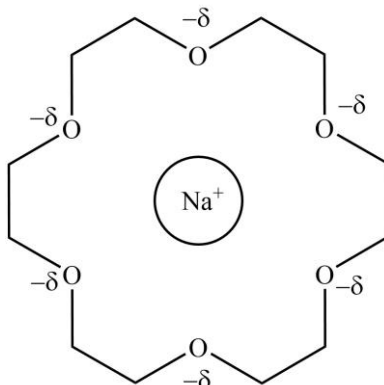
### ➤ Ion-Ion Interactions

Though ionic bonds are stronger than typical covalent bonds, the ion-ion interaction between a cation and organic anion is somewhat weaker than typical covalent interaction because of the bond energy in the range of 100–350 kJ mol.



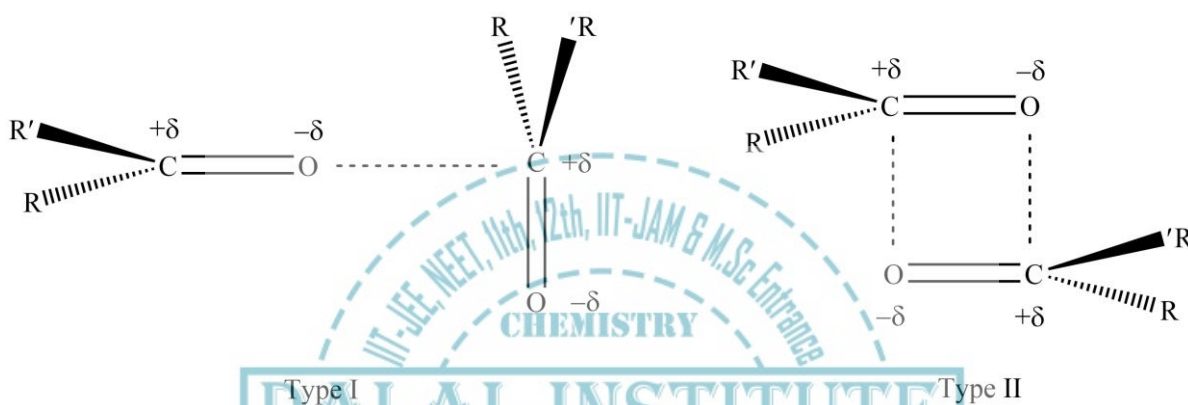
### ➤ Ion-Dipole Interactions

The interaction of an ion (like sodium) with a polar molecule (like water), is the case of ion-dipole interaction, whose bond energy ranges from 50–200 kJ mol<sup>-1</sup>. This type of interaction is observed both in the solution and in the solid state. The ion-dipole bonding in supramolecular systems of alkali cations' complexes with macrocyclic (large ring) ethers are labeled as crown ethers. The oxygen atoms of the ether play the same role as played by the polar H<sub>2</sub>O molecules, though the complex gets its extra stability from the chelate- and macrocyclic effects.



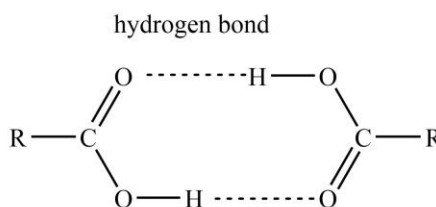
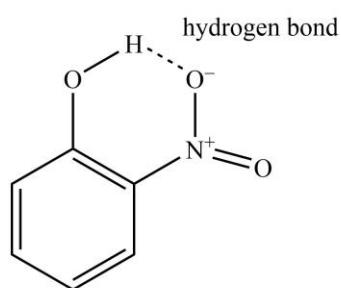
➤ **Dipole-Dipole Interactions**

The alignment of molecular dipoles with each other can produce substantial attractions. This can be of two types; the first is the matching of a single pair of poles on adjacent molecules, and the second one involves the opposing alignment of one dipole with the other. The bond energy of dipole-dipole interactions ranges from 5–50 kJ mol<sup>-1</sup>. Many carbonyl derivatives show this type of behavior in the solid state, and studies have proposed that the second type of interactions have energy around 20 kJ mol<sup>-1</sup>, which is quite comparable to a hydrogen bond of intermediate strength. Nevertheless, the lower boiling point of ketones suggests that dipole-dipole interactions of the second type are relatively weak in solution (acetone's boiling point = 56°C).



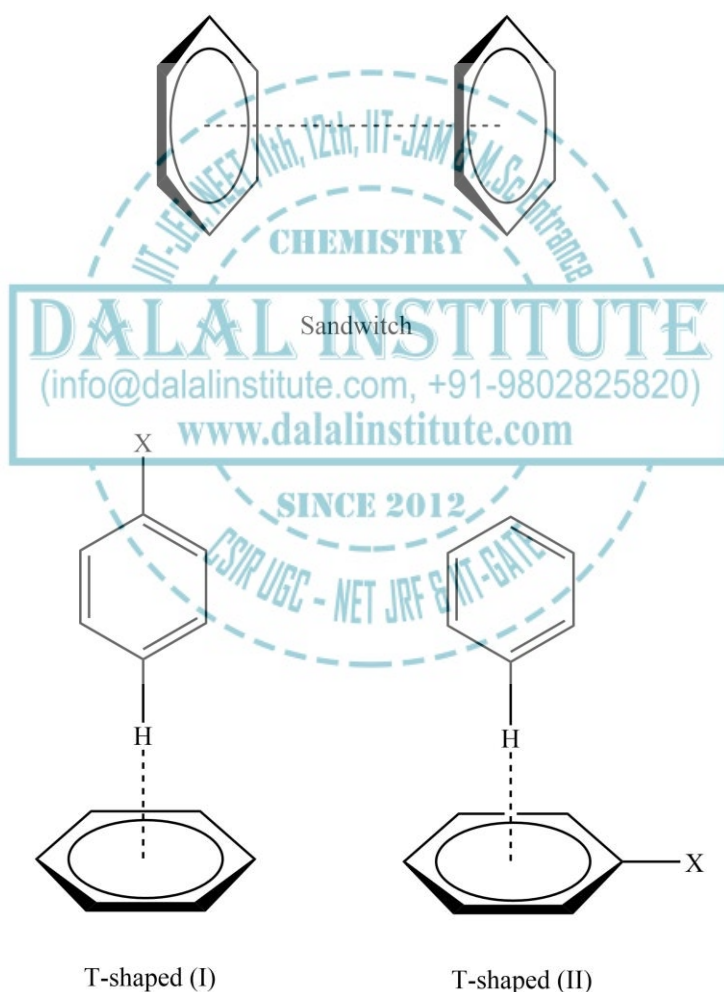
➤ **Hydrogen Bonding**

The hydrogen bonding or H-bonding may be considered as a special type of dipole-dipole interaction where an H atom is in quite strong attraction with an electronegative atom of the same or neighboring molecule. If the H-bonding takes place within the molecule itself, it is called as intramolecular H-bonding. On the other hand, if the H-bonding takes place between two molecules, it is called as intermolecular H-bonding. The bond energy for H-interactions ranges from 10–120 kJ mol<sup>-1</sup>. A typical case of H bonding in supramolecular systems is the generation of carboxylic acid dimers. H-bonds are ubiquitous, and are responsible for the overall shape of numerous proteins, recognition of substrates by many enzymes (along with  $\pi$ - $\pi$  interactions) and also for DNA's double helix structure.



➤  $\pi$ - $\pi$  Interactions

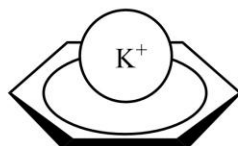
Since  $\pi$ - $\pi$  interactions happen to be present between aromatic rings, they are also known as aromatic  $\pi$ - $\pi$  stacking interactions, and generally involve one electron-deficient and one electron-rich species. The bond energy of these types of interactions ranges from 50–500 kJ mol<sup>-1</sup>. These  $\pi$ -interactions are two kinds; one is face-to-face, and the second one is edge-to-face. The face-to-face  $\pi$ - $\pi$  interactions are accountable for the slippery nature of graphite and its beneficial lubricant feature. Similar kind of  $\pi$ - $\pi$  interactions between the aryl rings of nucleobase pairs also helps the DNA double helix to get stabilized. The second type (i.e. edge-to-face interactions) may be considered as weak types of H-bonds between the electron-rich  $\pi$ -cloud of one aromatic ring and the slightly electron-deficient H atoms of another aromatic ring. Hence, they must not be called as  $\pi$ -stacking because no stacking of the  $\pi$ -electron surfaces is present.



The edge-to-face interactions are also accountable for the characteristic herringbone packing in the crystal lattice of a range of small aromatic hydrocarbons (benzene included).

➤ **Cation- $\pi$  Interactions**

Many cations of *d*-block metals (like  $\text{Fe}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$ ) are known to yield complexes with aromatic and olefinic systems such as ferrocene i.e.  $[\text{Fe}(\text{C}_5\text{H}_5)_2]$  and Zeise's salt i.e.  $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ . The nature of bonding in such systems is quite strong and could not be considered non-covalent, because it is closely linked with the partially filled *d*-orbitals of the metals. For instance, the bond between  $\text{Ag}^+$  and  $\text{C}_6\text{H}_6$  has a significant covalent character. Nevertheless, the bonding of alkali metals' cations or alkaline earth metals' cations with  $\text{C}=\text{C}$  double bonds is quite weak, and therefore, can be considered as non-covalent interaction. These interactions have also been proved to play a significant role in biological systems. For instance, the bond energy of the  $\text{K}^+$ -benzene bond in the gas phase is around  $80 \text{ kJ mol}^{-1}$ , which is quite comparable to  $\text{K}^+$ -water interaction ( $75 \text{ kJ mol}^{-1}$ ). This can be attributed to the fact that the  $\text{K}^+$  ion is more soluble in water than in  $\text{C}_6\text{H}_6$  as more water molecules can interact with the potassium ion, but only a few  $\text{C}_6\text{H}_6$  molecules can fit around it due to bulkier size.

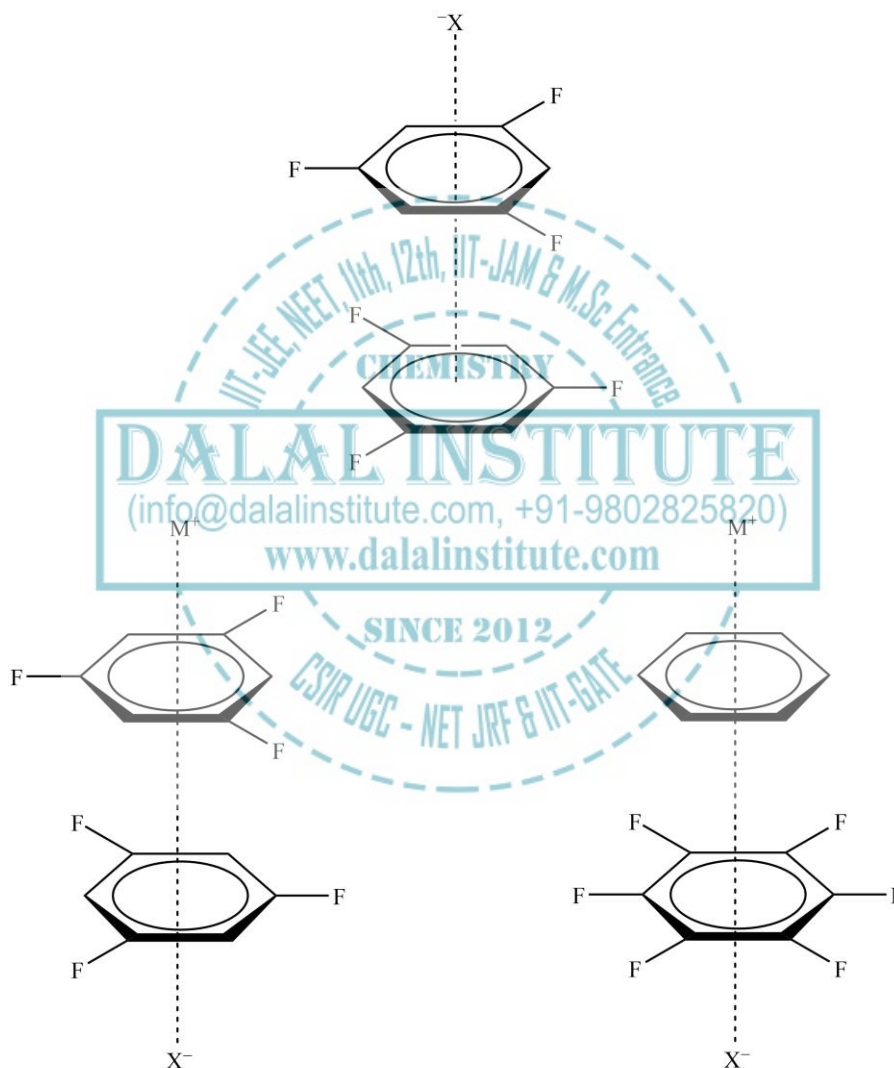


Cation- $\pi$  interactions in between  
 $\text{K}^+$  ion and benzene

The bonding of cations of non-metals like  $\text{RNH}_3^+$  with double bonds can be regarded as a type of  $\text{X}-\text{H} \cdots \pi$  H-interaction.

➤ **Anion- $\pi$  Interactions**

It seems that, unlike cation- $\pi$  interactions, anion- $\pi$  interactions should not be favorable as it appears to be repulsive; for instance, the affinity of the aromatic ring with cryptand for halides quickly drops in the order  $F^- \gg Cl^- > Br^- \sim I^-$  since repulsions arising from anion- $\pi$  interaction is more for bigger halides. Nevertheless, there is a difference in the charges between an anion and an overall neutral aromatic ring, and hence, there is a possibility of an electrostatic attraction. These kinds of short anion- $\pi$  interactions are noted for organometallic calixarene derivatives where the aromatic ring has a substantial positive charge.

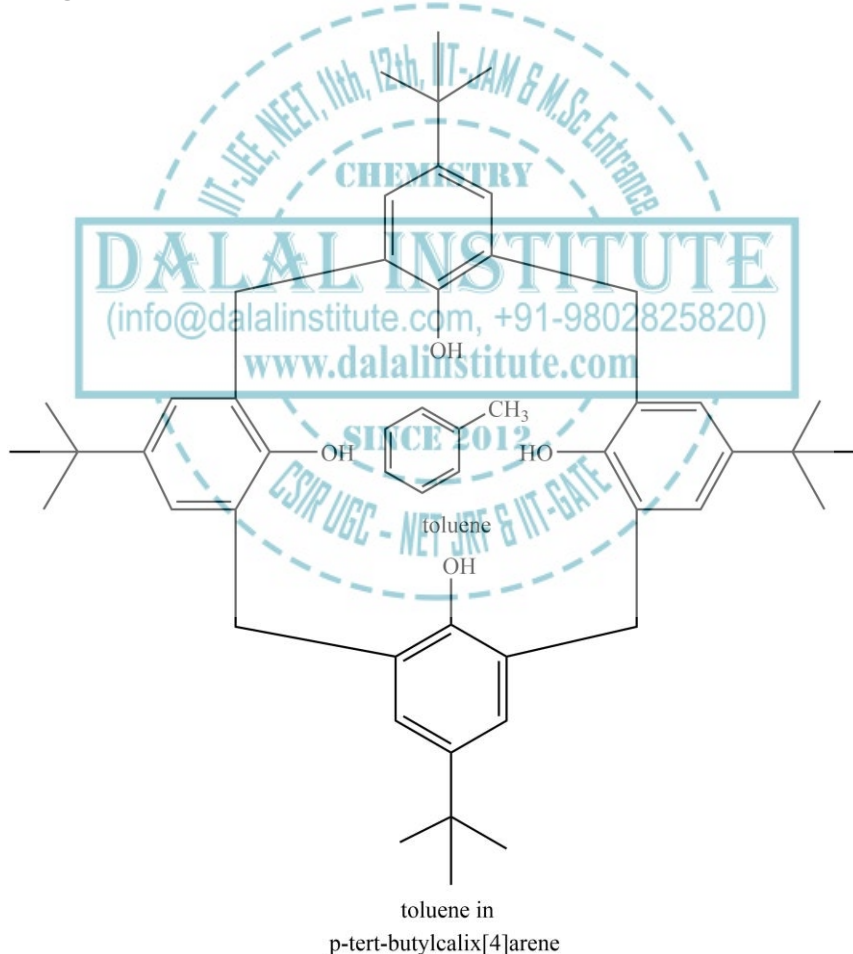


Anion- $\pi$  interaction

The anion- $\pi$  interactions are also caught up as controlling factors in self-assembly reactions of monovalent silver complexes with  $\pi$ -acidic aromatic rings.

➤ *Van der Waal's Forces*

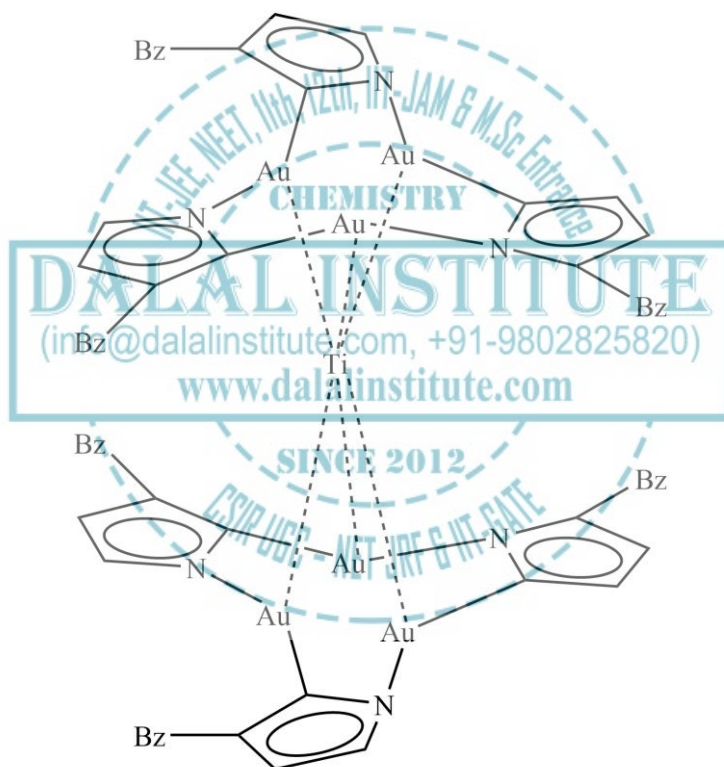
Van der Waals forces are attractive and arise from the polarization of an electronic cloud by the closeness of an adjacent nucleus, yielding a weak attraction of electrostatic nature. The characteristic range for Van der Waals forces ranges from 0.50–40 kJ mol<sup>-1</sup>. The Van der Waals forces are non-directional, and therefore, have only restricted scope in designing specific hosts for choosy complexation of specific guest molecules. Generally speaking, van der Waals forces deliver a generic attraction for most 'easily polarisable' (soft) species with the interaction energy relational to the surface area of direct contact. In the case of supramolecular systems, the van der Waals forces are extremely important in the generation of 'inclusion compounds', where very organic molecules small are loosely united within molecular cavities or crystal lattices; for instance, the inclusion of toluene into the molecular cavity of the *p*-tert-butylphenol-based macrocycle. In the case of molecular assemblies in solid-state, the effects of crystal close packing dictate the overall structural arrangement.



The hydrophobic interactions also perform a vital role in supramolecular systems as these are accountable for displacing the H<sub>2</sub>O molecules from the host's cavity by an organic molecular guest.

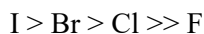
➤ **Closed Shell Interactions**

It is quite a well-known fact that an atom with partially filled electronic shells gives rise to a strong covalent bond. Nevertheless, many ions usually have fully-filled or closed valence electronic shells but feel strong attractions between oppositely charged pairs. Therefore, one might think that closed shell atoms of neutral or like charges should not show any significant interaction; though in some cases, they show significant attraction. These kinds of interactions are labeled as closed shell interactions and involve some secondary bonding interactions; one is halogen bonding and the other is metalophilic interactions. As far as the strength is concerned, these interactions are quite comparable to moderate H-bonds. These interactions are considered to originate from electron correlation effects, which are further strengthened by relativistic effects in the case of heavy metals like gold (i.e., aurophilic interactions). These interactions are very noticeable for heavy metals with electron configurations ranging from  $d^8$  to  $d^{10}s^2$ .



Closed Shell Interactions

Furthermore, it is also worthy to note the fact that the overall strength of halogen bonding decreases in the following order.



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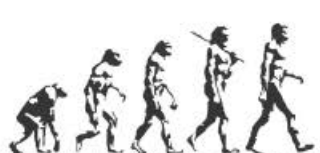
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# A TEXTBOOK OF ORGANIC CHEMISTRY

**Volume I**

**MANDEEP DALAL**



*First Edition*

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