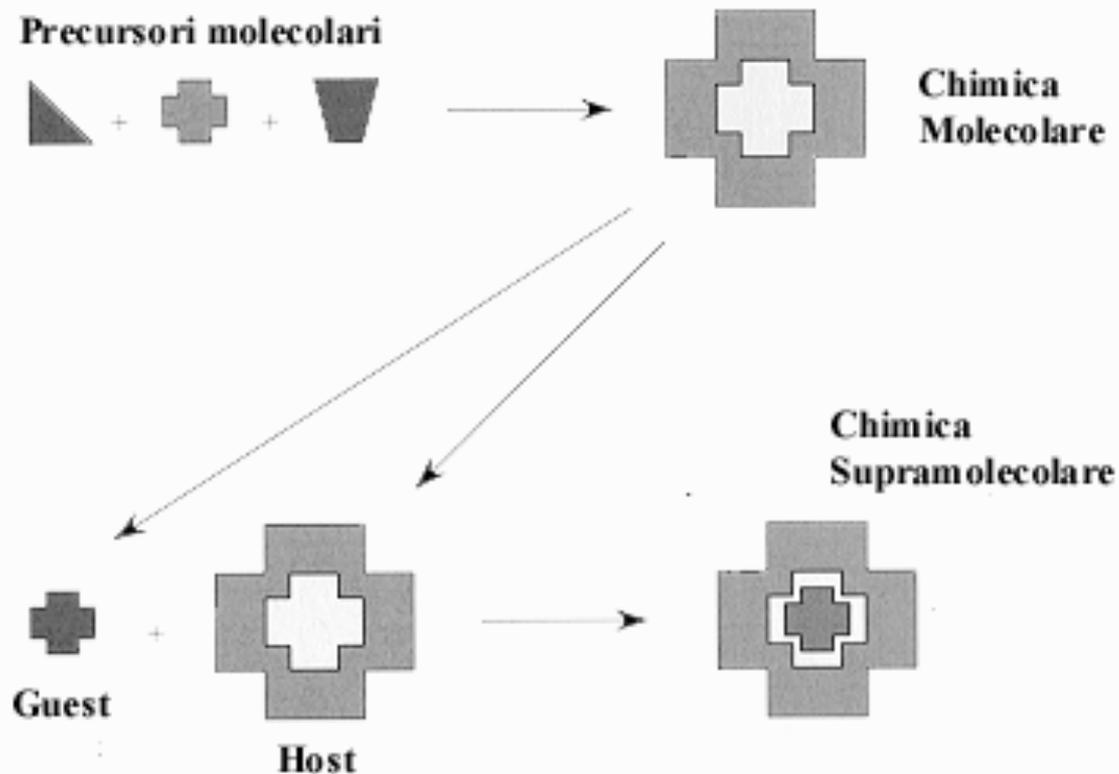


## Definizione di Chimica Supramolecolare

La **Chimica Supramolecolare** è stata definita da uno dei suoi fondatori, Jean-Marie Lehn (Premio Nobel 1987), la **‘chimica degli aggregati molecolari e del legame intermolecolare’**. Essa prende in esame le strutture e le funzioni di nuove entità chimiche che si formano in seguito all’associazione tra due o più specie chimiche diverse.

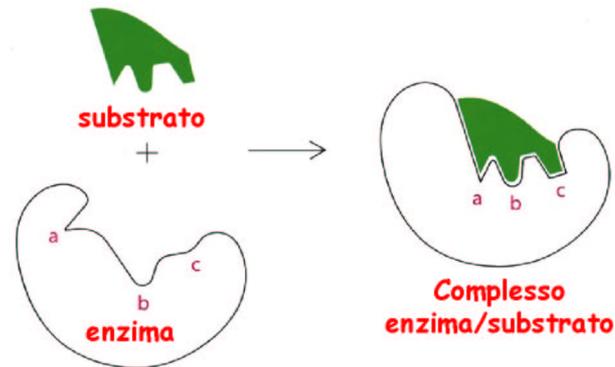
La **Chimica Supramolecolare** può essere definita come **‘la chimica oltre la molecola’**; la chimica delle interazioni intermolecolari (F. Voegtler, Bonn). In una supramolecola le informazioni sono conservate sotto forma di aspetti strutturali specifici

Differenza tra **chimica molecolare** e **chimica supramolecolare** in termini strutturali



Confronto fra la costruzione di un oggetto molecolare e di una entità supramolecolare (complesso Host-Guest)

**le radici:** Emil Fisher introduce il concetto di chiave-toppa per spiegare la selettività enzima substrato

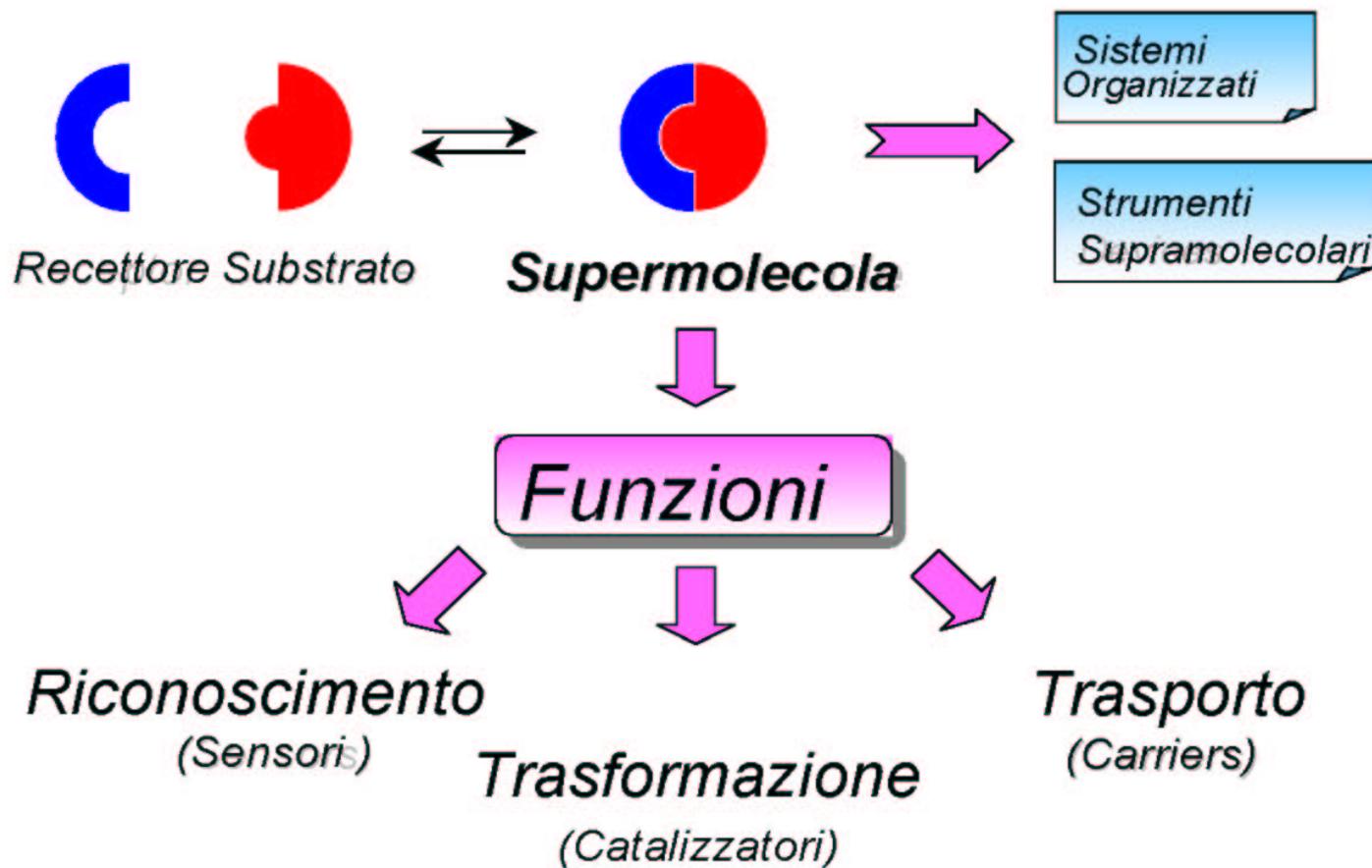


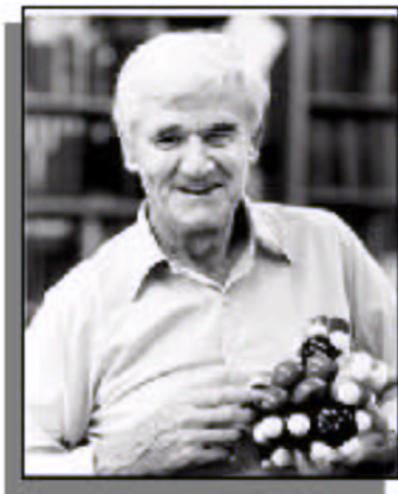
L' analogia “**lock and key**” ha posto le basi del riconoscimento molecolare, cioè la discriminazione da parte della specie **host** nell' ambito di una potenziale varietà di molecole **guest**

# OBIETTIVO DELLA CHIMICA SUPRAMOLECOLARE

La costruzione razionale di strutture complesse costituite da composti pre-programmati per specifiche applicazioni e organizzate per mezzo di interazioni deboli (forze elettrostatiche, legami a idrogeno, interazioni di Van der Waals, legami dativi-coordinativi)

# CHIMICA SUPRAMOLECOLARE

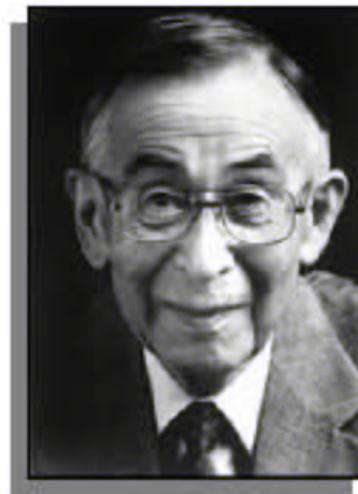




Donald J. Cram



Jean-Marie Lehn

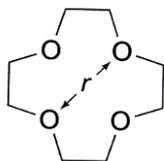


Charles J. Pedersen

**Gran parte della chimica supramolecolare ha avuto origine dagli sviluppi della chimica dei macrocicli negli anni sessanta, in particolare dei leganti macrociclici per cationi metallici.**

**(30 aprile 2014 Jean-Marie Lehn a Padova al Bo a al DiSC)**

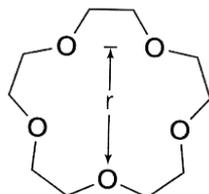
1.2–1.5 Å



**12-Crown-4**

Binds  $\text{Li}^+$  preferentially

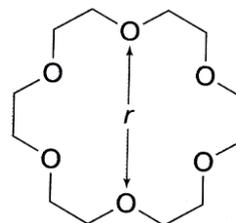
1.7–2.2 Å



**15-Crown-5**

Binds  $\text{Na}^+$  preferentially

2.6–3.2 Å



**18-Crown-6**

Binds  $\text{K}^+$  preferentially

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*Ionic radius (Å)*

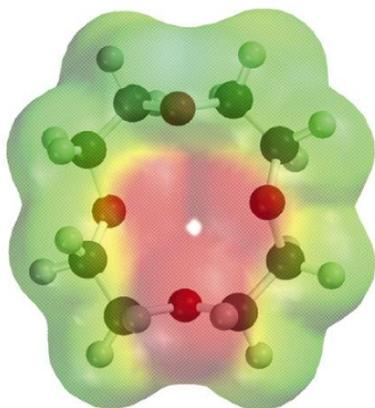
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$\text{K}^+$  2.66

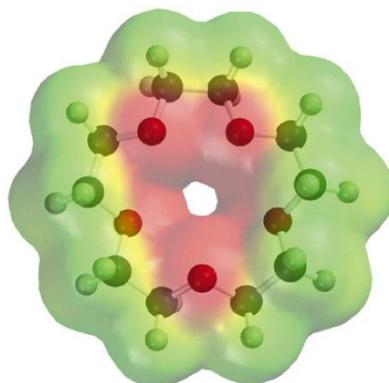
$\text{Na}^+$  1.80

$\text{Li}^+$  1.20

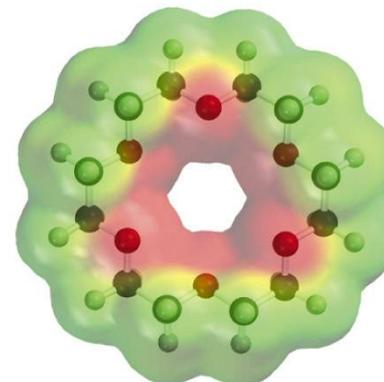
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**[12]-crown-4**



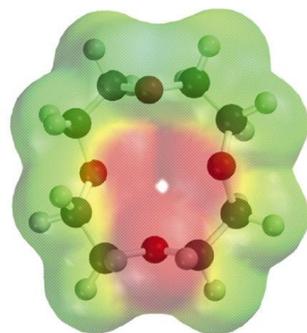
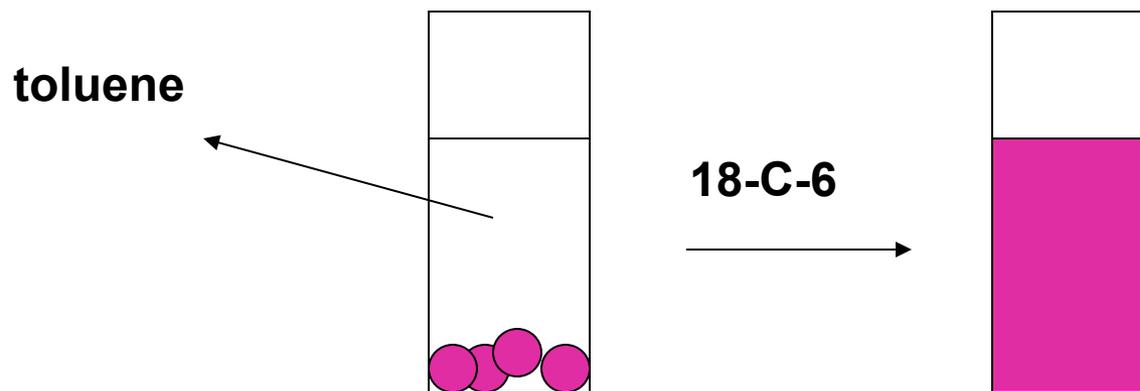
**[15]-crown-5**



**[18]-crown-6**

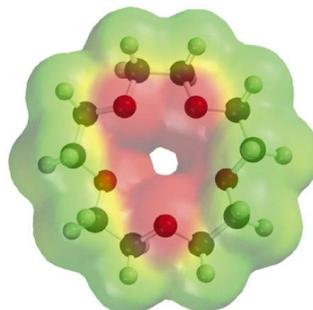
# Eteri corona

Solubilizzazione di sali in ambienti non acquosi



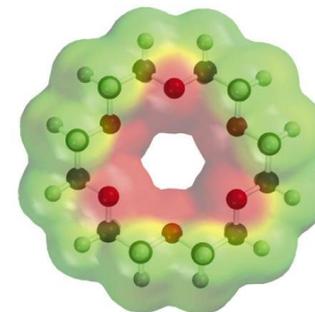
[12]-crown-4

**Li<sup>+</sup>, 1.36 Å**



[15]-crown-5

**Na<sup>+</sup>, 1.90 Å**



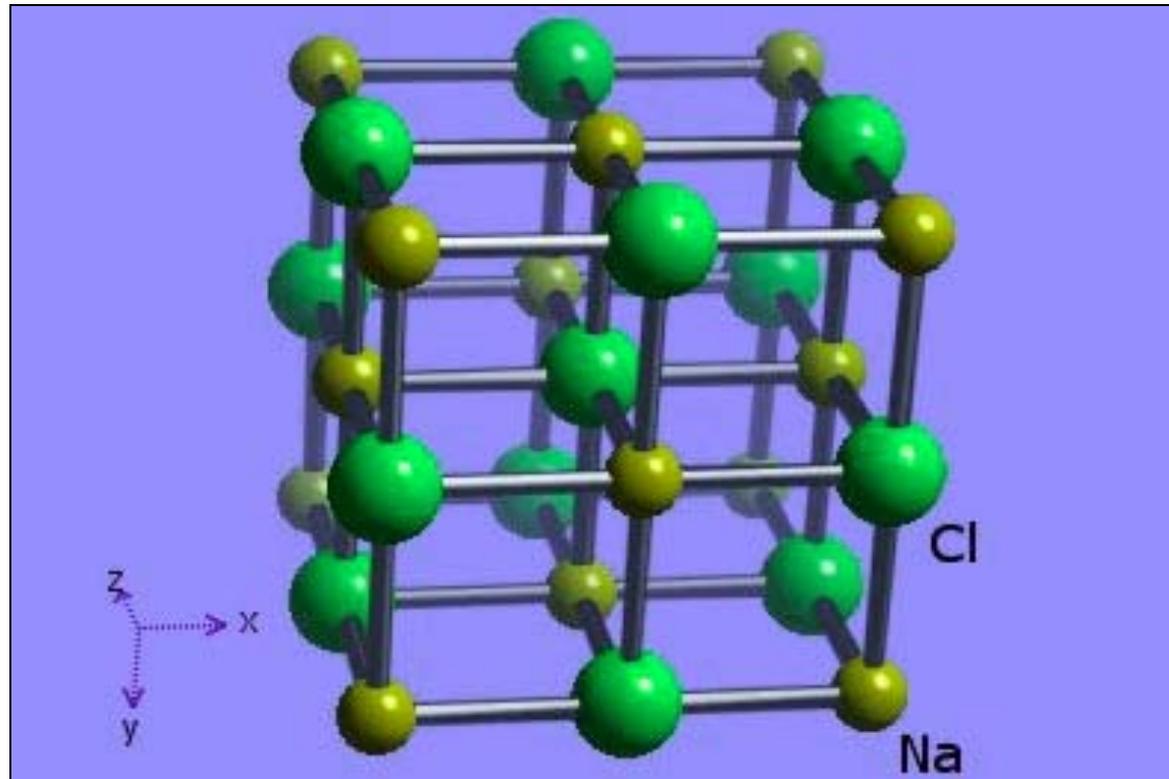
[18]-crown-6

**K<sup>+</sup>, 2.66 Å**

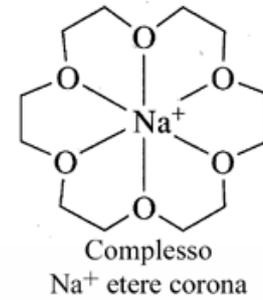
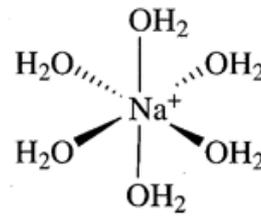
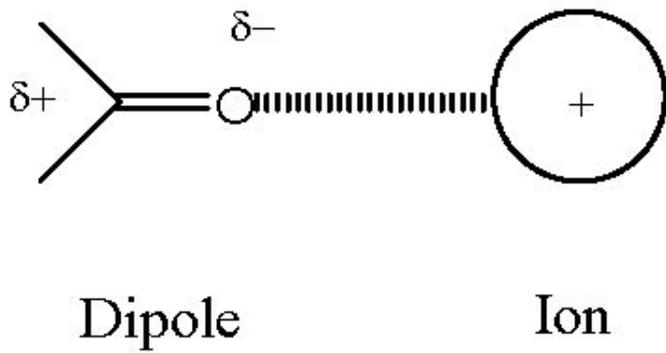
## *Nature of Supramolecular Interactions*

- 1 - Electrostatic (e.g. ion-ion, dipole-dipole)
- 2 - Hydrogen bonding (4 - 120 kJ/mol)
- 3 -  $\pi$ - $\pi$  stacking interactions (0 - 50 kJ/mol)
- 4 - Cation-  $\pi$  interactions (5 - 80 kJ/mol)
- 5 - Van der Waals forces (< 5 kJ/mol)
- 6 - Hydrophobic effects

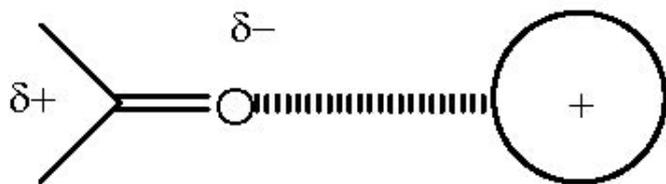
# Interazioni elettrostatiche



**ione-ione**  
(100-350 KJ mol<sup>-1</sup>)

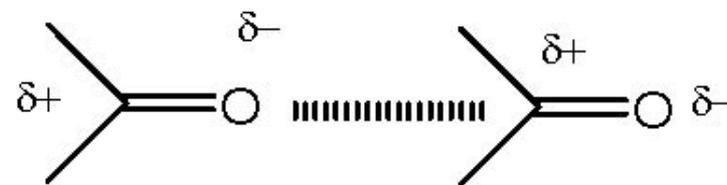


**Ione-dipolo  
(50 – 200 KJ mol<sup>-1</sup>)**



Dipole

Ion

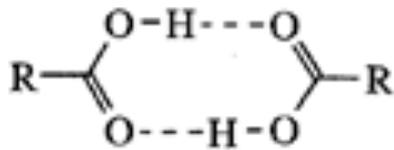


Dipole

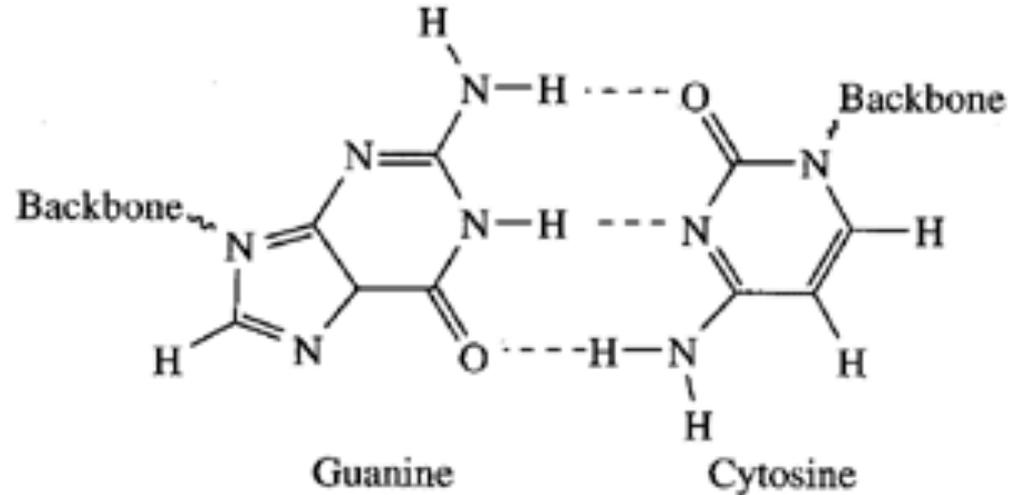
Dipole

**Dipolo-dipolo  
(5-50 KJ mol<sup>-1</sup>)**

# Legame a idrogeno (4-120 kJ mol<sup>-1</sup>)



2.50-2.80 Å



Legami d'idrogeno nei dimeri degli acidi carbossilici e nell'appaiamento delle basi del DNA

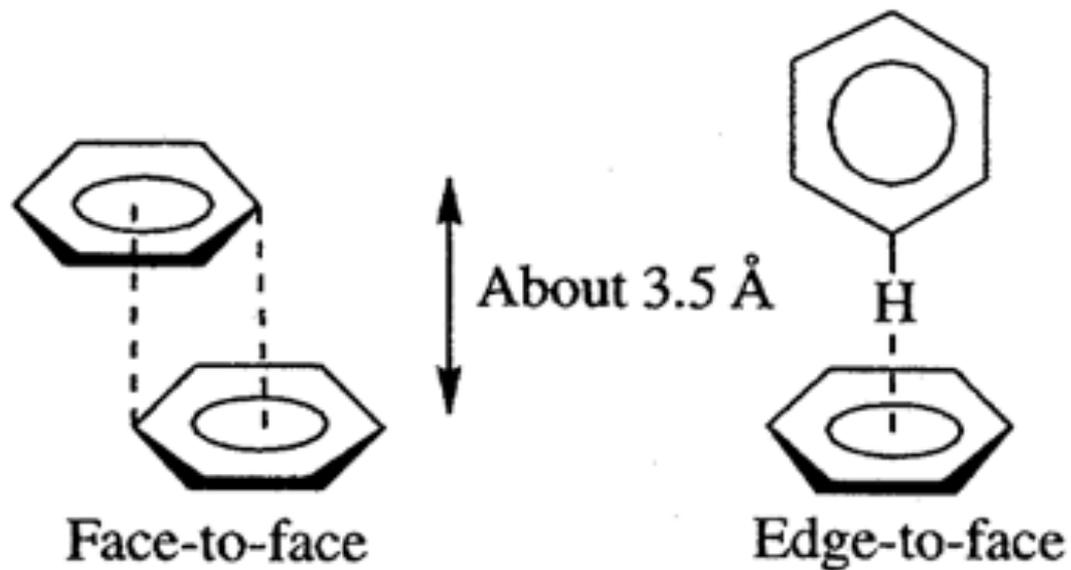
# Interazioni Catione- $\pi$ (5-80 kJ mol<sup>-1</sup>)



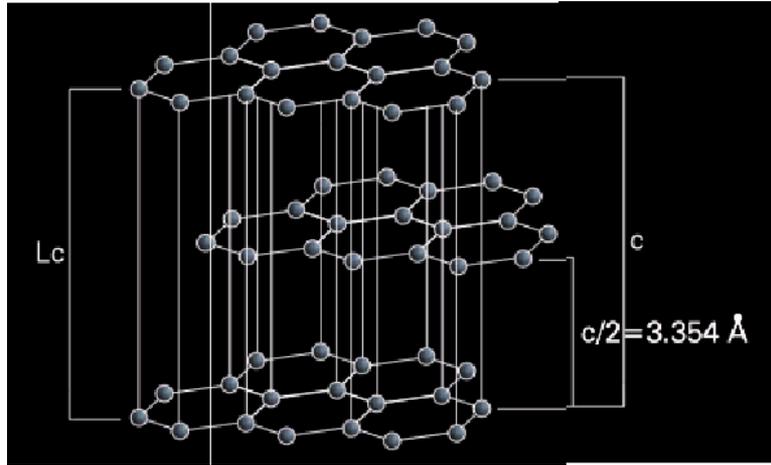
L'energia di interazione di  $K^+$  e benzene in fase gassosa è  
circa 80 kJ mol<sup>-1</sup>

(Per confronto, l'associazione di  $K^+$  con una singola  
molecola d'acqua è di 75 kJ mol<sup>-1</sup>)

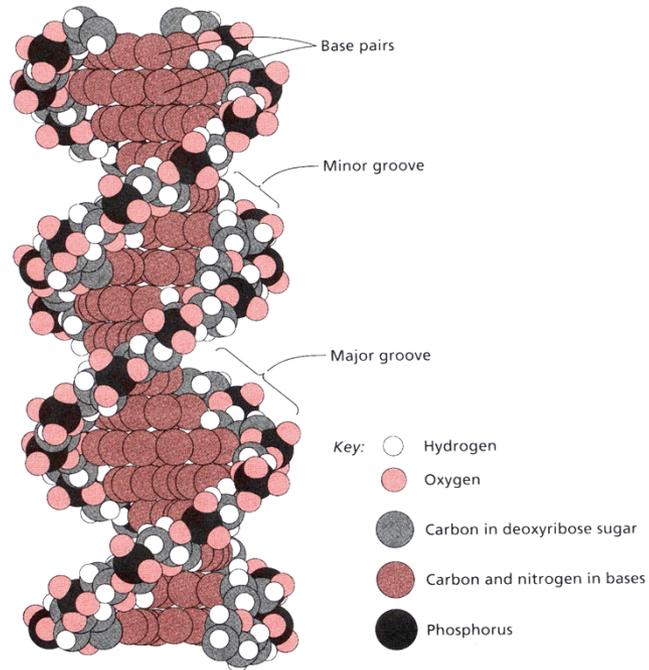
## Interazioni $\pi$ - $\pi$ (0-50 kJ mol<sup>-1</sup>)



Diversi modi di  $\pi$ - $\pi$  stacking.

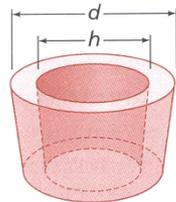
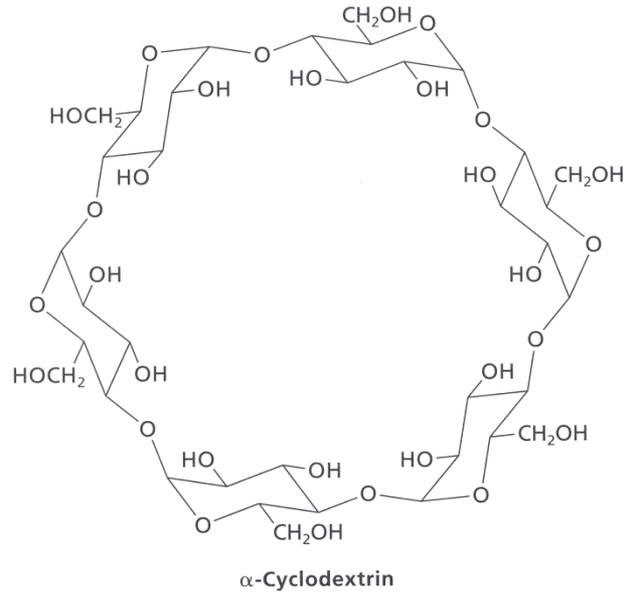


grafite

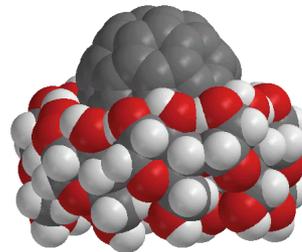
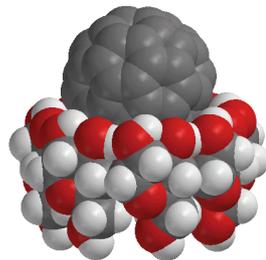
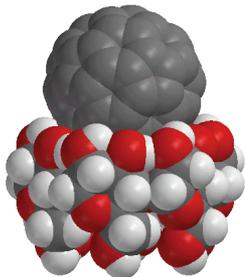


DNA

## effetti idrofobici



Cyclodextrin	No. glucose	d (nm)	h (nm)
$\alpha$	6	1.37	0.57
$\beta$	7	1.53	0.78
$\gamma$	8	1.69	0.95



complesso di inclusione fullerene-ciclodestrina

*“A **halogen bond** occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity” (IUPAC)*

