

# Molecole dalla Forma Curiosa

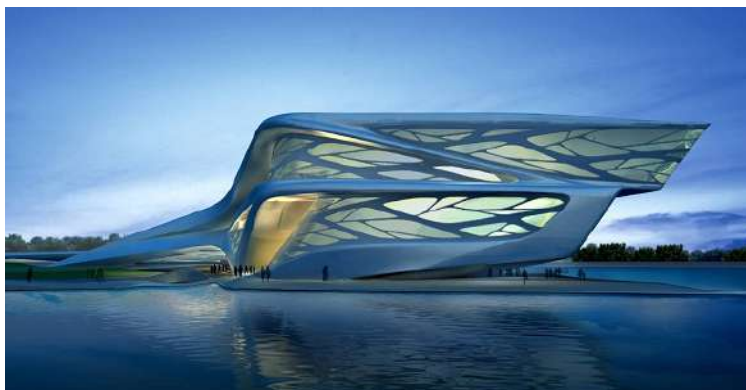


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**Università degli Studi di Perugia**  
**Dipartimento di Chimica, Biologia e Biotecnologie**



# Motivazioni

- ❖ Stimolare la curiosità degli studenti verso la disciplina chimica parlando della forma e bellezza delle molecole.
- ❖ Evidenziare l'affascinante mondo della chimica parlando delle forme molecolari come sculture dalle dimensioni **nano-scopiche**, che richiamano la forma di **oggetti macroscopici**.



Così come un architetto, un ingegnere, uno scultore o un pittore modellano e rappresentano la materia dando forme ad oggetti dalle dimensioni macroscopiche (**mm - metri**).

Il chimico organizza e unisce gli atomi creando forme (*sculture molecolari*) dalle dimensioni dei nanometri (**nm, cioè  $10^{-9}$  m**).

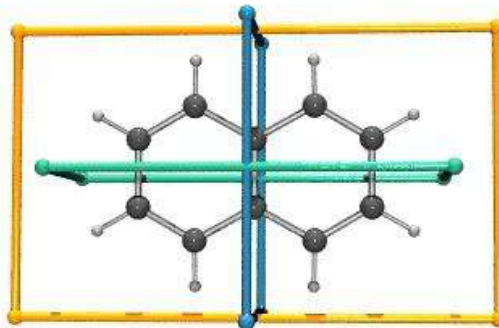
# Forma delle molecole

**La forma di una molecola è legata alla struttura ciò è :**

- Dal tipo e numero di atomi presenti nella molecola;
- Dai legami che essi instaurano (*distanze di legame, angoli*);
- Dalle conformazioni (*legate alle interazioni deboli intermolecolari ed intramolecolari*).

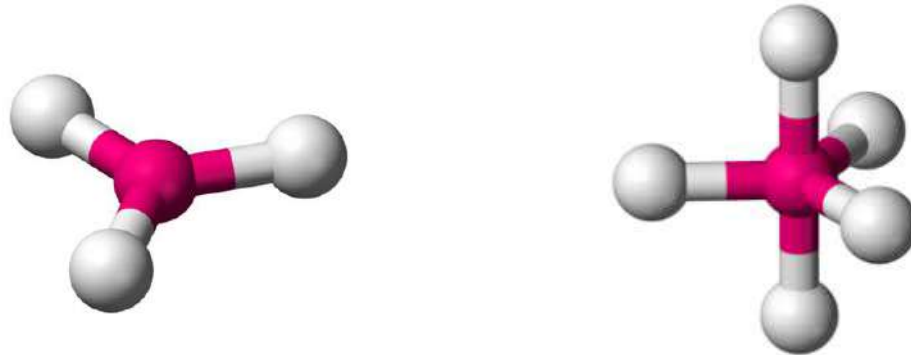
L'estetica di una molecole, la sua bellezza (*di un qualsiasi oggetto*) è spesso relazionata alla simmetria della sua forma.

La presenza di elementi di simmetria come l'asse, il piano, il centro di inversione della struttura molecolare rende la percezione della molecola (**oggetto**) molto più armoniosa.



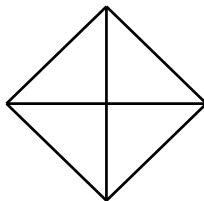
# Forma delle molecole

Le molecole possono presentare forme **bidimensionali** o **tridimensionali**.

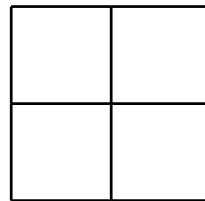


Spesso molte molecole prendono dei nomi particolari, che sono relazionati alla forma degli oggetti macroscopici che esse richiamano. Ad esempio:

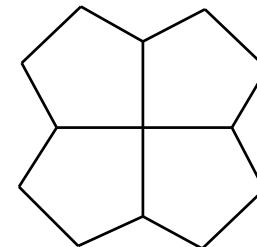
Molecole chiamate **Finestrani**



**[3,3,3,3]Finestrano**



**[4,4,4,4]Finestrano**



**[5,5,5,5]Finestrano**



# Forme Molecolari 2D

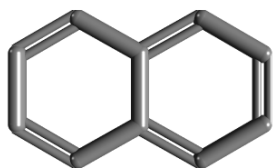
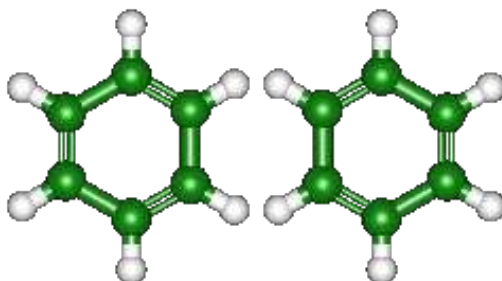
Il benzene è il capostipite di queste **molecole bidimensionali**. Dalla condensazione di  **$n_1$ -benzeni** si possono avere diverse forme. Le mattonelle del benzene possono combinarsi tra loro in moltissimi modi.



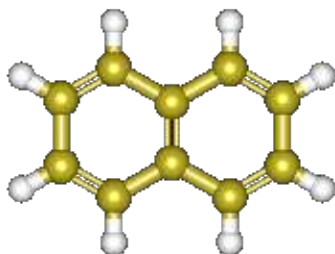
Benzene



Mattonella esagonale



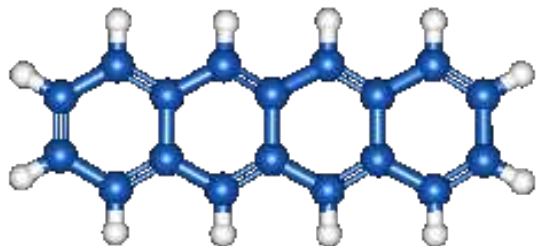
Naftalene



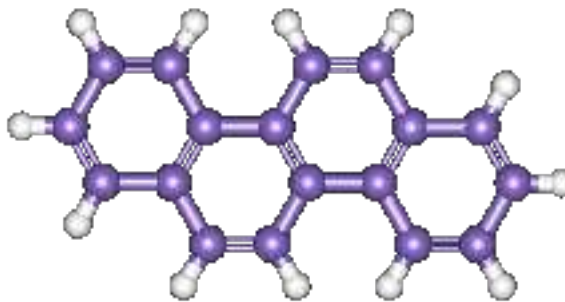
Antracene



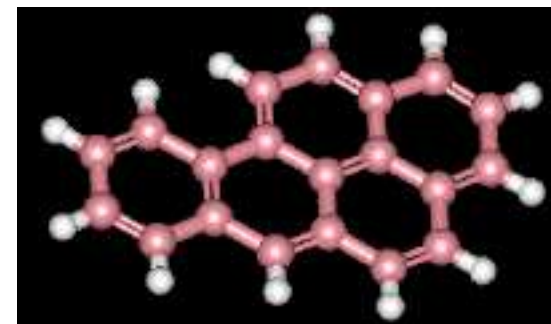
Fenantrene



Tetracene

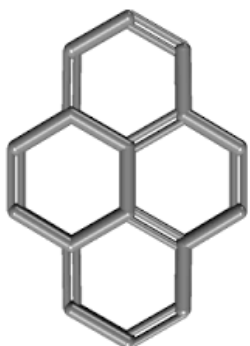


Crisene

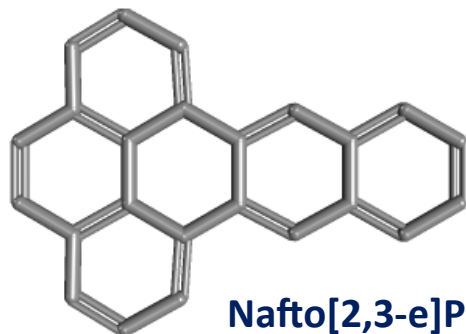


Benzopirene

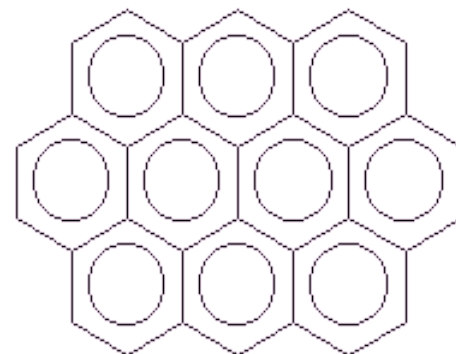
# Forme Molecolari 2D



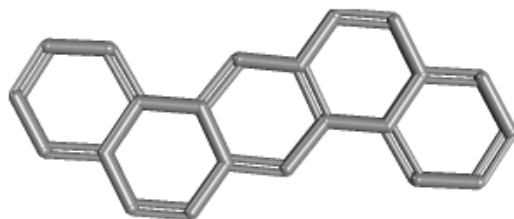
Pirene



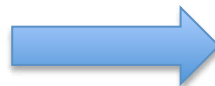
Nafto[2,3-e]Pirene



Ovalene

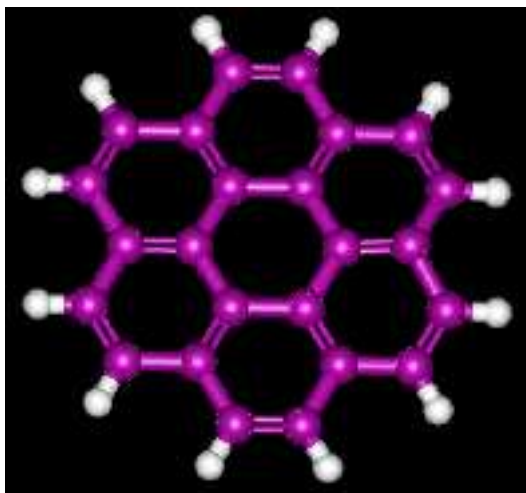


Dibenzo[a,h]antracene

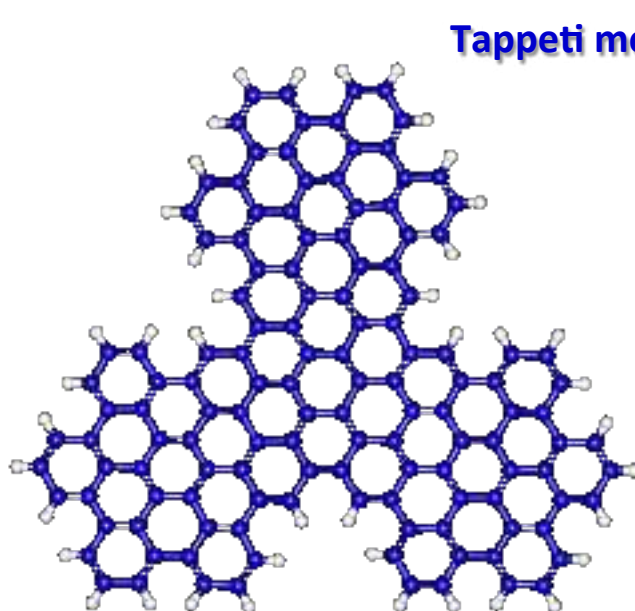


Grafene

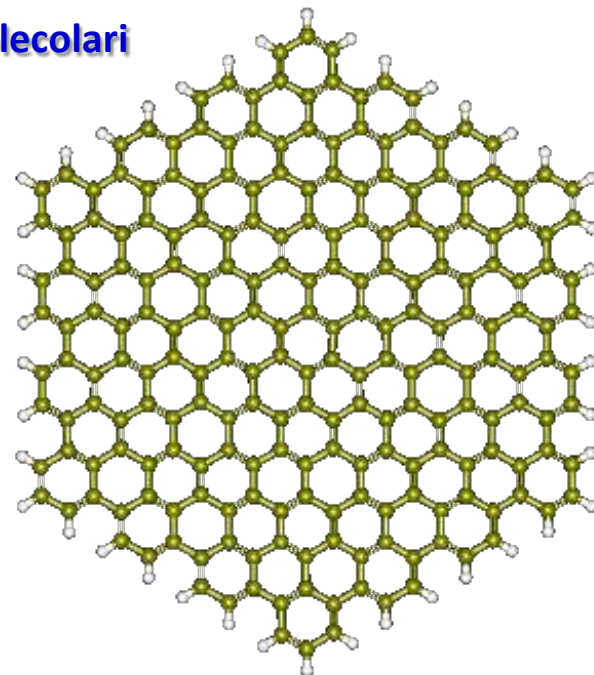
Tappeti molecolari



Coronene

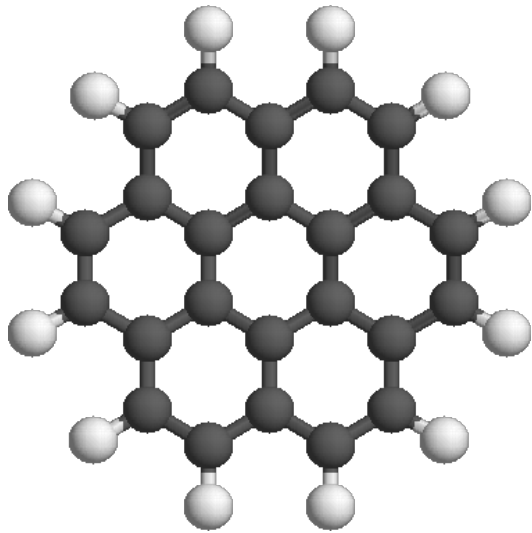


Composti poli-aromatici giganti

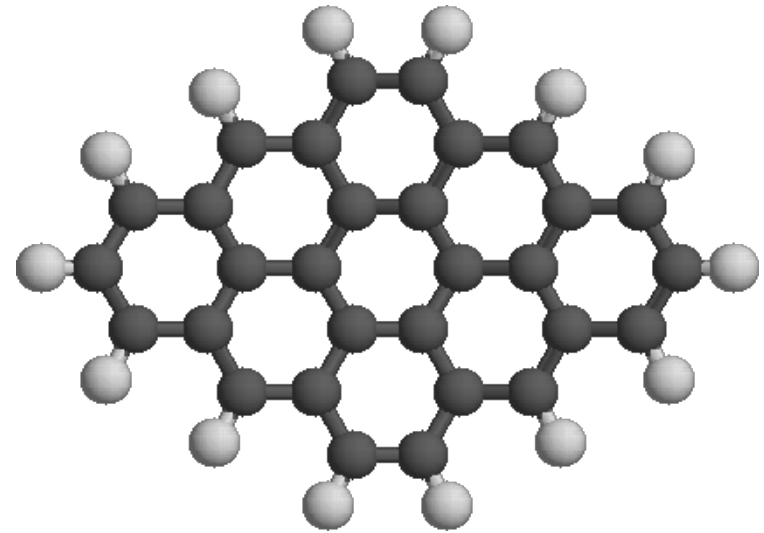


Composti poli-aromatici giganti

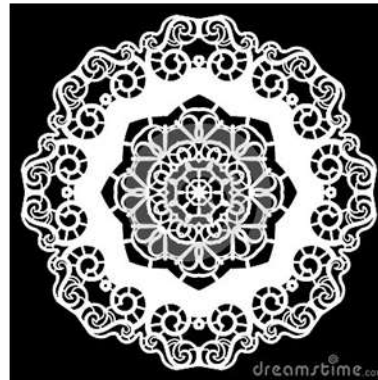
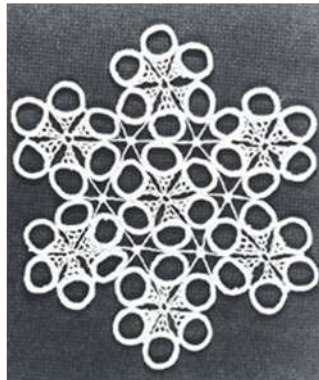
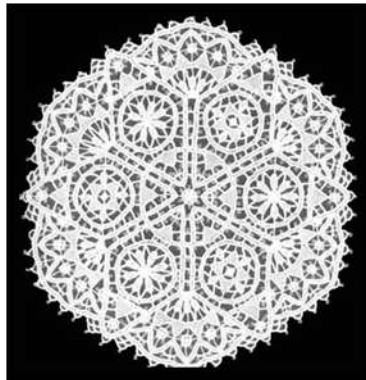
# Merletti Molecolari



Coronene

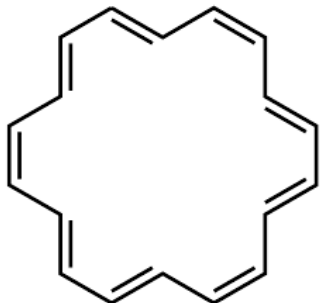


Dibenzo bc-kl coronene

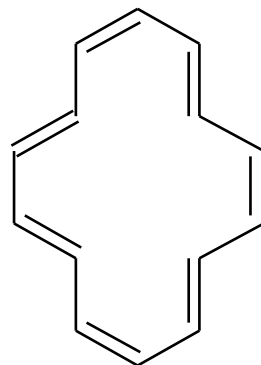


# Gli Annuleni

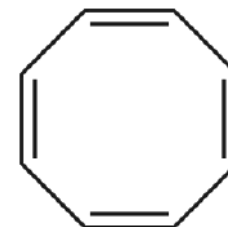
Prendono nome dalla loro forma circolare ad anello. Tutti i carboni sono ibridizzati  $sp^2$ , in base al numero di elettroni  $\pi$  (regola di Huckel) alcuni sono aromatici altri no.



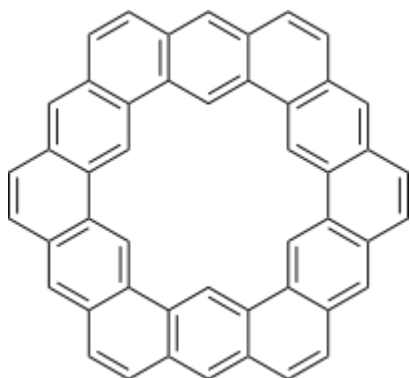
Aromatici =  $[4n + 2] e^-$   
Non Aromatici =  $[4n] e^-$



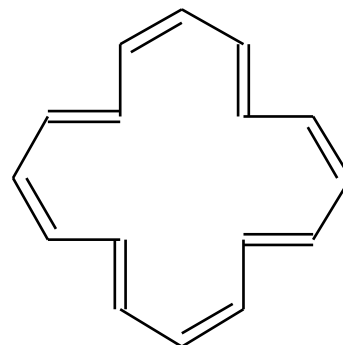
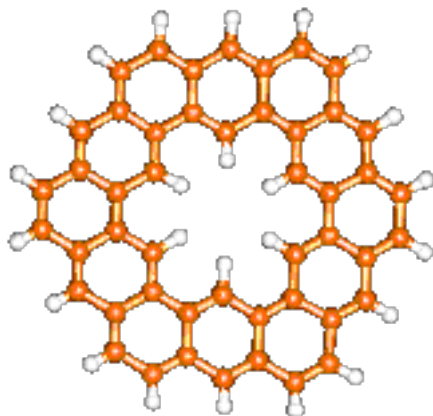
[14]-Annulene  
Aromatico



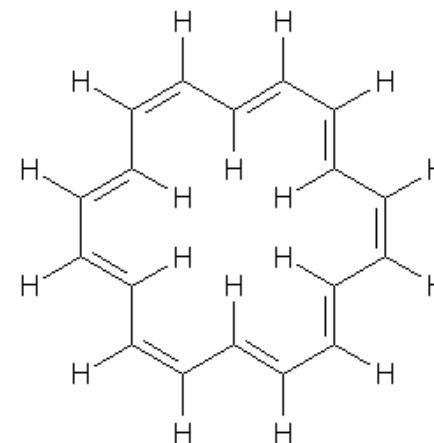
[8]-Annulene  
Non aromatico



Kekulene  
 $C_{48}H_{24}$



[16]-Annulene  
Non aromatico

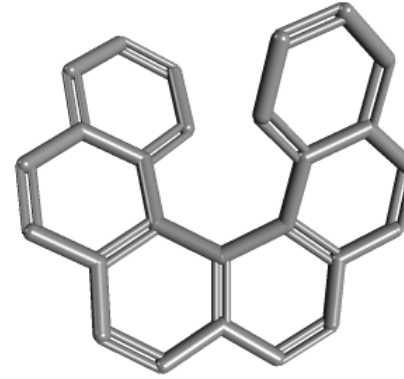
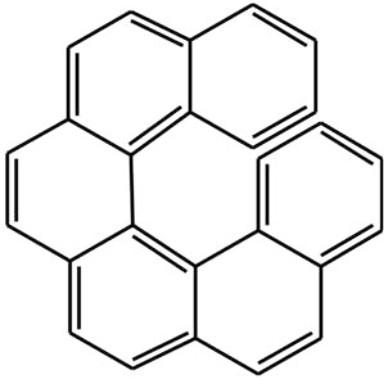


[18]-Annulene  
Aromatico

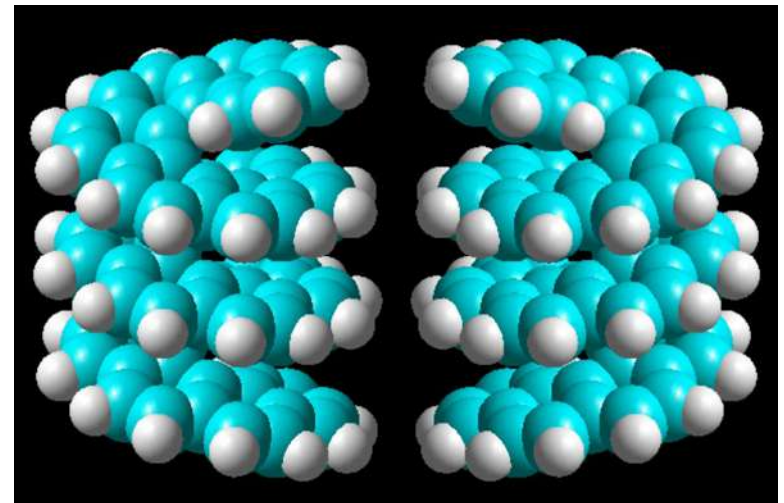


# Forme Molecolari 3D da blocchi 2D

## Gli Eliceni

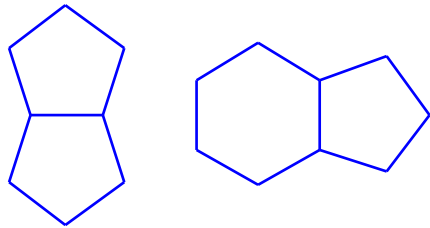


Come si evince dal nome sono molecole che presentano una forma elicoidale, sono molecole chirali: sinistrorse o destrorse.

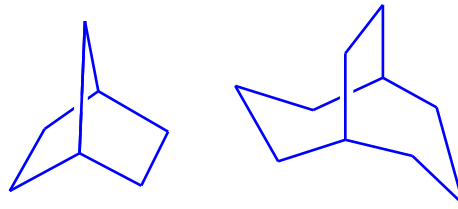


# Forme Molecolari 3D

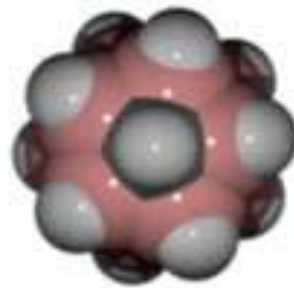
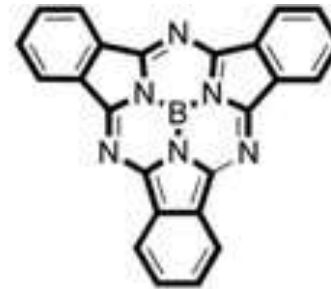
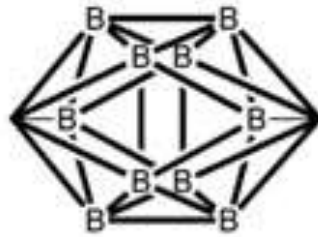
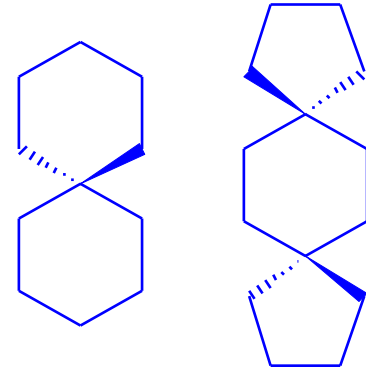
**Fuse**



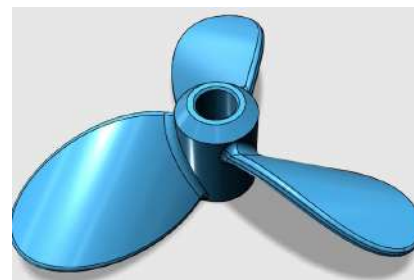
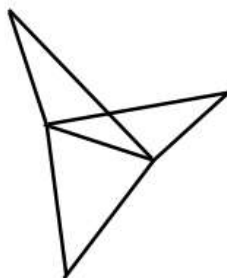
**a Ponte**



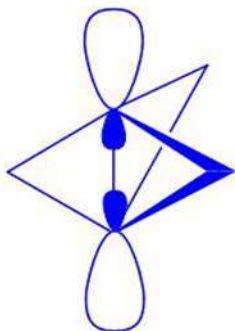
**Spiro**



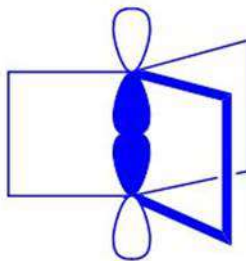
# Singole Molecole a Forma di Elica



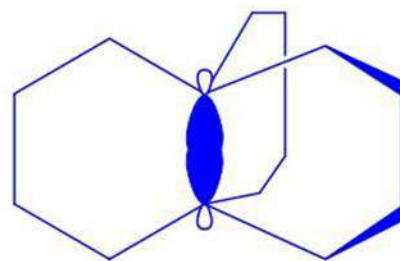
I **Propellani** sono molecole che ricordano la forma delle eliche a tre pale.



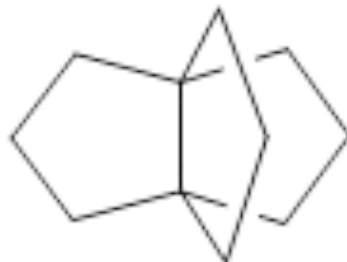
[1,1,1] propellane



[2,2,2] propellane



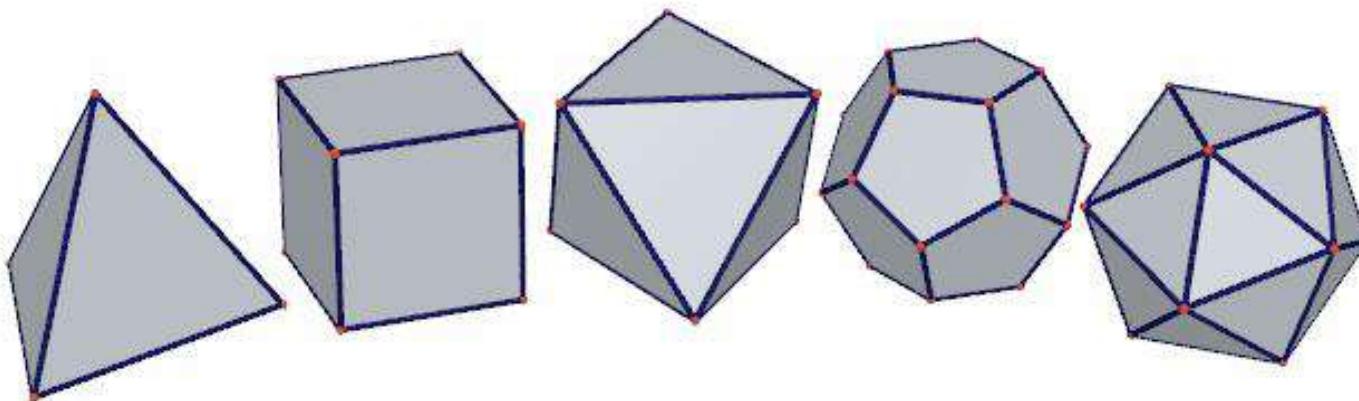
[4,4,4] propellane



# Gabbie Molecolari

## Solo gruppi C-H

### I cinque Solidi Platonici



**Tetraedro**  
**Fuoco**

**Cubo**  
**Terra**

**Ottaedro**  
**Aria**

**Dodecaedro**  
**Etere**

**Icosaedro**  
**Acqua**

Negli anni molti chimici si sono cimentati nella sintesi di molecole aventi la struttura dei cinque corpi Platonici  $(CH)_n$ . Queste molecole appartengono alla famiglia degli:

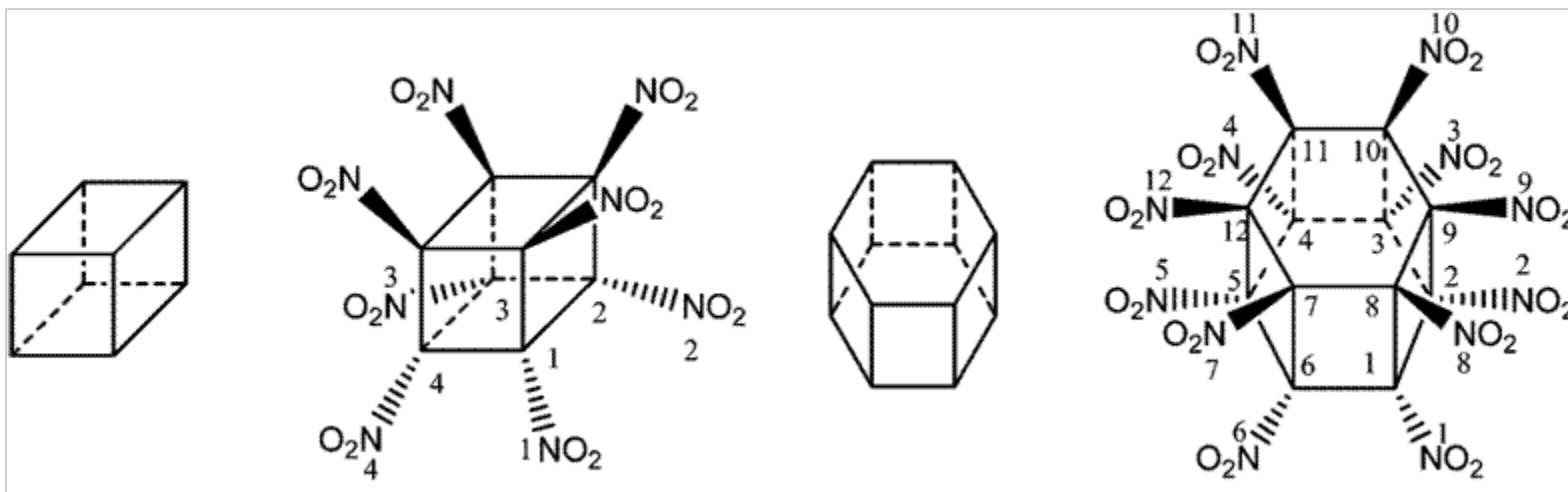
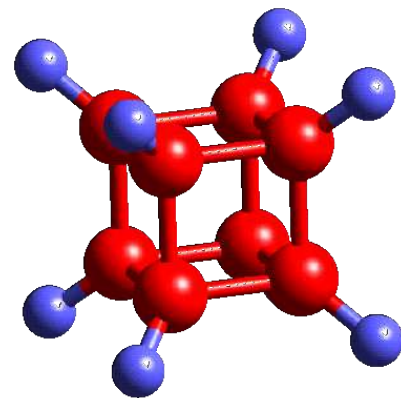
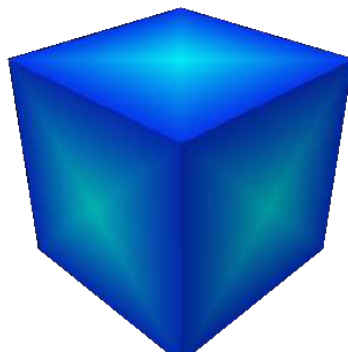
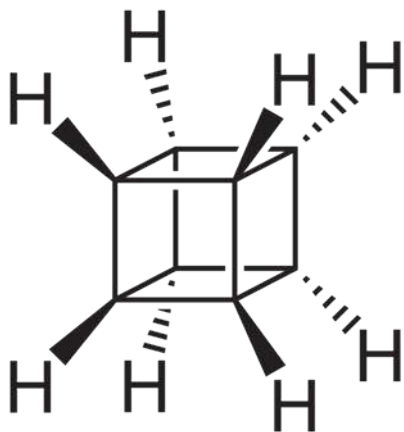


**Idrocarburi Platonici**



# Idrocarburi Platonici

Il **cubano** è una molecola con 8 atomi di carbonio ( $C_8H_8$ ), sono legati tra di loro a formare un **cubo**, da qui il nome cubano. È una delle strutture dei solidi Platonici.



Cubano

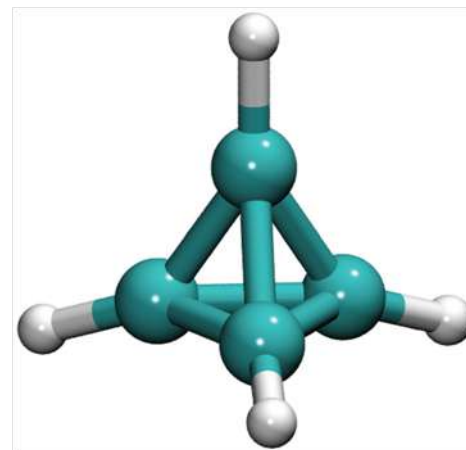
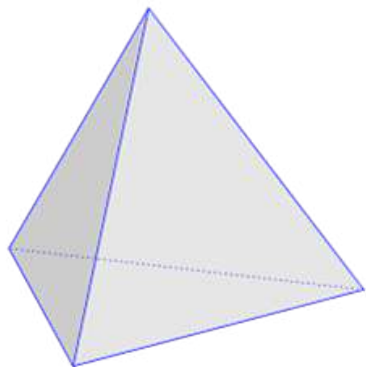
Ottanitrocubano

Esaprismano

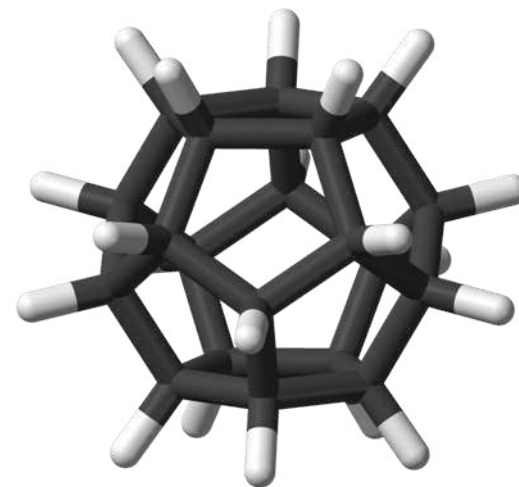
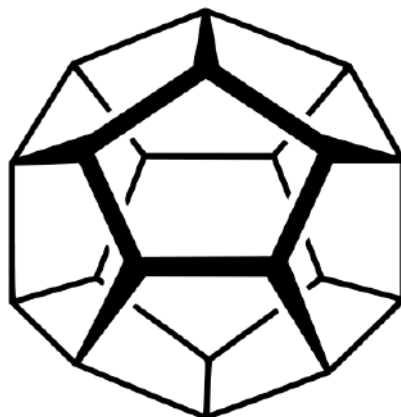
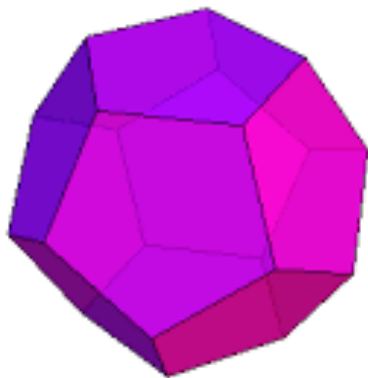
Dodecanitroesaprismano

# Idrocarburi Platonici

Il **tetraedrano** è una molecola con 4 atomi di carbonio ( $C_4H_4$ ), sono legati tra di loro, tramite legami  $\sigma$  a formare un **tetraedro**, da qui il suo nome. È una delle strutture dei solidi Platonici.

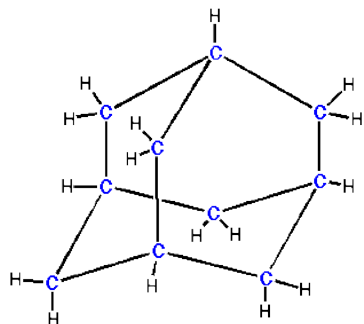


Il **dodecaedrano** è una molecola con 20 atomi di carbonio ( $C_{20}H_{20}$ ), sono legati tra di loro a formare un **dodecaedro**, da qui il suo nome. È una delle strutture più belle dei solidi Platonici.

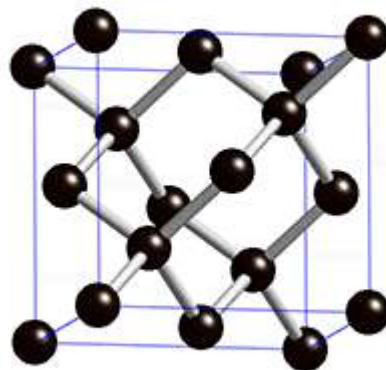


# Altre Molecole a Struttura rigida

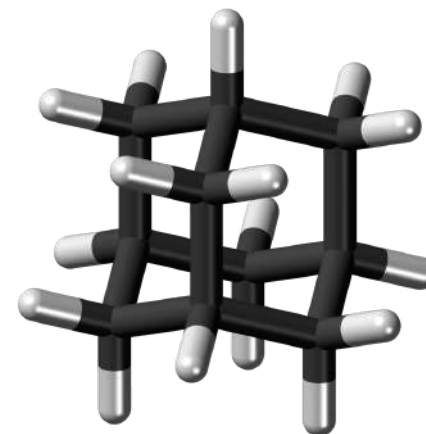
L' **adamantano** è una molecola con 10 atomi di carbonio ( $C_{10}H_{14}$ ), sono legati tra di loro a formare l'unità **strutturale del diamante**, da qui il nome adamantano.



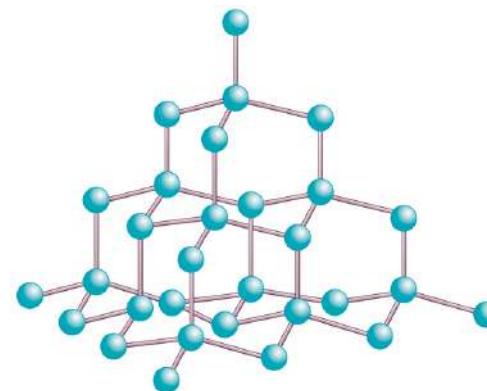
**adamantano**



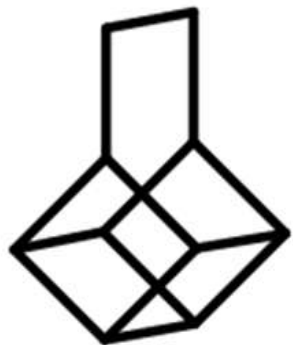
**Struttura diamante**



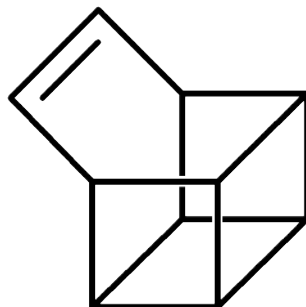
- L'adamantano presenta una forma altamente simmetrica, si possono tracciare **4 cicloesani** nella loro conformazione a sedia.
- Ha lo stesso scheletro di base del diamante.



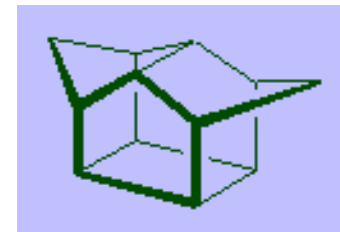
# Molecole a Struttura rigida



**Basketano**



**Basketene**



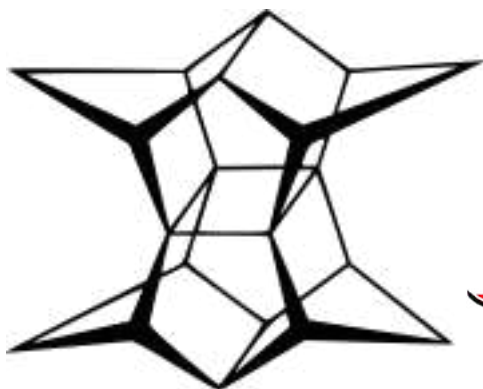
La forma di questa molecola richiama la gabbietta degli uccellini.

La forma di queste due molecole parenti richiama la struttura di un cestino, da qui i loro nomi.



**Housane**

I nomi di questi due idrocarburi sono ovviamente correlati alle forme che ricordano: quella di una casa e di una chiesa di campagna.



**Pagodane**



Questo idrocarburo ( $C_{20}H_{20}$ ) a causa della sua forma ricorda due pagode unite per la base.



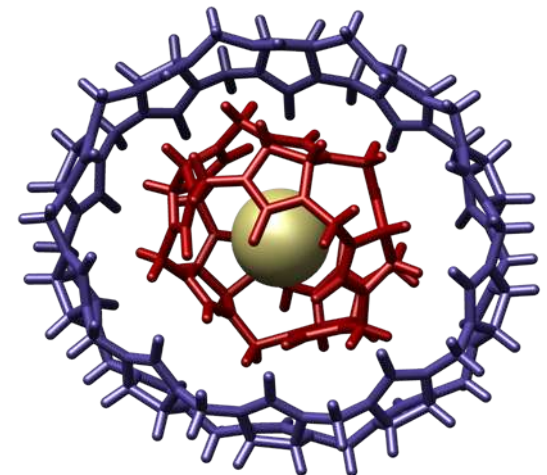
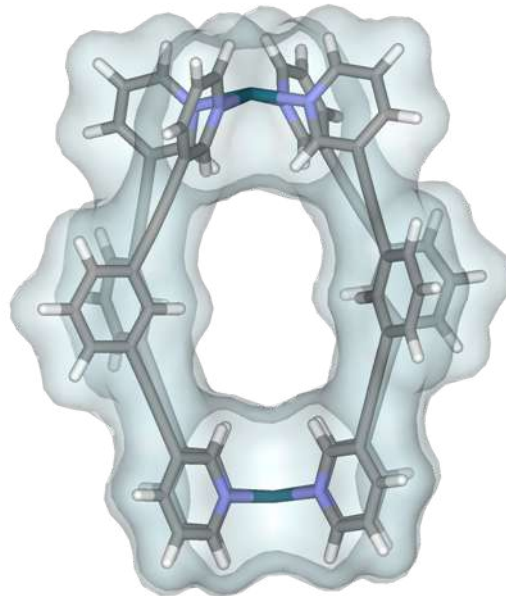
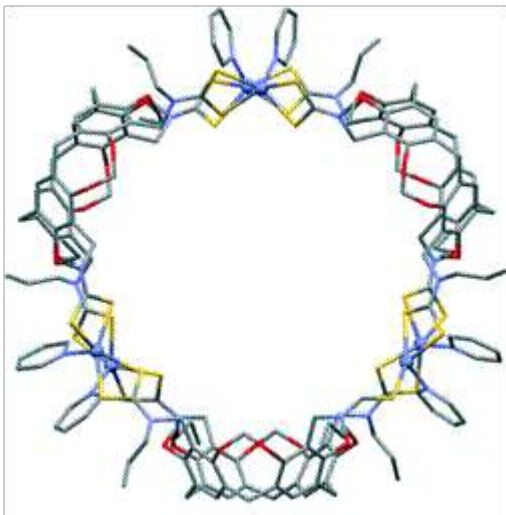
**Churchane**





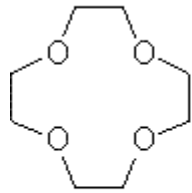
# I Cavitandi

I **cavitandi** sono molecole in cui gli atomi sono legati tra di loro a formare delle strutture tali che la molecola presenta una cavità. Questa cavità è sempre presente sia che la molecola sia in fase gassosa, liquida o solida, o in soluzione. All'interno di questo spazio possono essere ospitate altre molecole o ioni (**formazione di sistemi supramolecolari**).

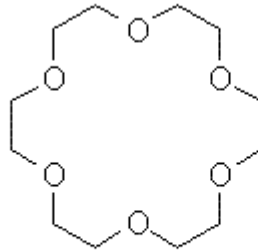


# Cavitandi: gli Eteri Corona (Crown Ethers)

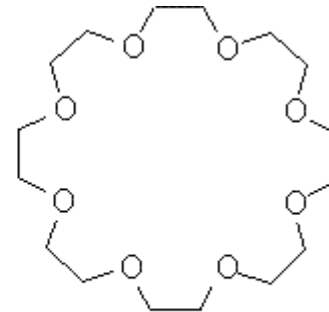
Gli **eteri corona** sono degli eteri macrociclici in cui gli atomi sono legati tra di loro a formare una struttura ciclica che assomiglia ad una corona regale.



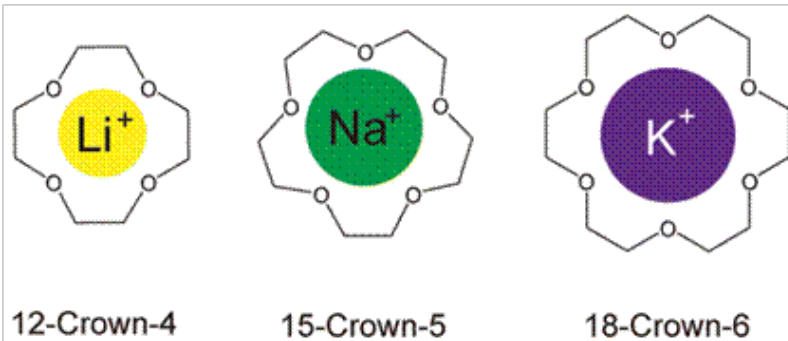
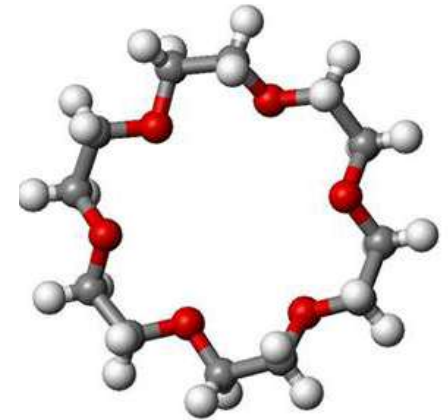
[12]-crown-4



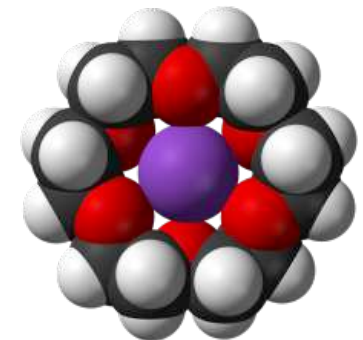
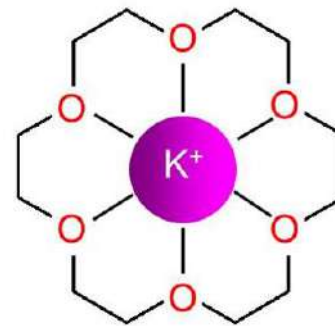
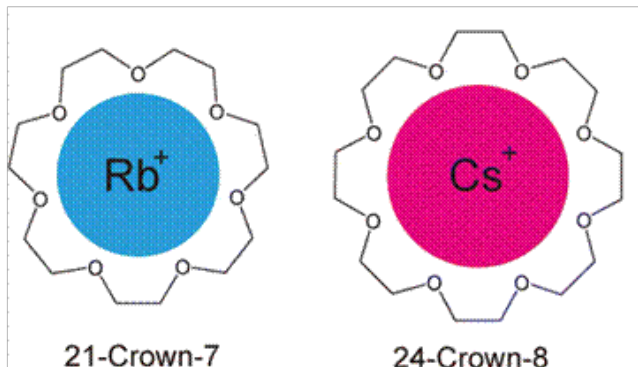
[18]-crown-6



[24]-crown-8

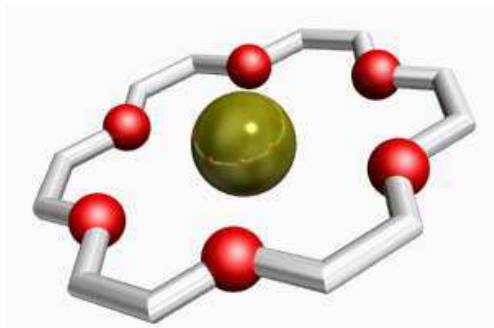


- La cavità è adatta per ospitare cationi dei metalli alcalini o alcalino terrosi.

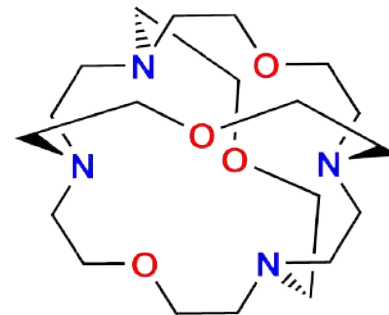
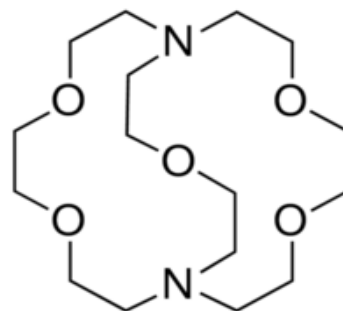


# Criptandi e Sepulcrati

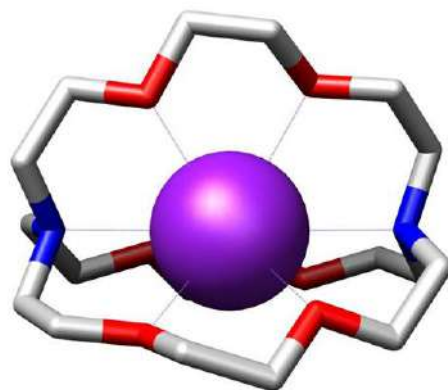
Anche queste due classi di composti appartengono ai cavitandi, rispetto agli eteri corno sono sistemi bi- o triciclici.



Etere corona



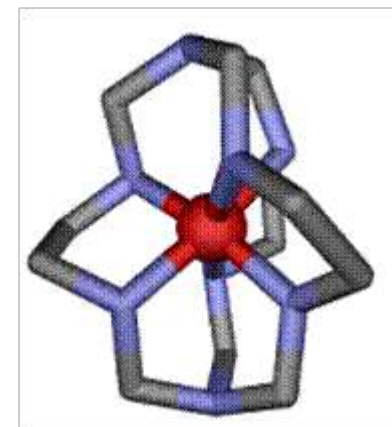
*cripta*



Complesso [K<sup>+</sup>-criptando-2,2,2]



*sepulcro*



Sepulcrato

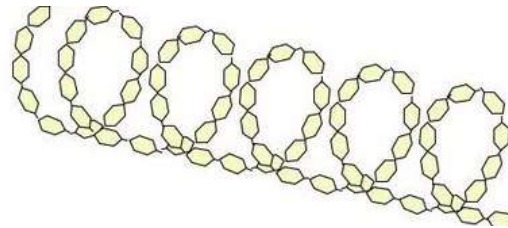
I nomi di queste molecole sono associati a luoghi da cui non si può più venir via (*cripta*, *sepulcro*). Sono molecole che per la loro struttura riescono ad associare tenacemente una specie ospite (catione metallico) in maniera tale che l'ospite ha poca possibilità di liberarsi.



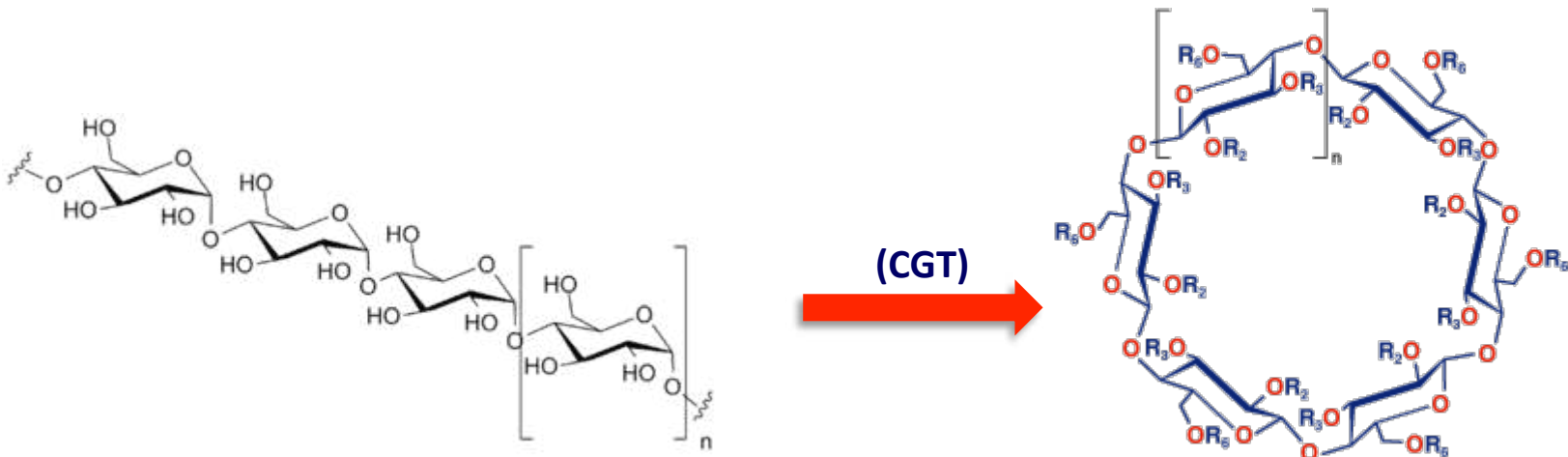
# Cavitandi: Le Ciclodestrine

❖ Le ciclodestrine (CDs) sono oligosaccaridi non-riducenti ciclici a forma tronco-conica, consistenti di 6 ( $\alpha$ -CD), 7 ( $\beta$ -CD) o 8 ( $\gamma$ -CD) unità D-(+) glucopiranosiche legate tramite legami glucosidici  $\alpha$ -1,4.

- ✓ Presentano la cavità idrofobica e la superficie esterna idrofila.
- ✓ Oggi le CDs sono prodotte, in grande quantità, per degradazione enzimatica dell'amido per opera di differenti *ciclodestrina glicosil transferasi (CGTase)* ottenute da diversi microorganismi.

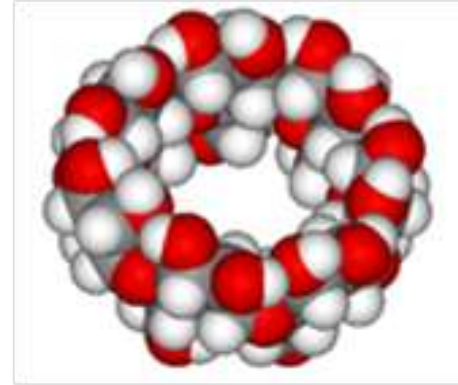
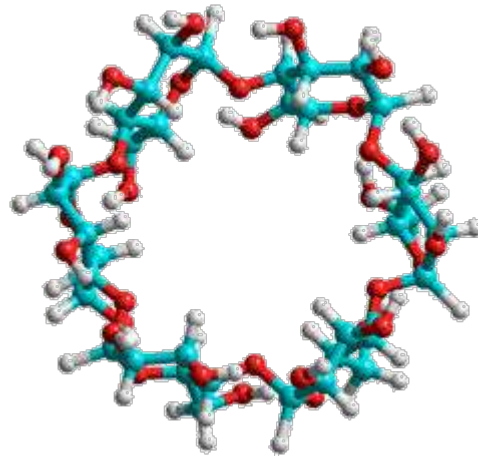
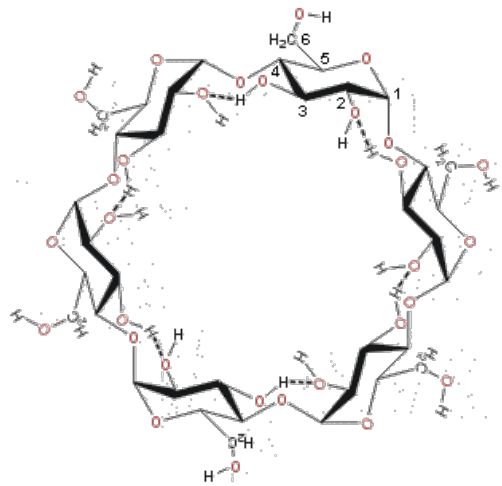


L'enzima ciclodestrina glicosil transferasi (CGT) agisce sulla catena lineare polisaccaridica dell'amido scindendo il legame glucosidico e ricostituendolo formando oligomeri ciclici:

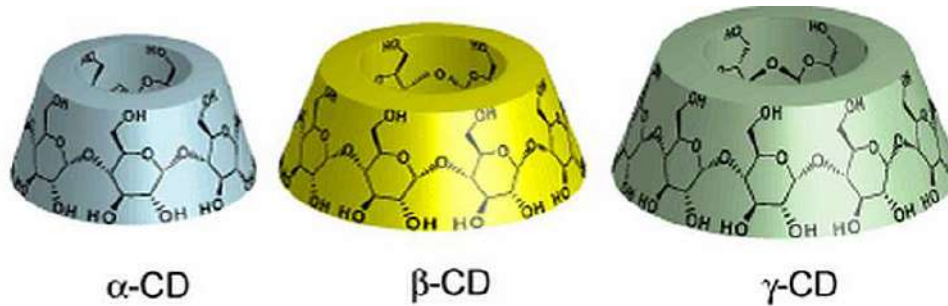




# Le Ciclodestrine



Forma tronco conica

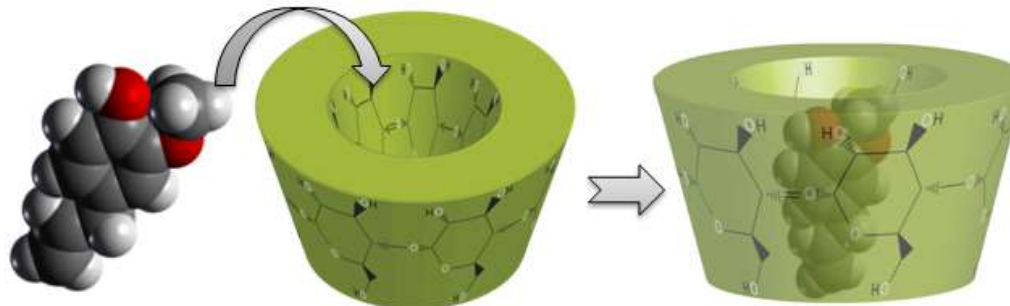


$\alpha$ -CD

$\beta$ -CD

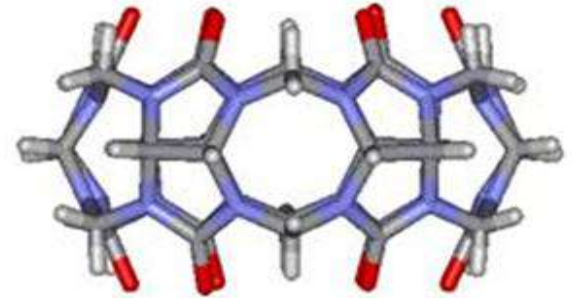
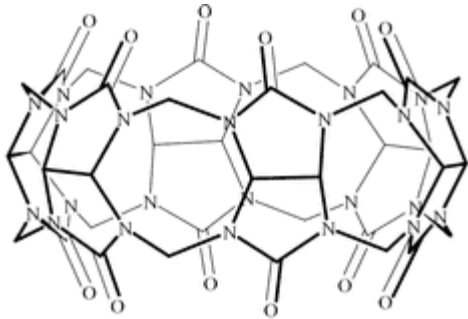
$\gamma$ -CD

- ❖ Per le loro caratteristiche le CDs permettono **“l’impacchettamento a livello molecolare”** di numerose molecole, tale processo trova molteplici applicazioni.

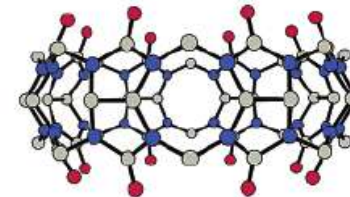
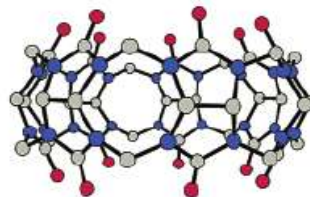
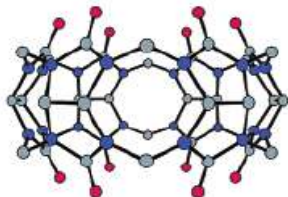
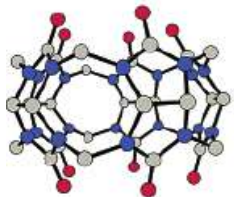
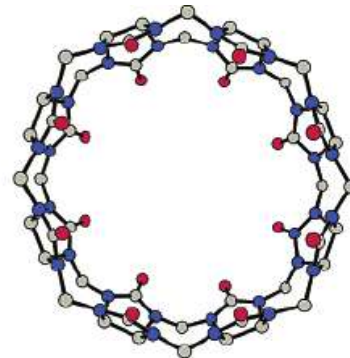
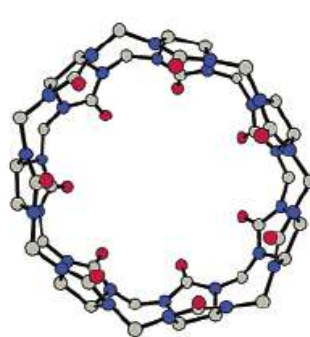
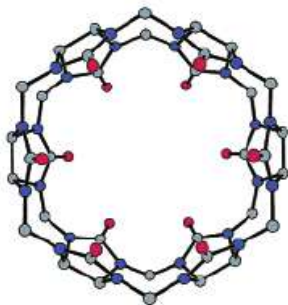
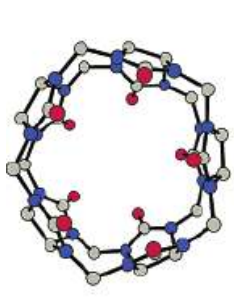


# Altre Molecole con una Cavità

**Cucurbiturili**, il loro nome deriva dalla loro forma che ricorda le cucurbitacee (Zucche)



Come tutti i cavitandi possono associare ospiti molecolari.

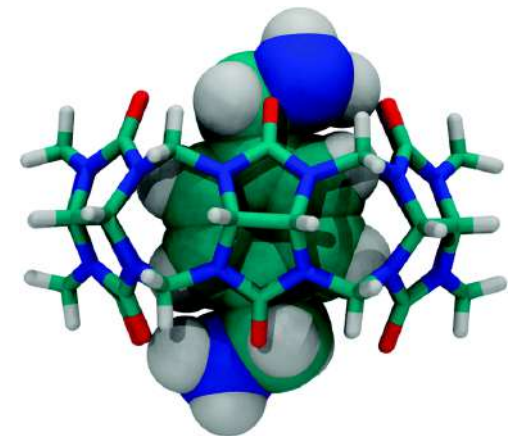


CB[5]

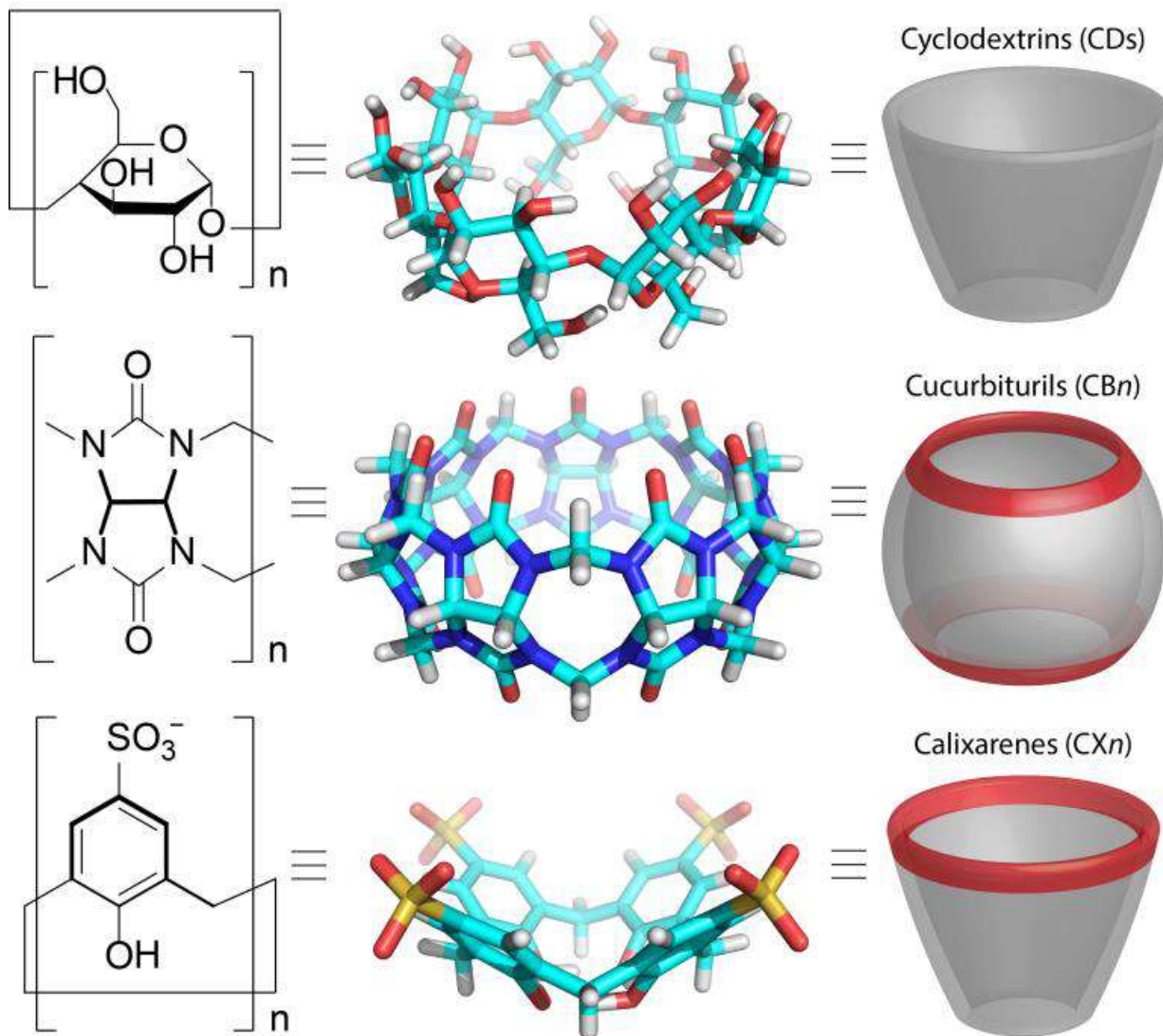
CB[6]

CB[7]

CB[8]

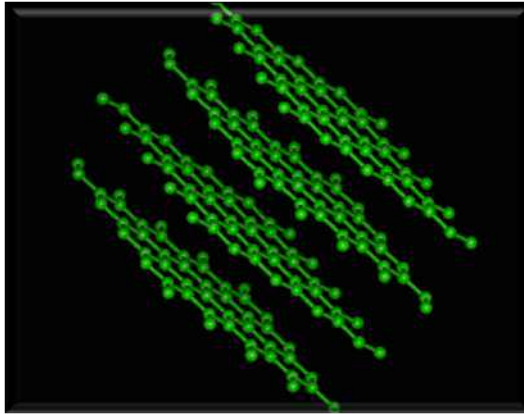


# Cavitandi a Confronto

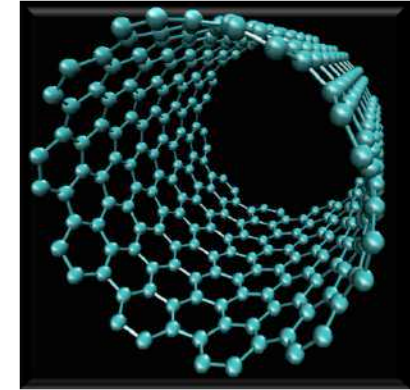




# Il Carbonio

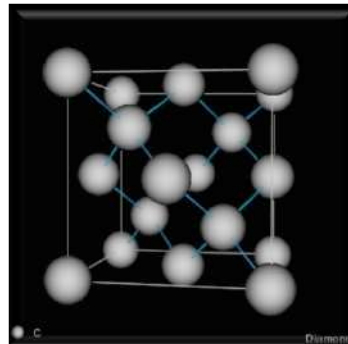


**Grafite**

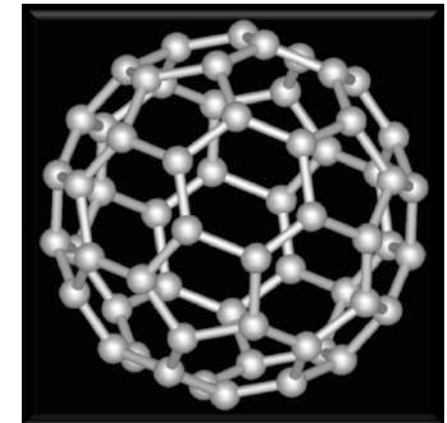


**Nanotubo**

**Materiali costituiti solo da atomi di Carbonio (forme allotropiche )**



**Diamante**



**Fullerene**

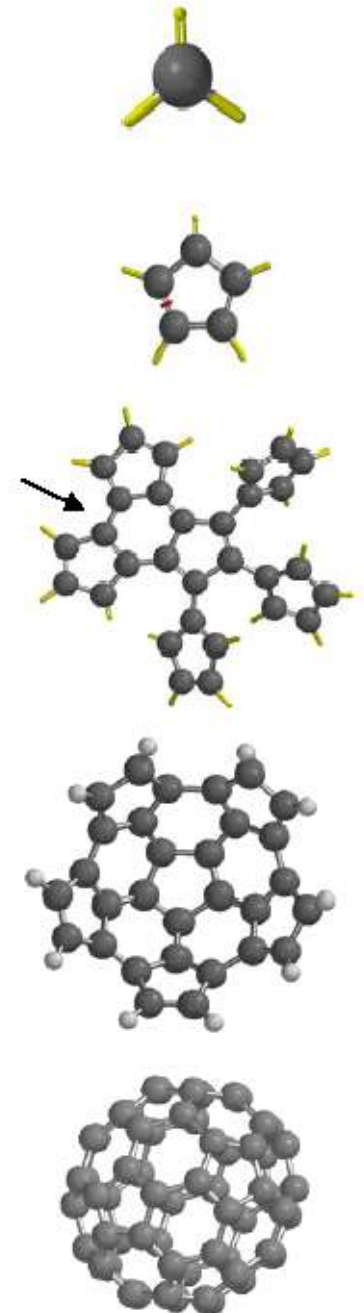
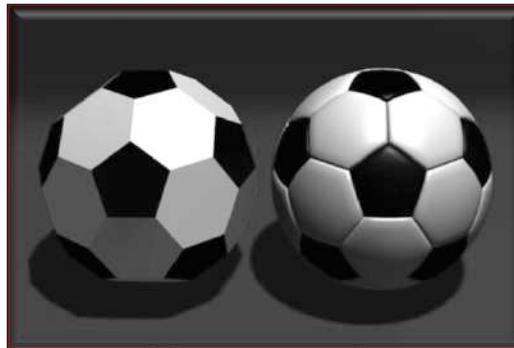
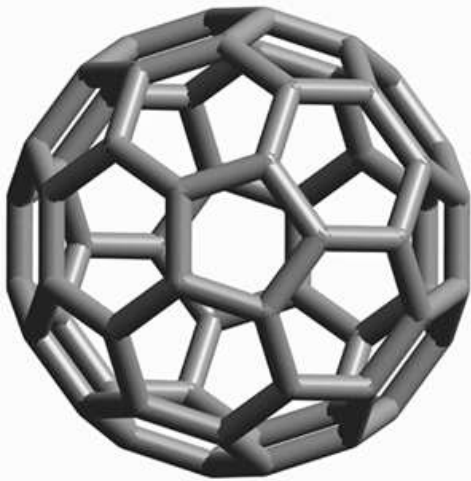


# Fullereni

Strutture covalenti di **forma sferica** fatte da atomi di Carbonio. Il Buckminsterfullerene, anche noto come C<sub>60</sub> o [60]fullerene è una molecola costituita da 60 atomi di C, che ricorda la forma di un pallone da calcio.

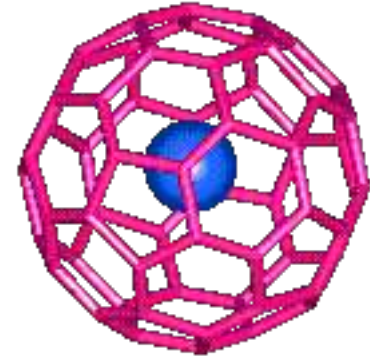
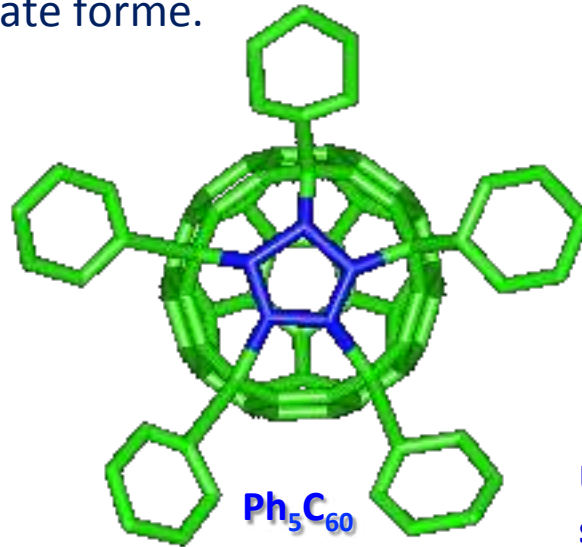
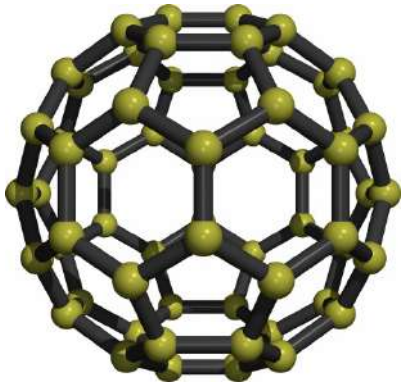
Il C<sub>60</sub> fu scoperto nel 1985. Nel 1996 premio Nobel in Chimica per la loro scoperta (Robert F. Curl, Harold W. Kroto, Richard E. Smalley).

I 60 atomi di carbonio sono  
arrangiati in forma di sfera  
costituita  
da **12** pentagoni e **20** esagoni

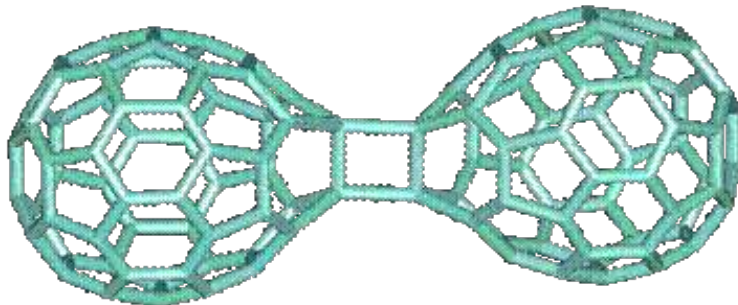


# Fullereni

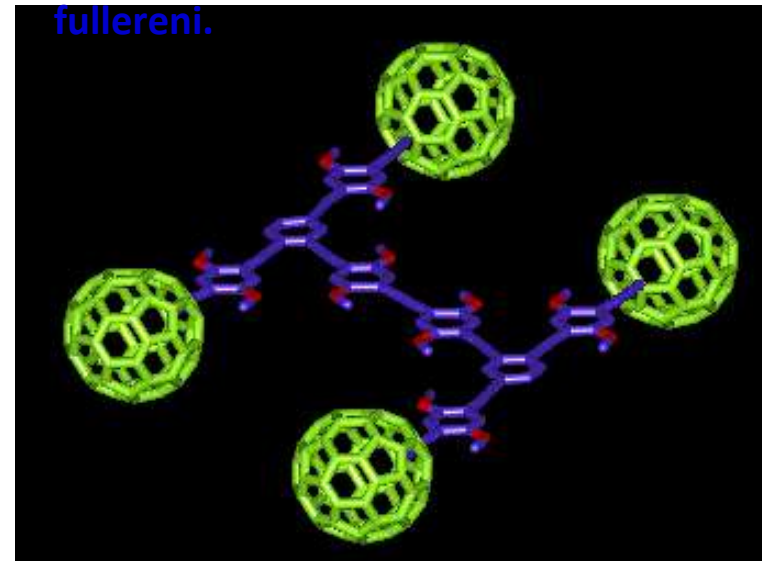
I fullereni possono essere usati per ingabbiare ioni o possono essere funzionalizzati in vario modo dando origine a svariate forme.



Un nanocar's "chassis" è costruito solidamente a base di anelli benzenici e di legami tripli carbonio-carbonio, le ruote sono quattro fullereni.

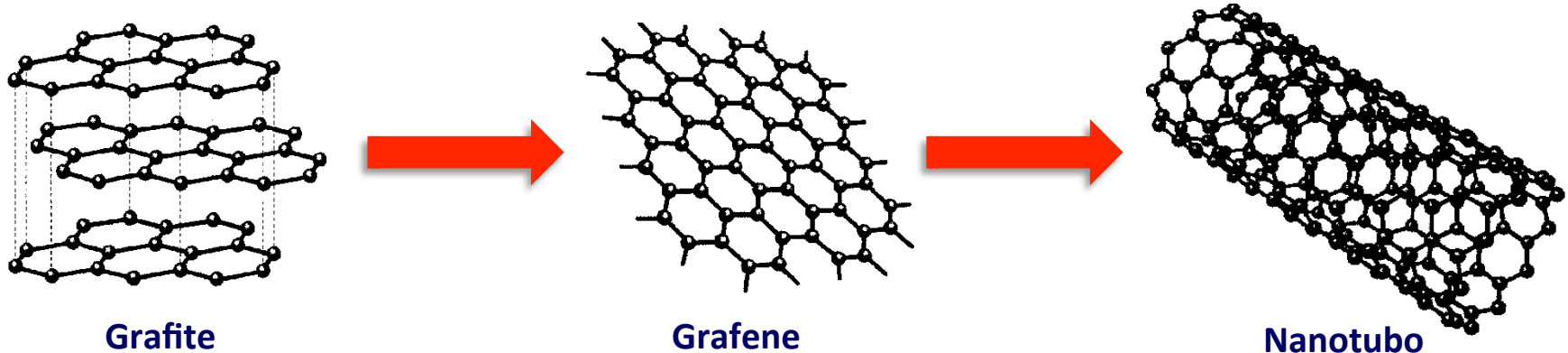


Bucky dumbbell

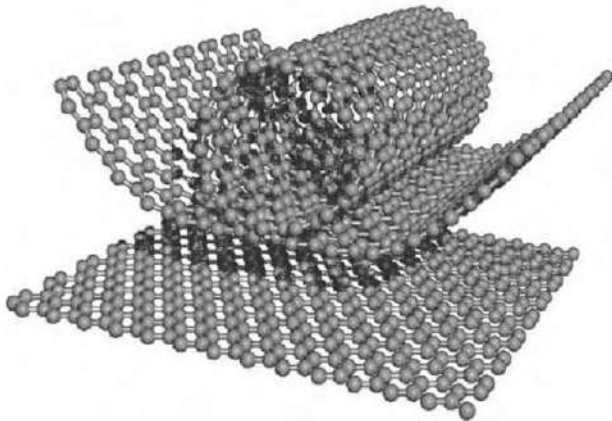


# Dalla Grafite ai Nanotubii

Possiamo idealmente immaginare i nanotubi di carbonio (CNT) come un foglio di grafene ripiegato su se stesso a formare un cilindro.



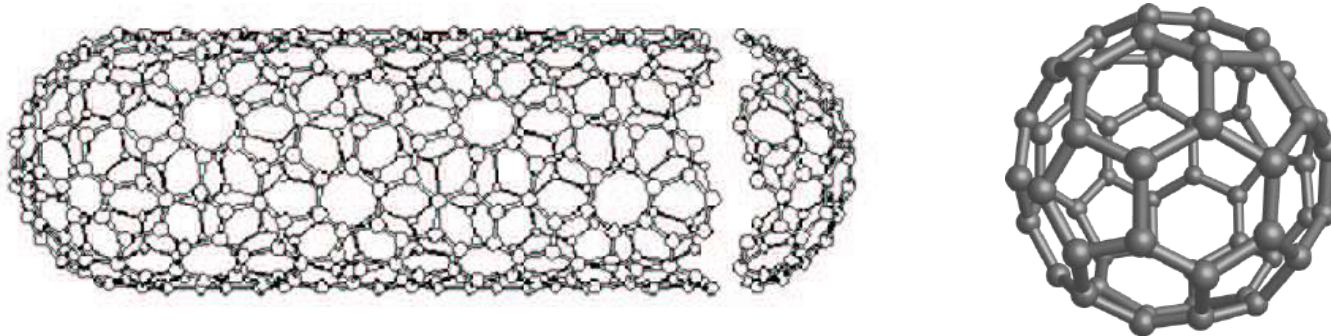
Questi cilindri presentano un rapporto **lunghezza/diametro** molto elevato (pochi nm di diametro per lunghezze superiori a 1 mm) (**1-D**)  
Sono 50.000 volte più sottili di un capello



Furono scoperti nel **1991** da  
Sumio Iijima – NEC Laboratory in Tsukuba (Giappone)  
tramite microscopia TEM ad alta risoluzione

# Nanotubi di Carbonio (CNTs)

Un CNT ideale può essere descritto come un tubo costituito solo da atomi di carbonio, formato da uno foglio di grafite arrotolato su se stesso a formare un cilindro, chiuso all'estremità da 2 calotte emisferiche.

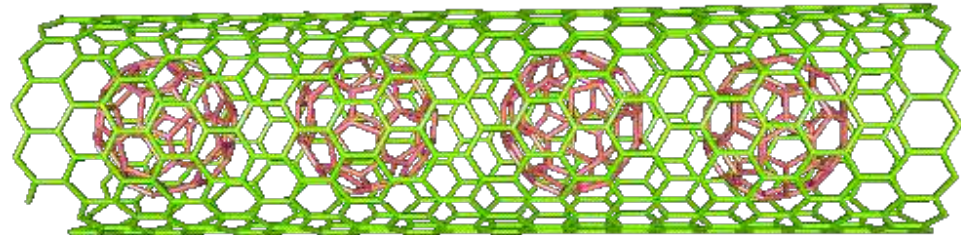


Il corpo del CNT è formato da sole **unità esagonali**, mentre le calotte terminali sono costituite da mezza molecola di fullerene, pertanto contengono sia strutture **esagonali** che **pentagonali**.

## Tipiche dimensioni:

Diametro  $\sim 0.7 \div 10$  nm

Rapporto Lunghezza/Volume  $\sim 10^4 \div 10^5$





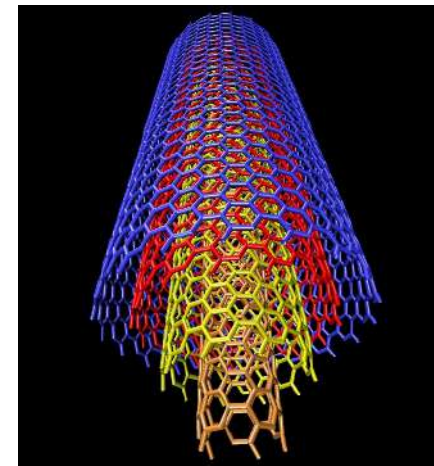
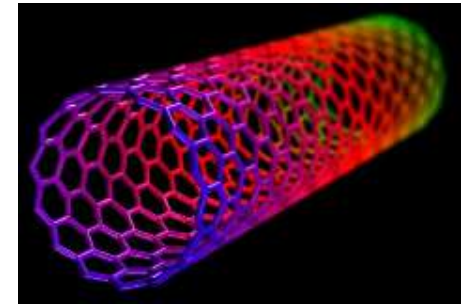
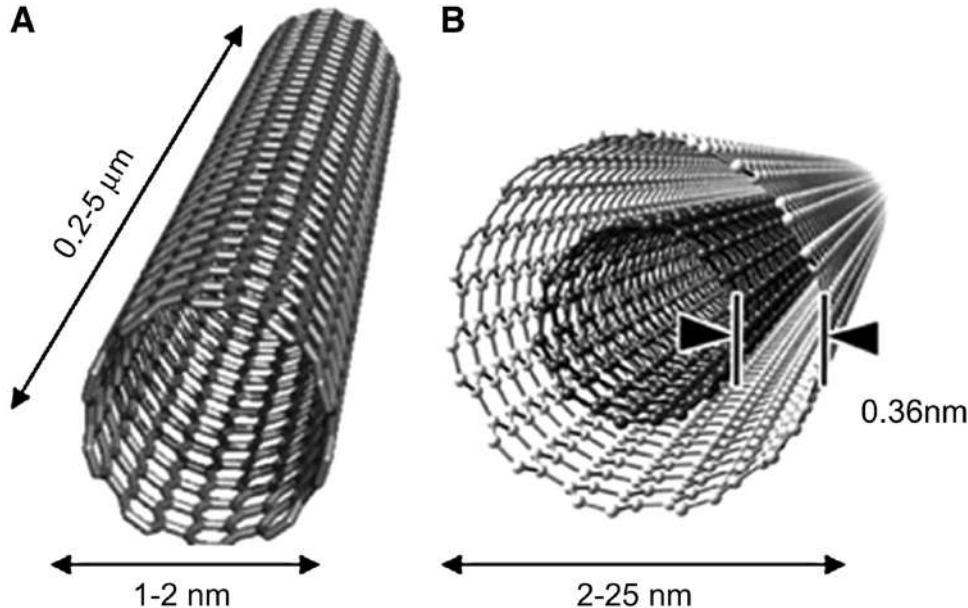
# Nanotubi di Carbonio (CNTs)

I **CNT** si dividono in nanotubi a singola parete (Single Wall Carbon Nanotubes; **SWCNT**) e nanotubi a pareti multiple (Multi Wall Carbon Nanotubes; **MWCNT**), strutture formate da diversi SWCNT concentrici di diverso diametro, che possono essere tra di loro interconnessi.



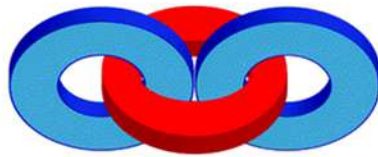
## Nanotubi

- A singola parete A
- A pareti multiple B

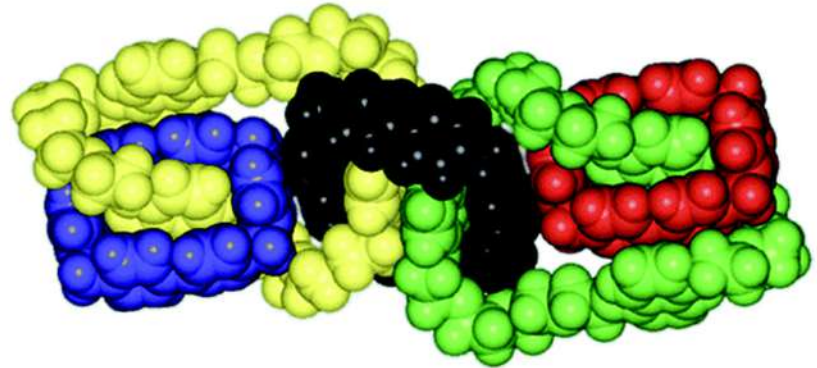
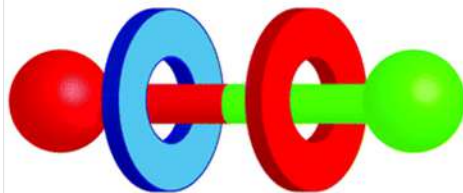


# Catene e Ingranaggi Molecolari: Catenani & Rotaxani

Catenano



Rotaxano



Premi Nobel per la Chimica 2016



Sauvage



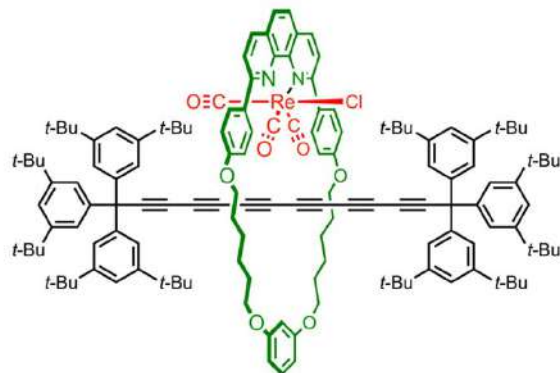
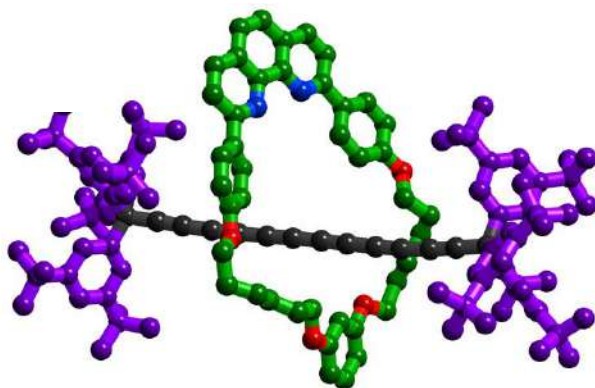
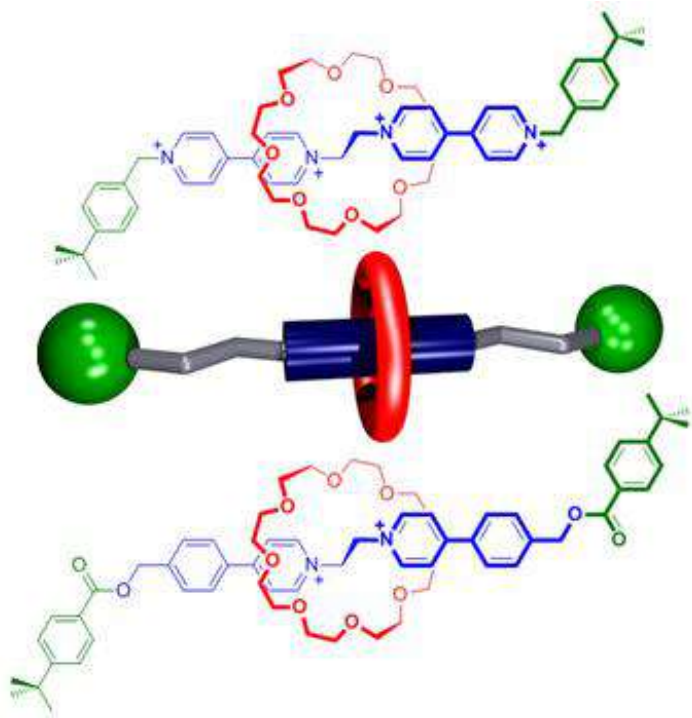
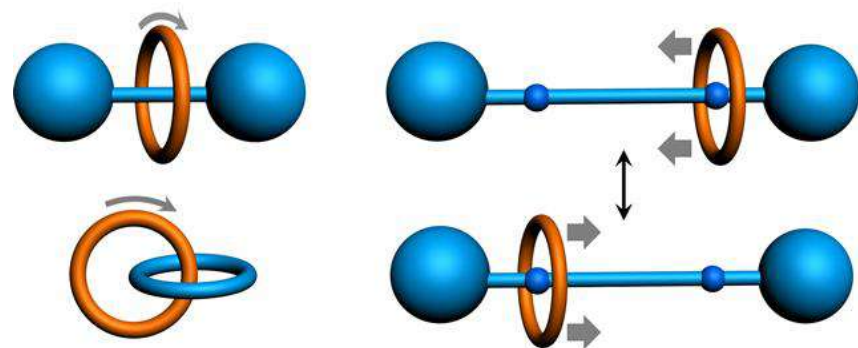
Stoddart



Feringa

# Molecular Machines

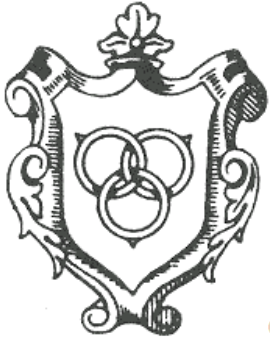
I movimenti molecolari possono essere indotti da variazioni di pH, di concentrazione di specie ioniche, da assorbimento di radiazioni (UV-Vis) o da processi redox.



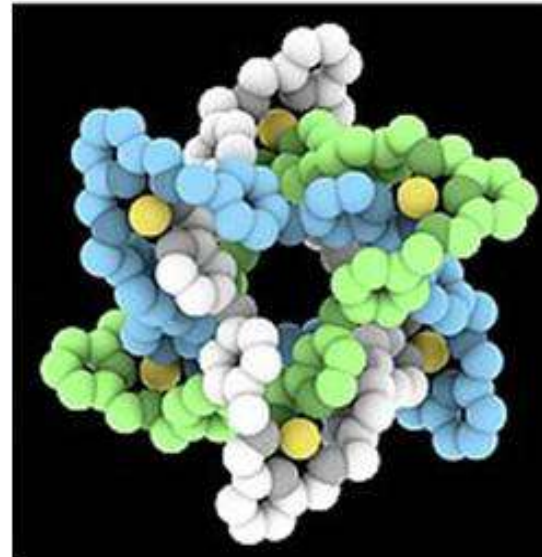
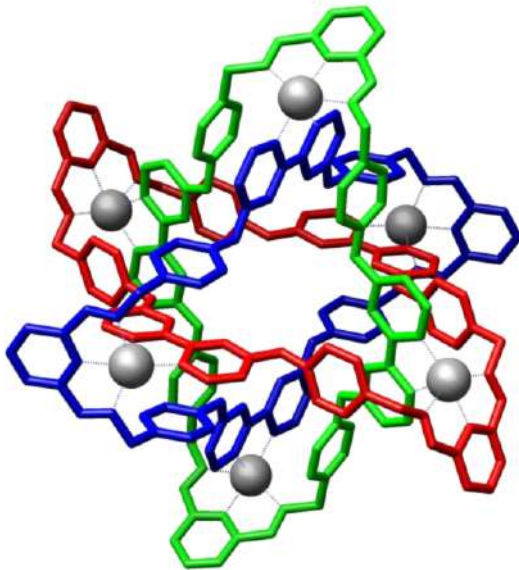
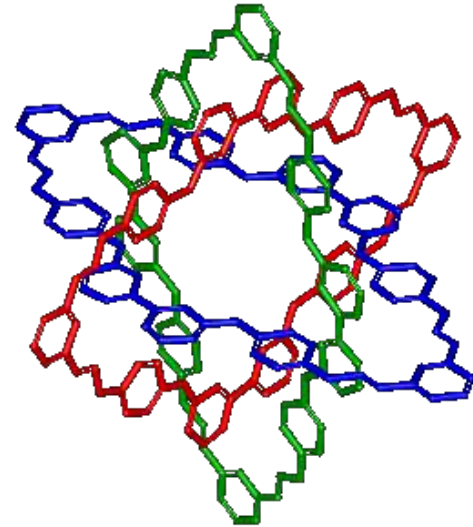
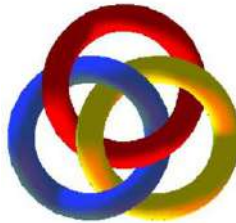


# Anelli Molecolari Borromiani

Molecole a forma di anelli Borromiani sono stati preparati dal prof. Stoddart nel 2004. Il nome deriva dal simbolo di una famiglia aristocratica dell'Italia medievale i Borromeo. Ha una proprietà interessante che i tre anelli sono collegati tra di loro, ma rompendo uno qualsiasi dei tre anelli, si ottiene due anelli non collegati.



**Nodo Borromiano**

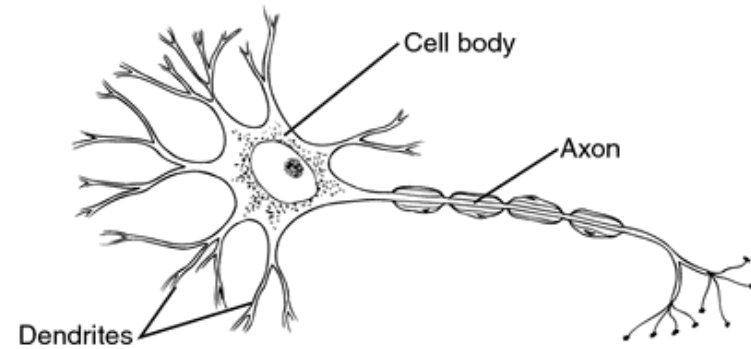




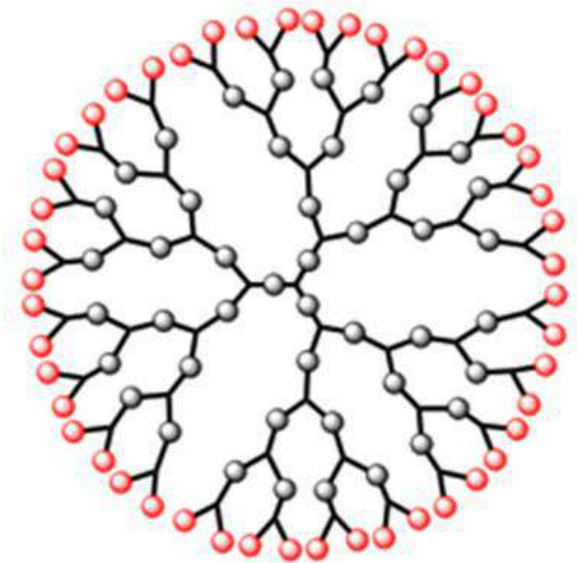
# Arborols & Dendrons



Sono strutture molecolari polimeriche che presentano una forma di crescita dendritica come si riscontra in molti esempi di materiali naturali.

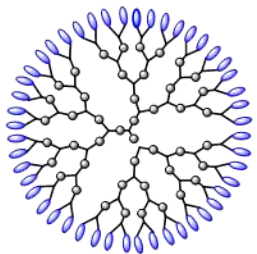
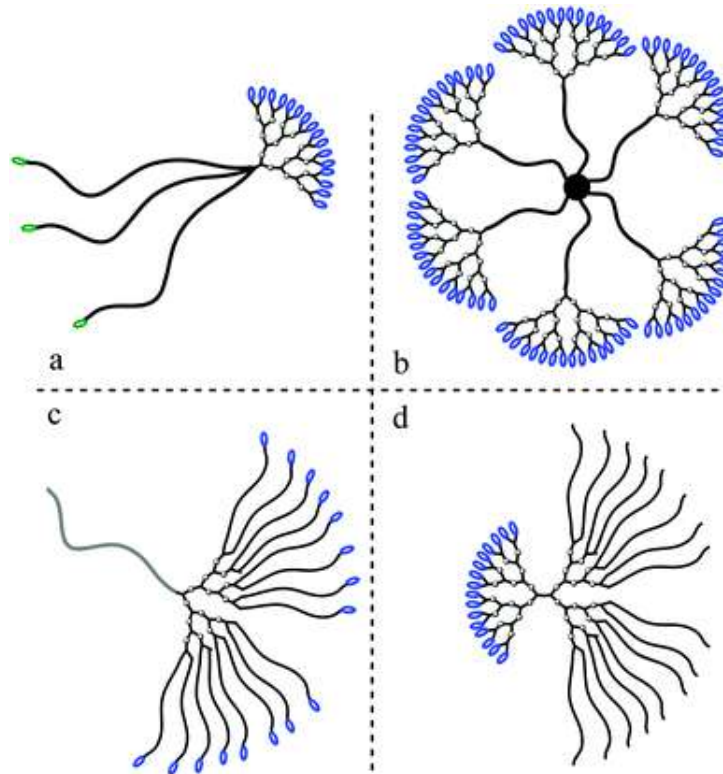


**Esempi di crescite dendrimeriche**

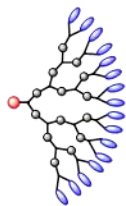


**Molecola a Struttura dendrimerica**

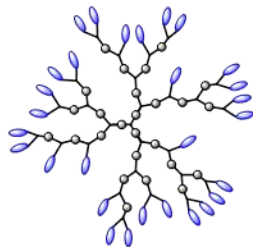
# Macromolecole Dendritiche



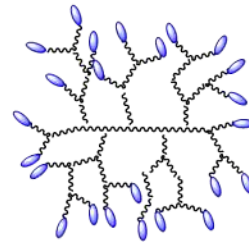
Dendrimers



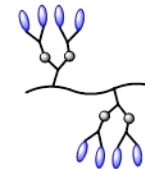
Dendrons



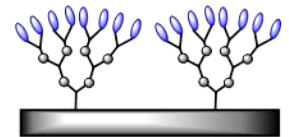
Hyperbranched  
Polymers



Dendrigraft



Dendritic-Linear  
Hybrids

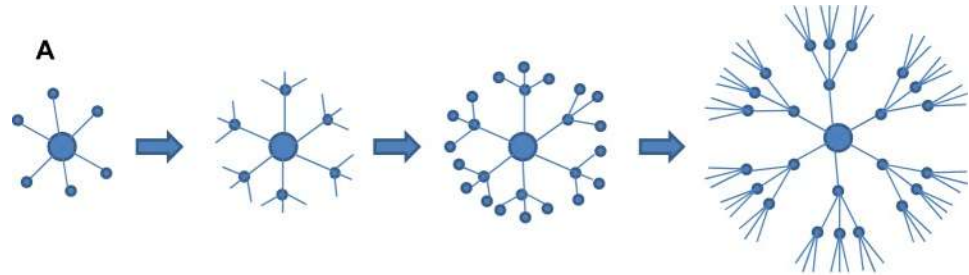


Dendritic-Surface  
Hybrids

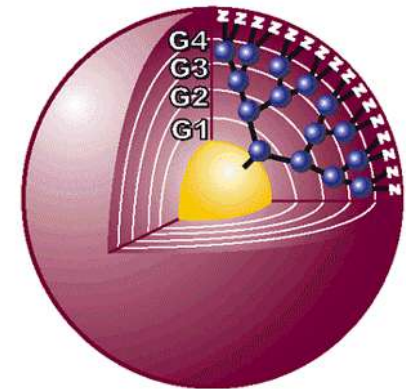
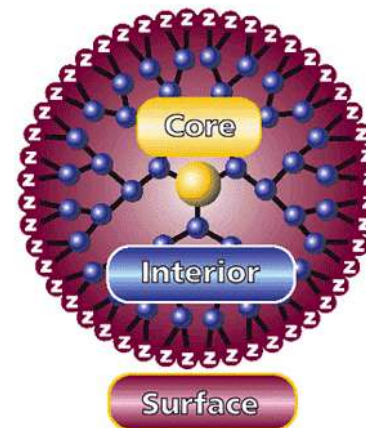
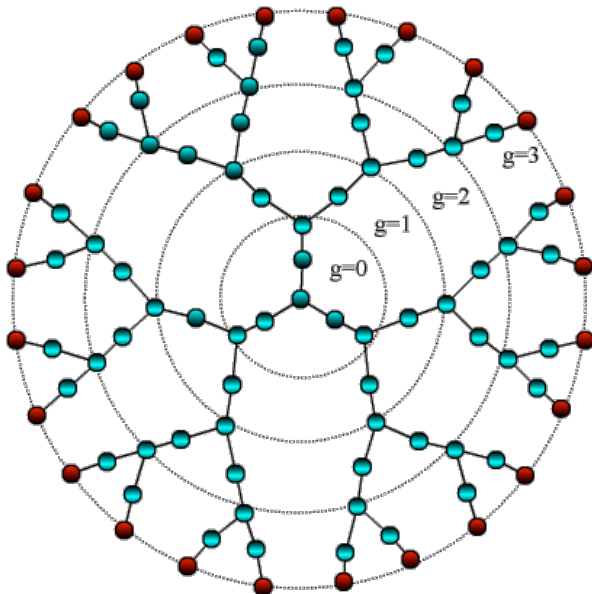
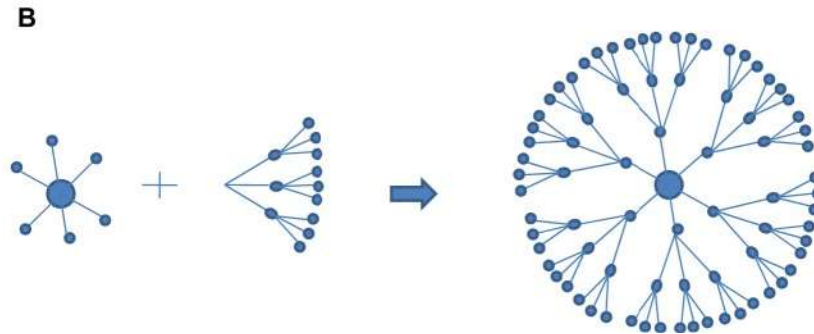
# Sintesi Dendrimeri

- Fondamentalmente ci sono due metodologie sintetiche

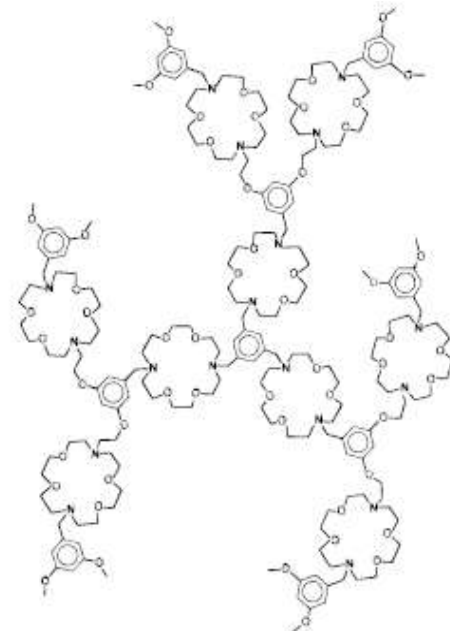
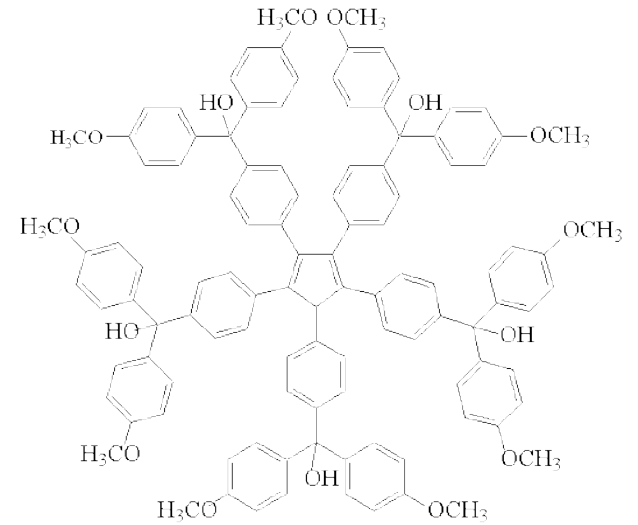
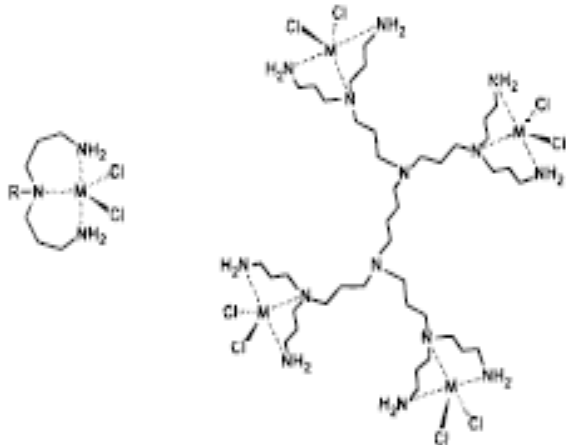
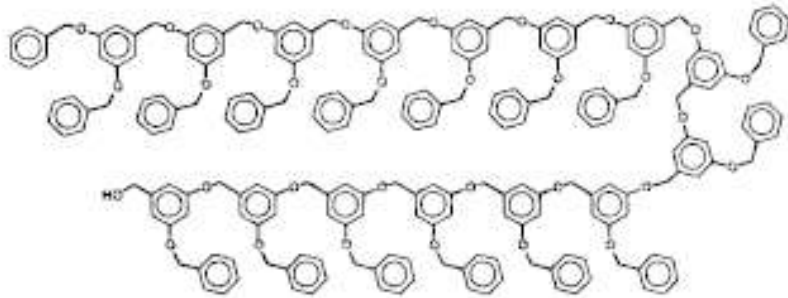
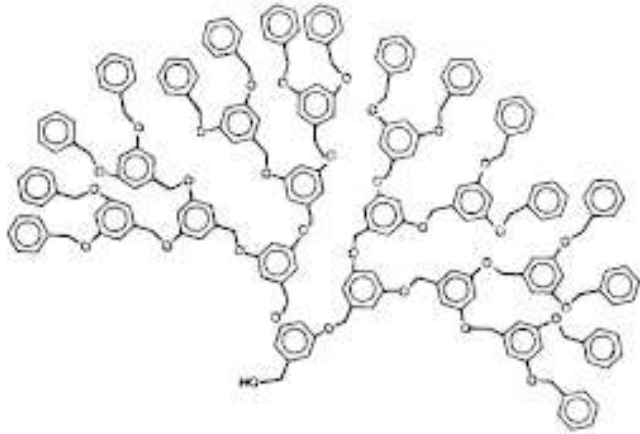
➤ Sintesi divergente (1978) A



➤ Sintesi convergente (1990) B

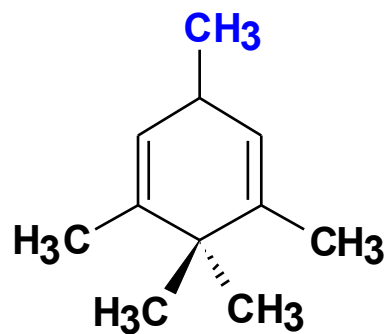


# Esempi di Molecole Dendrimeriche





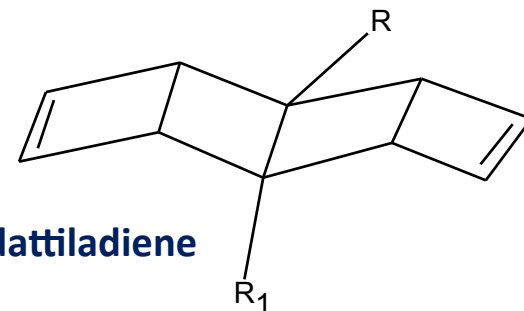
# Molecole Zoomorfe



**Pinguinone**

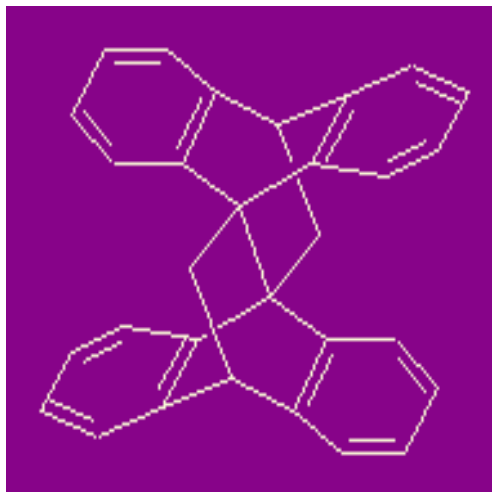


**Pterodattiladiene**



I gruppi R, R<sub>1</sub> sono variabili in maniera da dare differenti forme e dimensioni alla testa e alla coda.

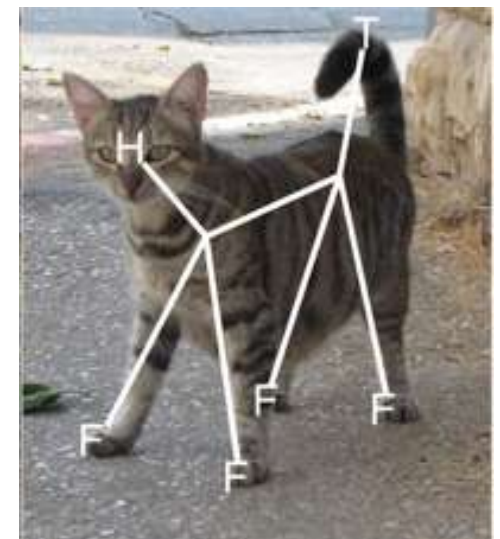
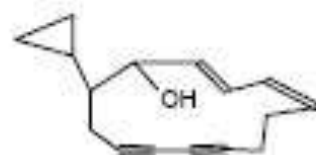
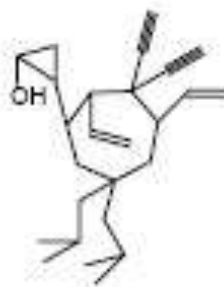
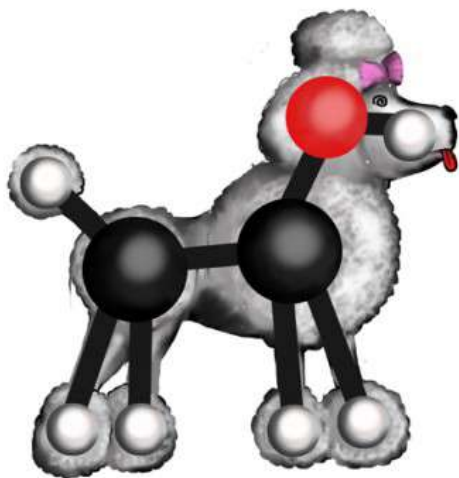
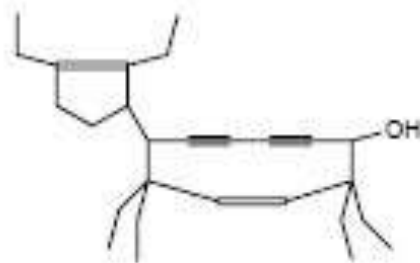
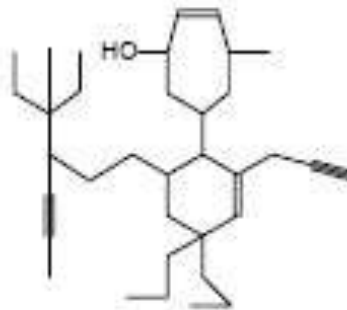
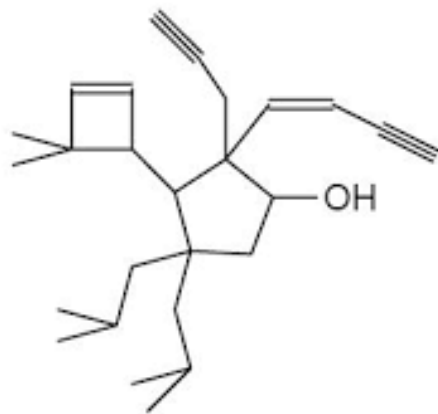
Questa molecola il 3,4,4,5-tetrametilcicloesa-2,5-dienone nella sua rappresentazione 2D assomiglia ad un pinguino.



**Lepidopterene o Biplanene**

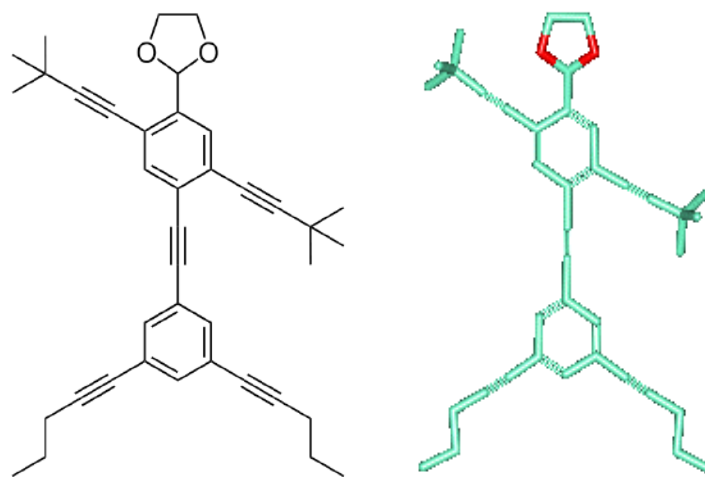
Sono famiglie di molecole che prendono nome dalla loro somiglianza con la forma dei lepidotteri o con quella dei biplani.

# Molecole Zoomorfe



# NanoPutians: Molecole Antropomorfe

Sono una serie di molecole organiche la cui struttura ricorda la forma di un essere umano, sintetizzate nel 2003 (James Tour della Rice University). Il termine **nano-puziani** deriva dagli abitanti del paese immaginario di Lilliput, i **Lillipuziani** (I Viaggi di Gulliver).

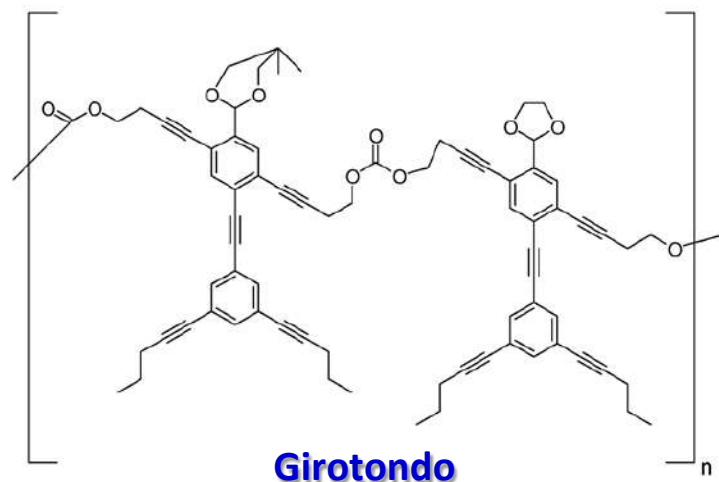
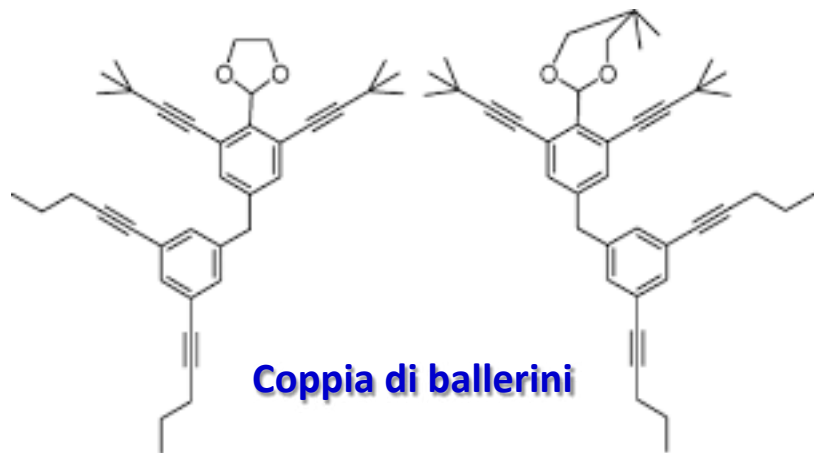
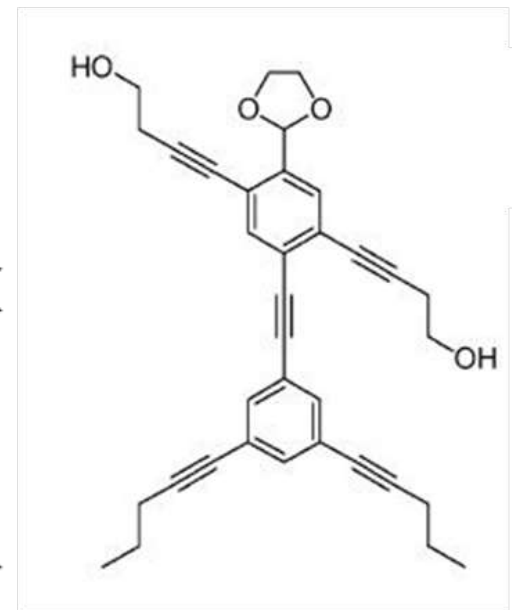
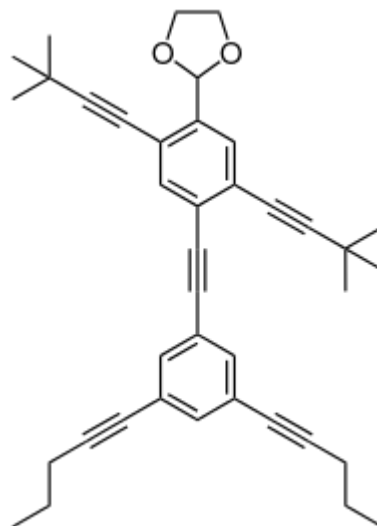
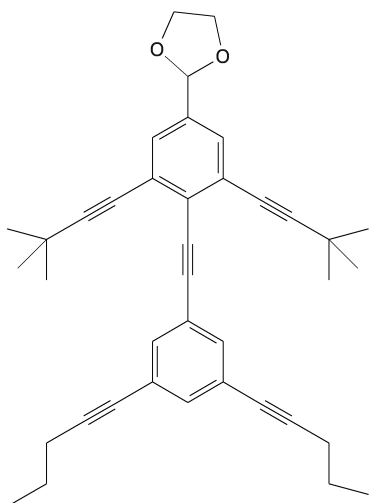


**Nano-kid**  
Blocco di base

Il corpo è costituito da due **anelli benzenici** collegati da uno spaziatore **alchinico**. Stesso spaziatore è utilizzato per costruire le braccia e le gambe, mentre due gruppi alchilici differenti costituiscono le mani (**tert-butile**) e i piedi (**n-propil**). Come testa è stato utilizzato un gruppo **1,3-diossolano**.

# NanoPuziani: Molecole Antropomorfe

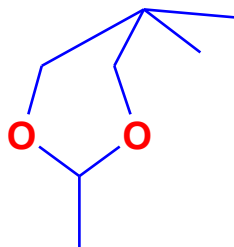
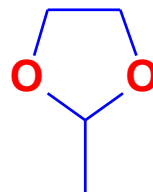
Combinando diversi residui e i punti di congiunzione si possono ottenere forme umanoidi variabili.



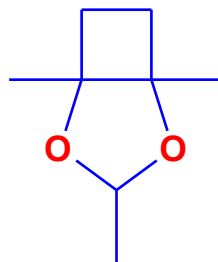


# NanoPuziani: Tante teste

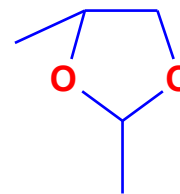
Modificando il residuo **1,3-diossolano** è possibile avere facce diverse del Nanoputian. Sotto sono riportate alcune strutture che ricordano (vedi nomi) diversi personaggi umani.



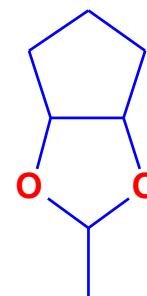
**NanoAthlete**



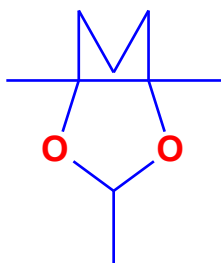
**NanoPilgrim**



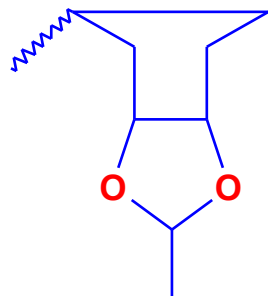
**NanoGreenBeret**



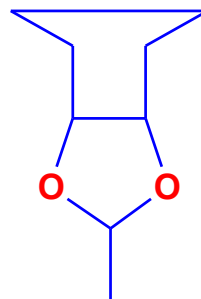
**NanoJester**



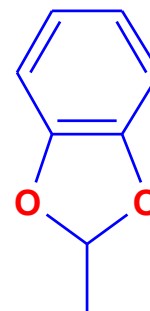
**NanoTexan**



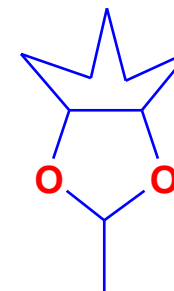
**NanoScholar**



**NanoBaker**

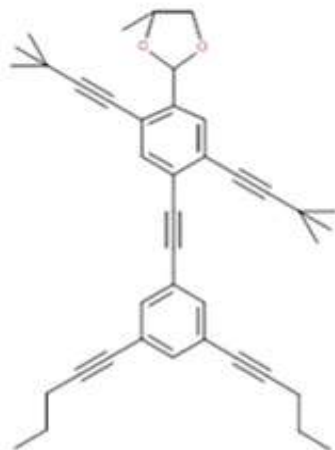


**NanoChef**

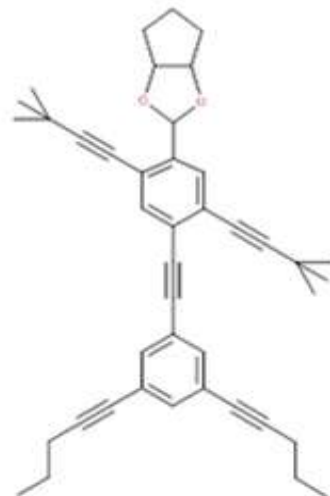


**NanoMonarch**

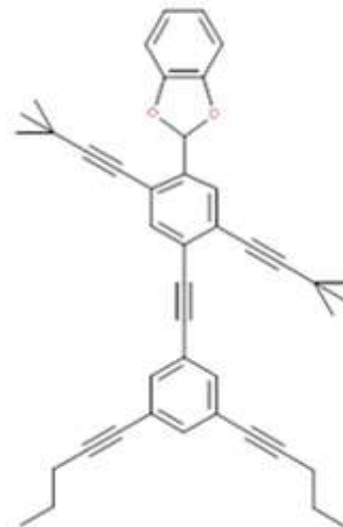
# Tante Teste per Personaggi Diversi



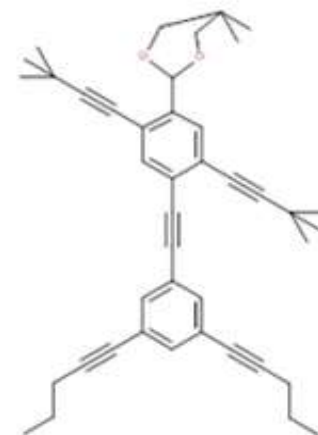
**NanoGreenBeret**



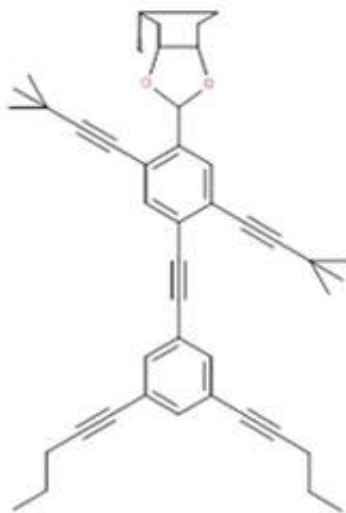
**NanoJester**



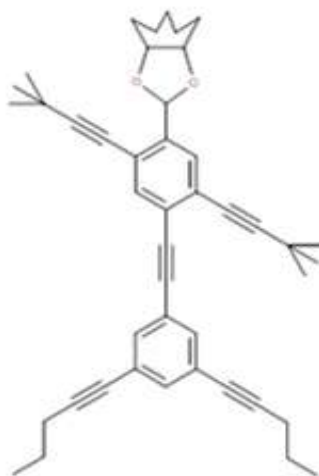
**NanoChef**



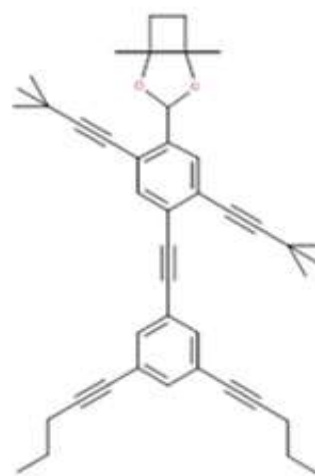
**NanoAthlete**



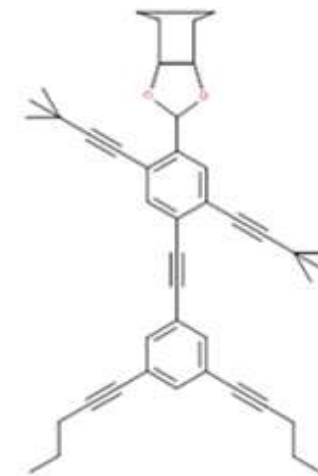
**NanoScholar**



**NanoMonarch**

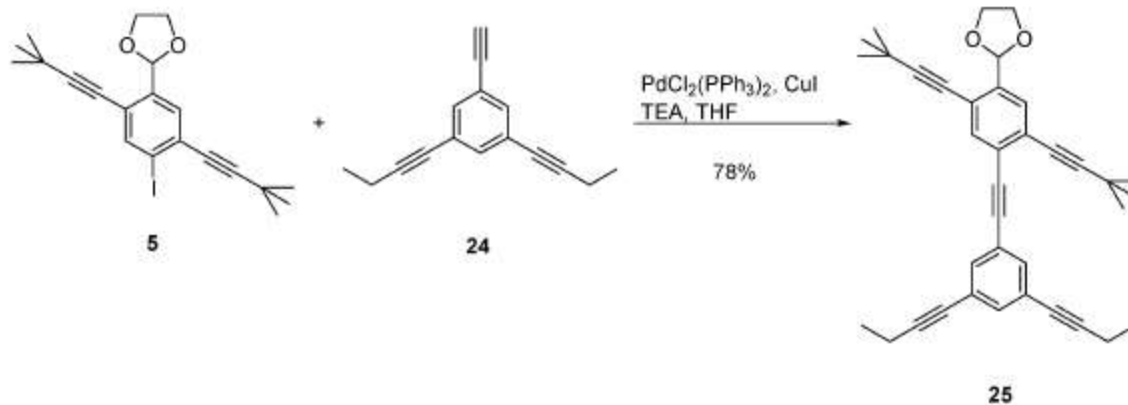
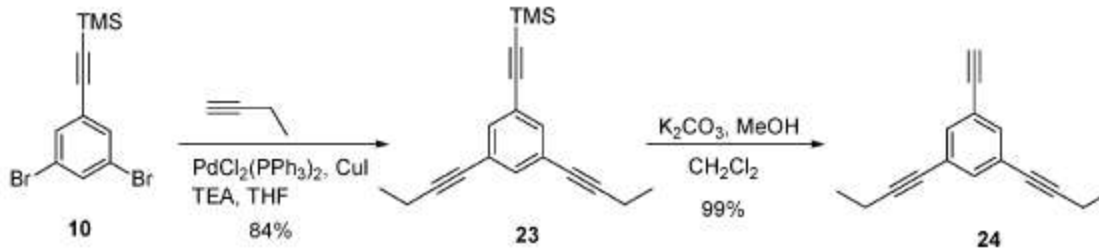
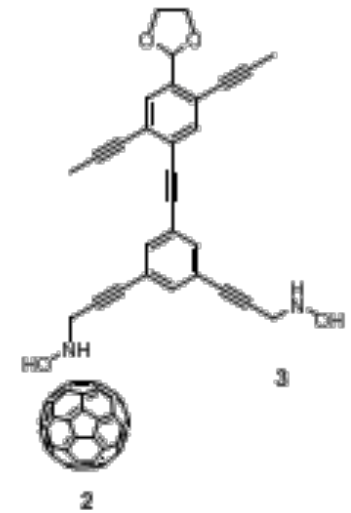
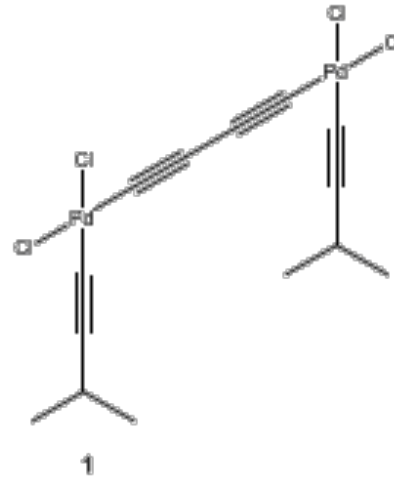
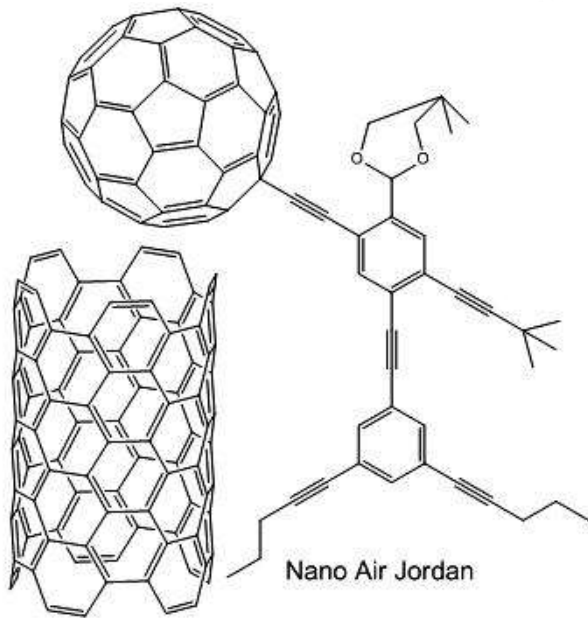


**NanoPilgrim**



**NanoBaker**

# NanoPuziani e Sport



# Fiori Molecolari

