Recettori per molecole neutre

Legami idrogeno

Effetto idrofobico

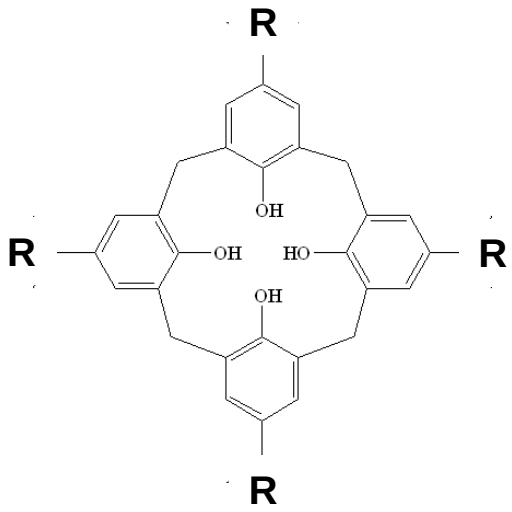
Interazioni CH-π

Interazioni π stacking

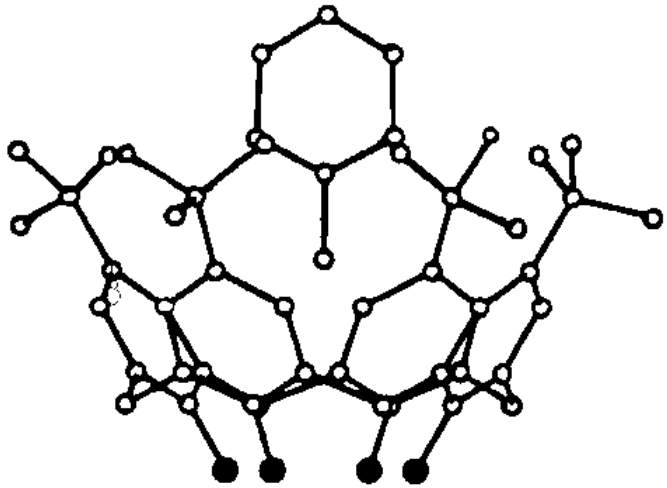
pre organizzazione

Recettori per molecole neutre

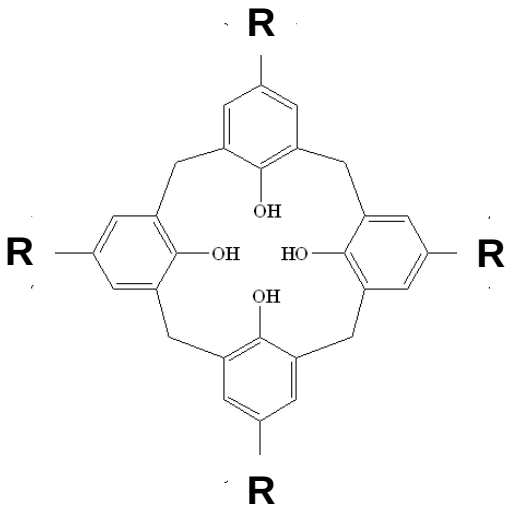
Interazioni CH-π pre organizzazione (cavità profonde e rigide)

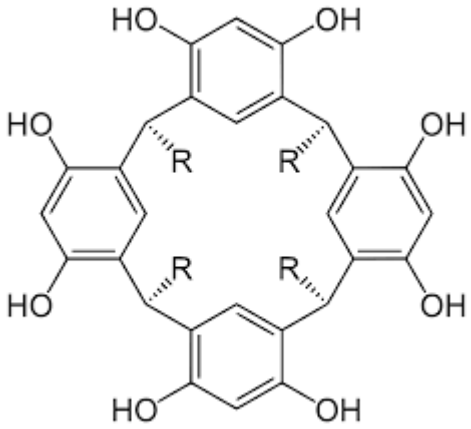


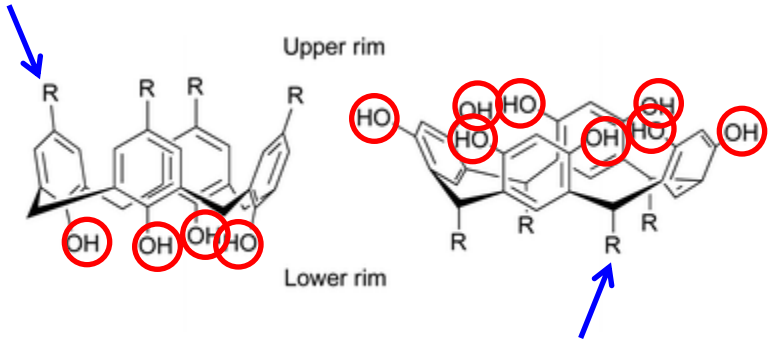
calix[4]arene



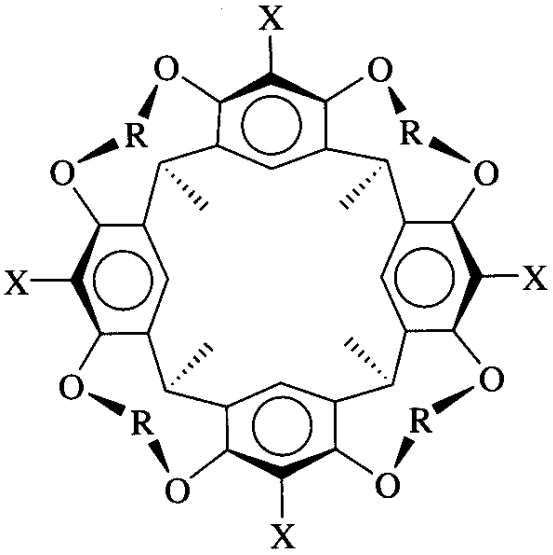
p-tert-Butylcalix[4]arene-toluene inclusion complex

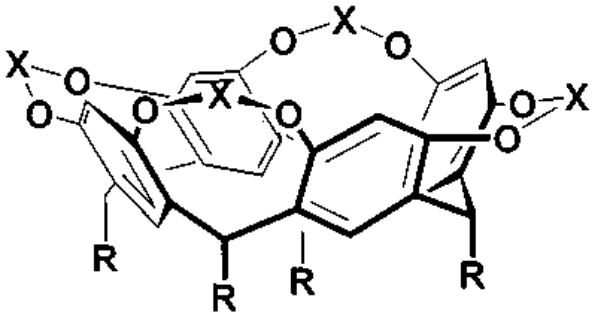

R
R
R
R
OH
OH
HO
OH


HO
OH
HO
OH
R
R
R
R
HO
OH
HO
OH


Upper rim
Lower rim
R
R
R
R
OH
OH
OH
HO
HO
OH
HO
OH
HO
OH
R
R
R
R

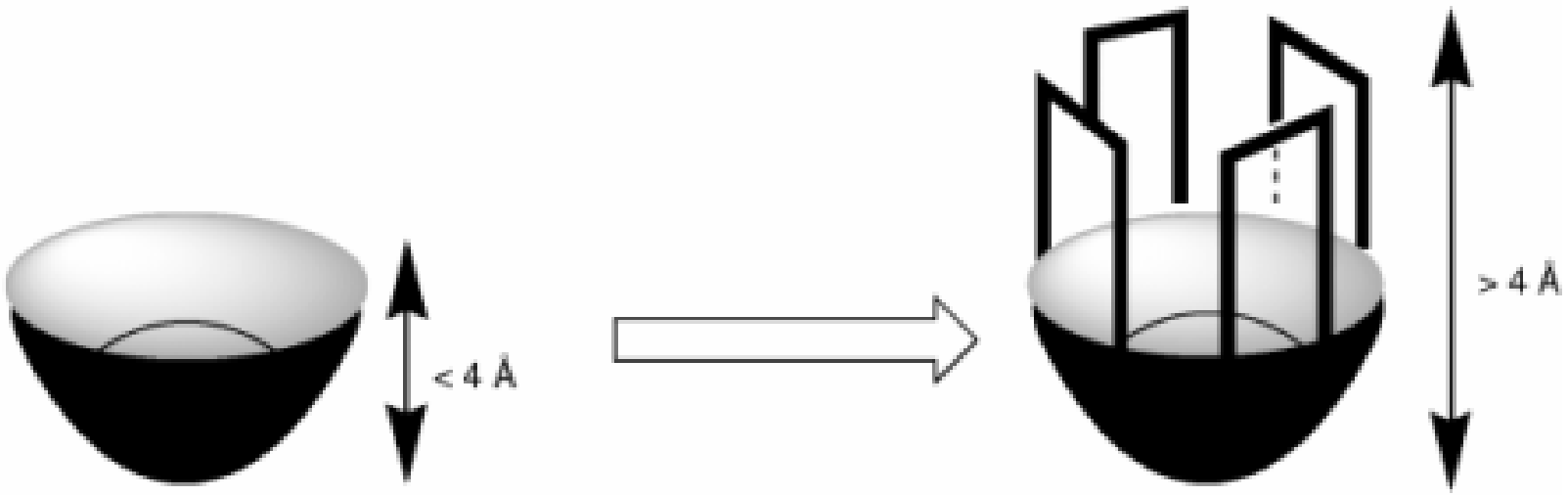
[4] resorcinarene



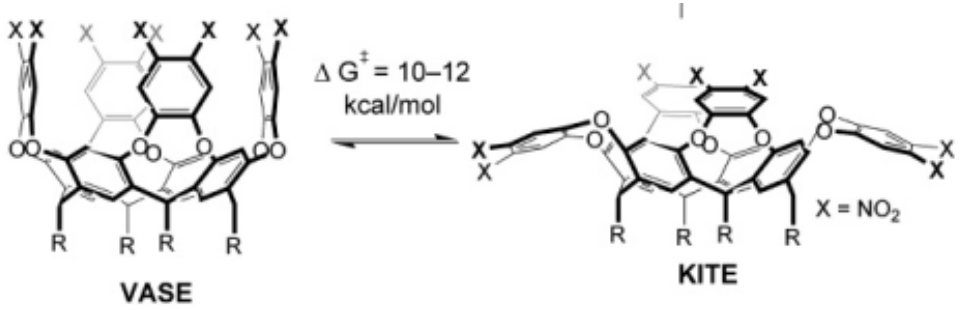


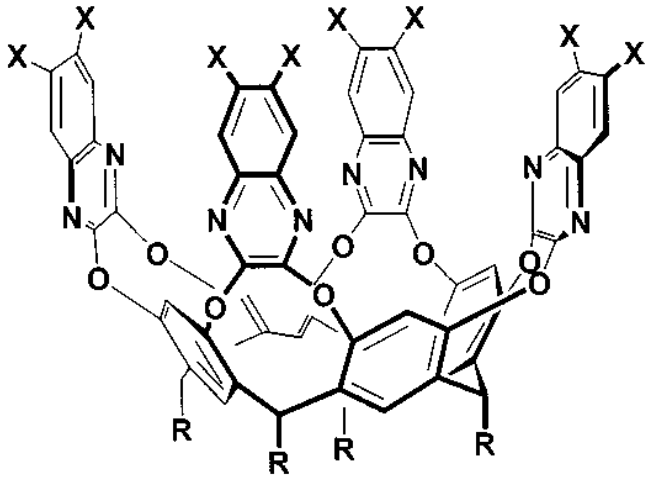
2 R = Alkyl, Ar;
X = $(CH_2)_n$, $SiAlk_2$

Ciclofani concavi ⟹ Cavitandi

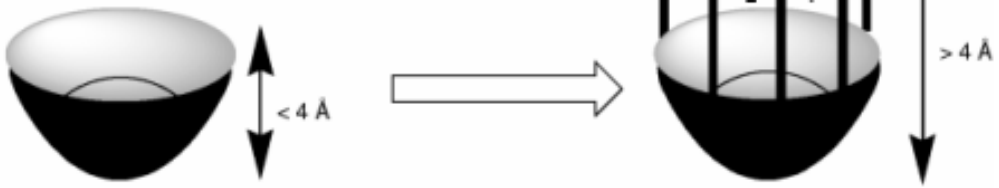


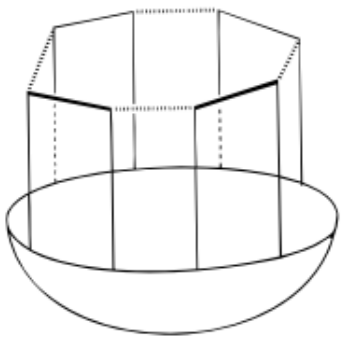
The studies of Cram[13] had established a barrier of some 10 to 12 kcal mol^{-1} for the vase-to-kite interconversion. If this

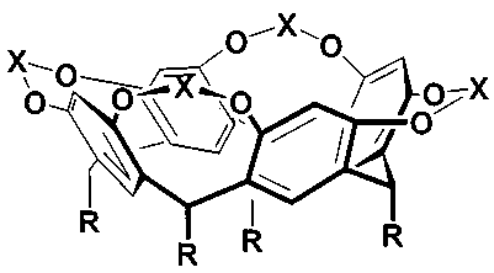




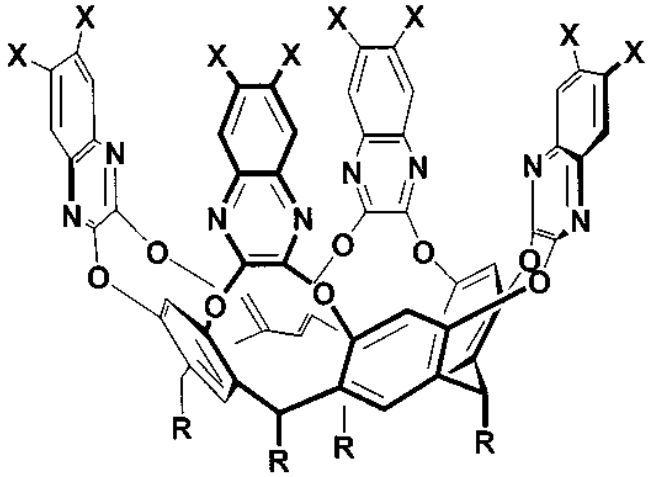
3 R = Alkyl;
X = H, CH_3, Hlg


< 4 Å
> 4 Å

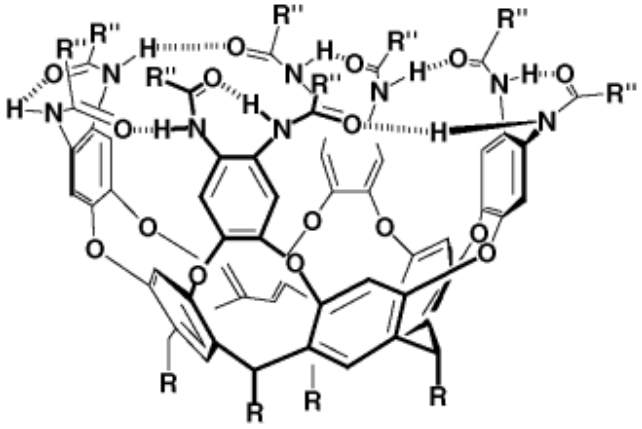


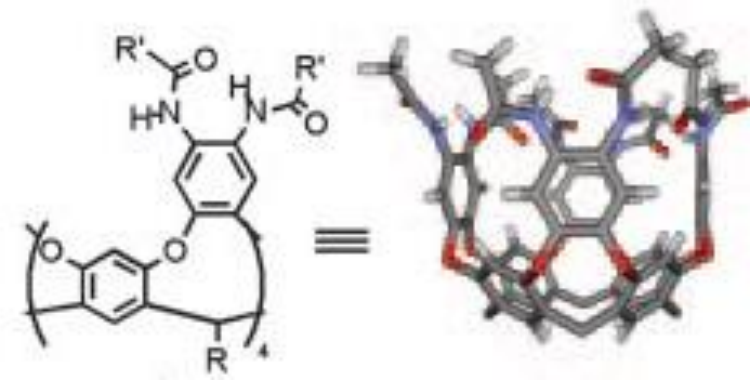


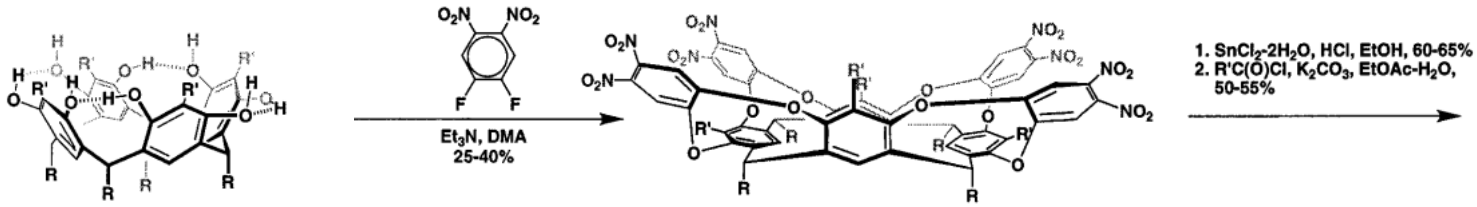
2 R = Alkyl, Ar;
X = $(CH_2)_n$, $SiAlk_2$

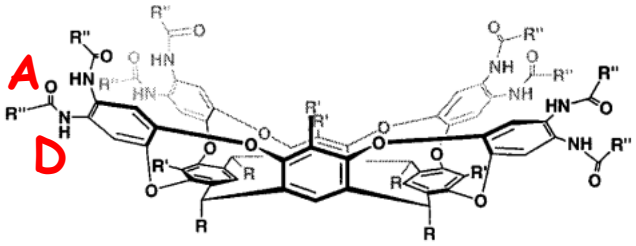


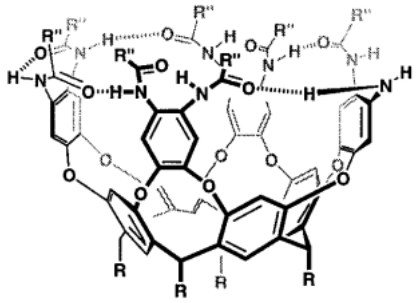
3 R = Alkyl;
X = H, CH_3, Hlg

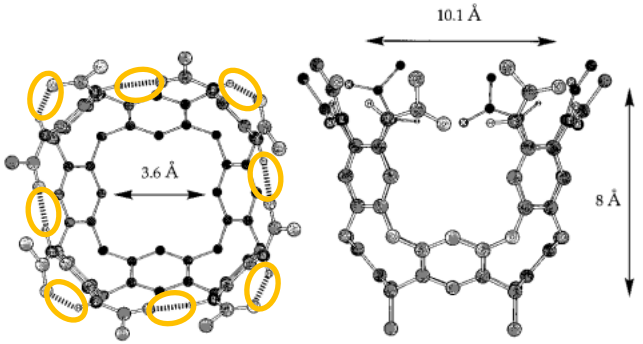


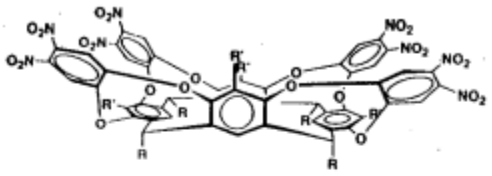



Et3N, DMA
25-40%
1. SnCl2-2H2O, HCl, EtOH, 60-65%
2. R'C(O)Cl, K2CO3, EtOAc-H2O,
50-55%


A
D

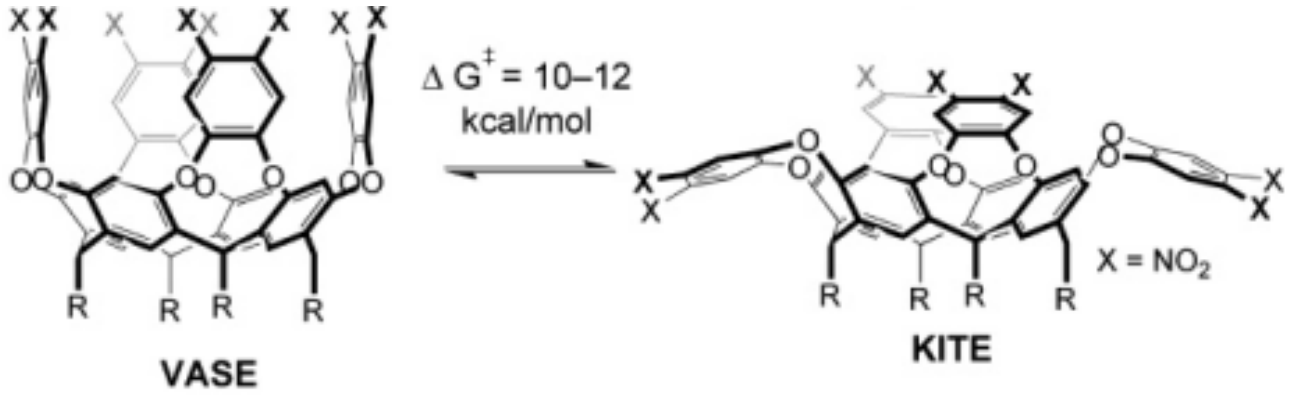


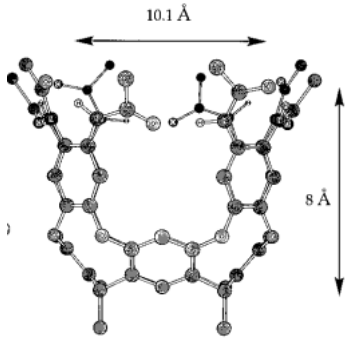

10.1 Å
3.6 Å
8 Å



4 c R = $C_{11}H_{23}$, R' = H

$CDCl_3$, 295 K



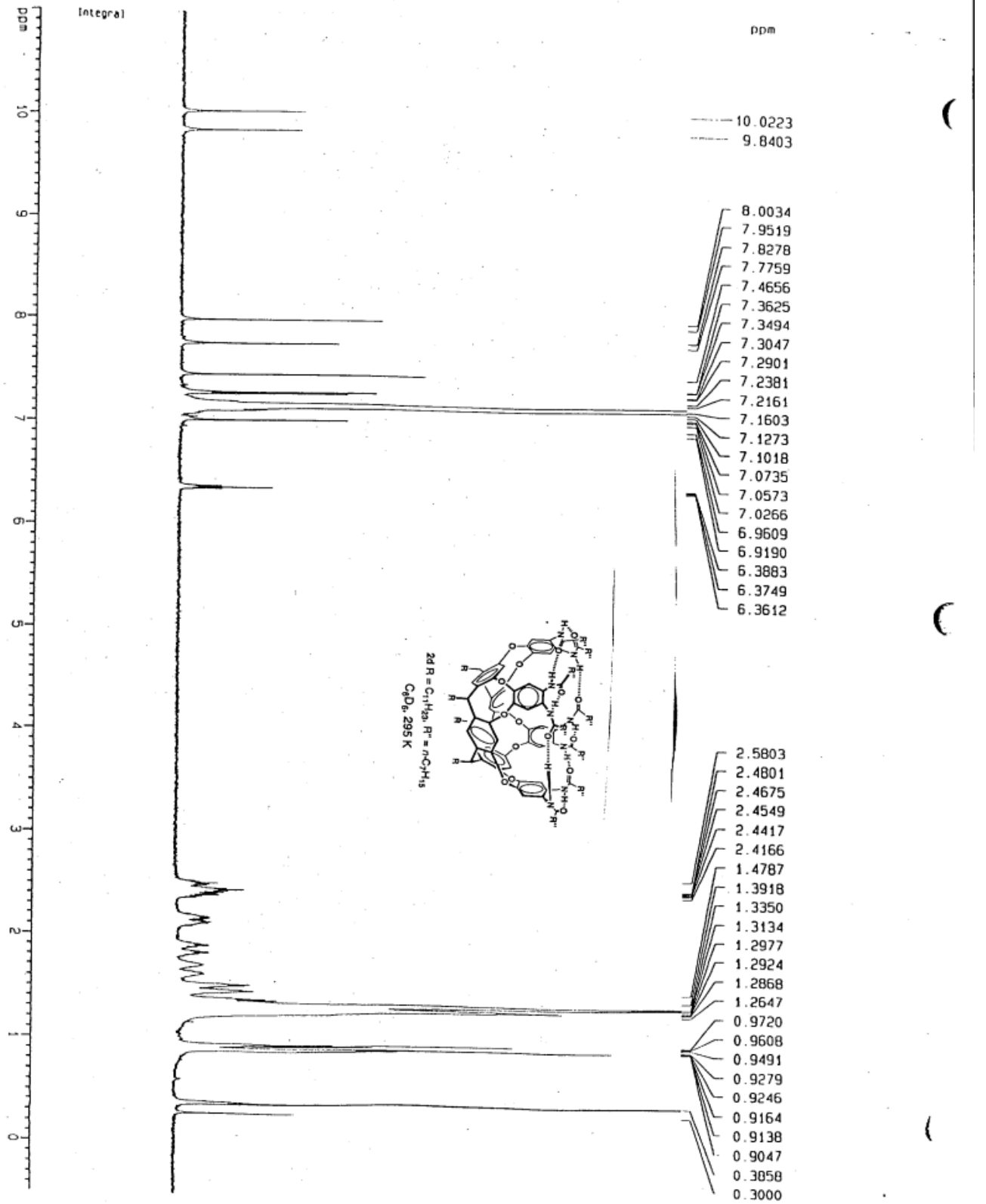


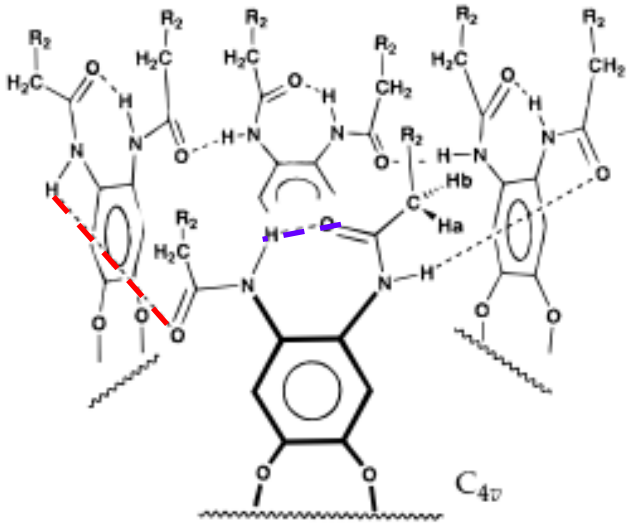
Spettro ^{1}H NMR affilato
Segnale –NH spostato a campi bassi,

Spettro ^{1}H NMR non varia con la concentrazione

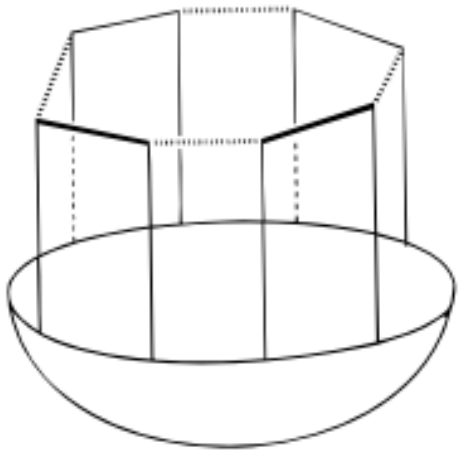
Aggiunta solvente competitivo (dmso-d_6):
allargamento dei segnali

Stretching NH (IR)

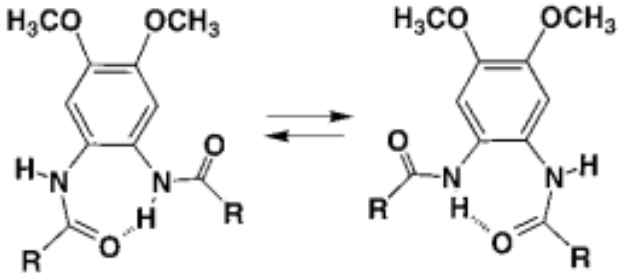

[integral]
ppm
10.0223
9.8403
8.0034
7.9519
7.8278
7.7759
7.4656
7.3625
7.3494
7.3047
7.2901
7.2381
7.2161
7.1603
7.1273
7.1018
7.0735
7.0573
7.0266
6.9609
6.9190
6.3883
6.3749
6.3612
2.5803
2.4801
2.4675
2.4549
2.4417
2.4166
1.4787
1.3918
1.3350
1.3134
1.2977
1.2924
1.2868
1.2647
0.9720
0.9608
0.9491
0.9279
0.9246
0.9164
0.9138
0.9047
0.3058
0.3000
2d R = C11H23, R'' = nC7H15
C6D6, 295 K



=

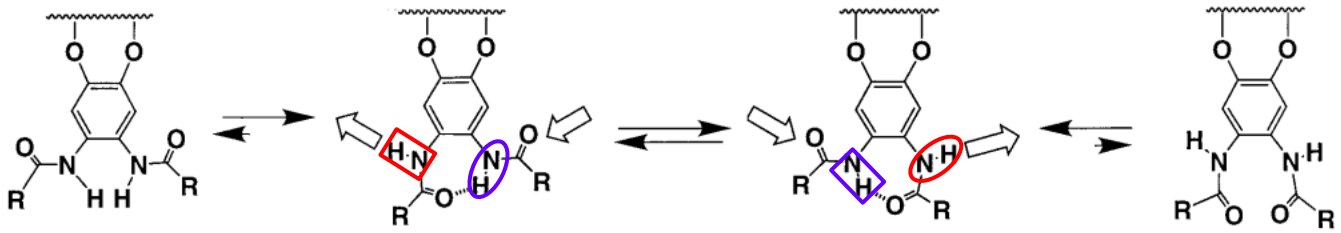


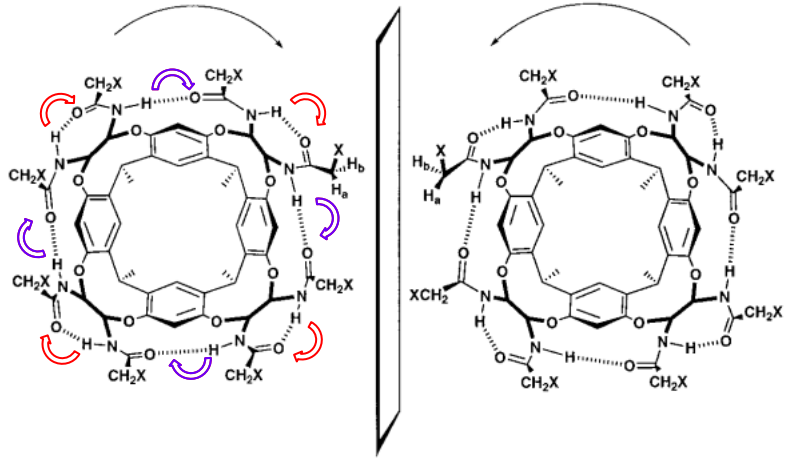
3 $R_1 = C_{11}H_{23}$, $R_2 = C_6H_{13}$

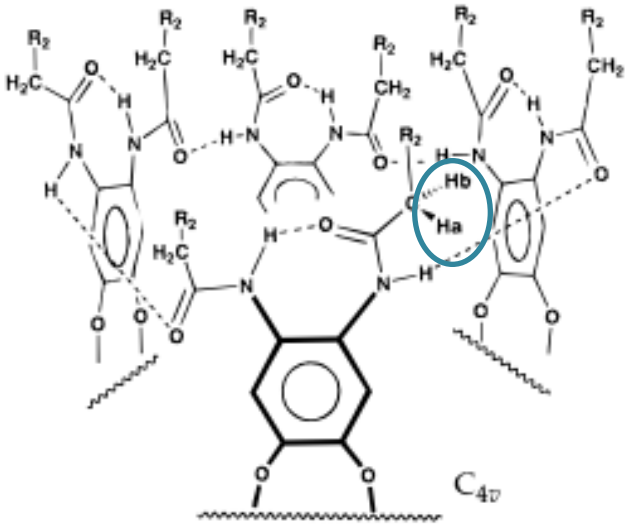


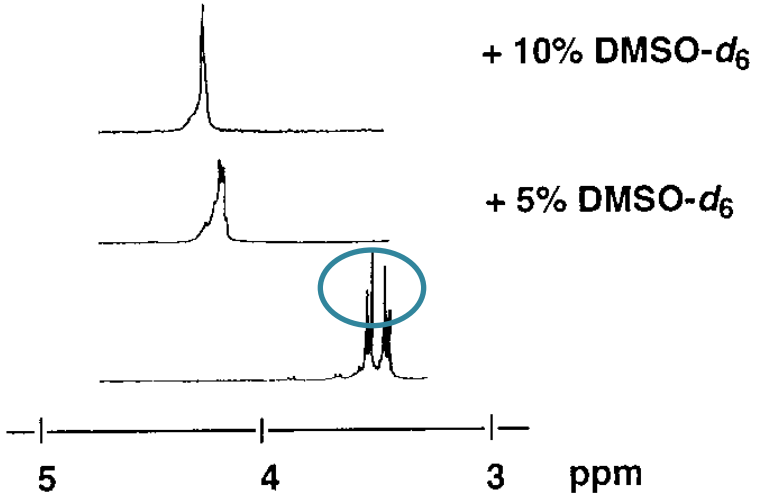
4

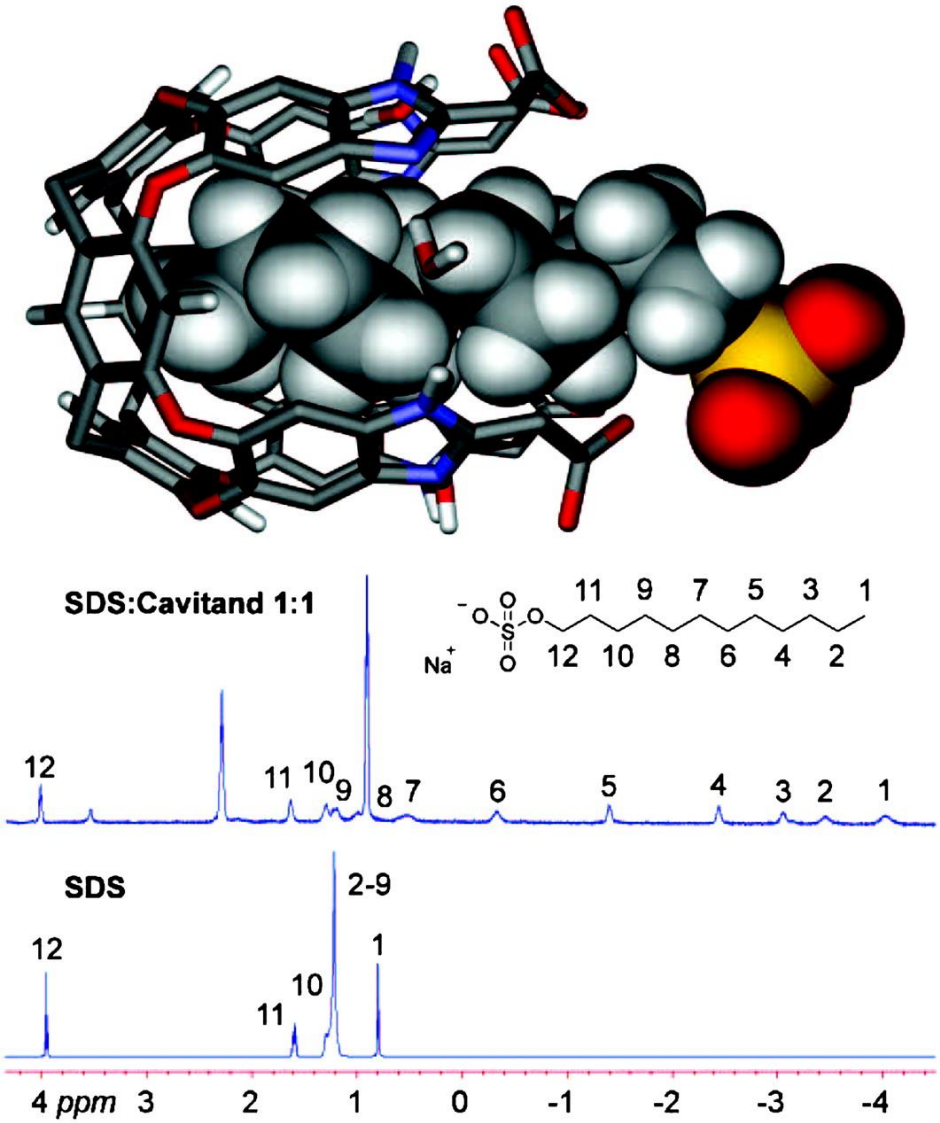
cavitand, four hydrogen bonds need to be broken: those that hold together adjacent rings. The typical costs of such ruptures in organic solvents are roughly 1 to 2 kcal mol^{-1} per hydrogen bond,[17] so the additional 5 to 7 kcal mol^{-1} is quite reasonable for the overall 17 kcal mol^{-1} activation barrier to racemization.

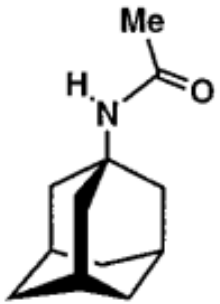


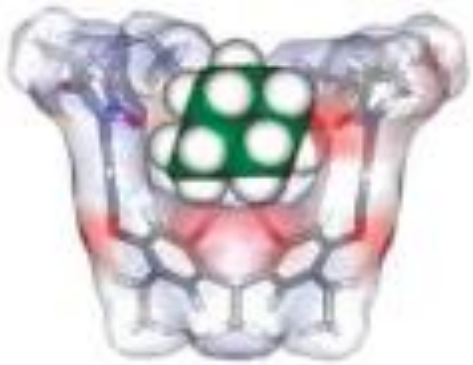


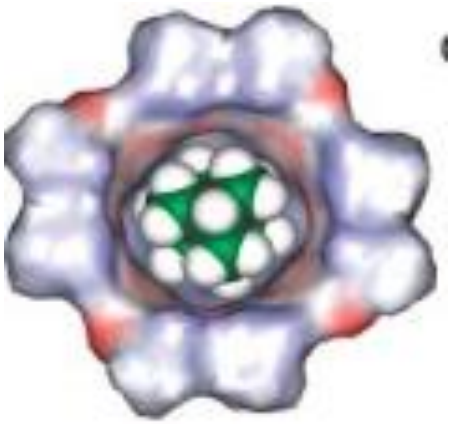

Hb
Ha
C47


+ 10% DMSO-d6
+ 5% DMSO-d6
5
4
3
ppm


SDS:Cavitand 1:1
11 9 7 5 3 1
12 10 8 6 4 2
Na+
12
11 10 9 8 7 6 5 4 3 2 1
SDS
2-9
12
1
10
11
4 ppm 3 2 1 0 -1 -2 -3 -4

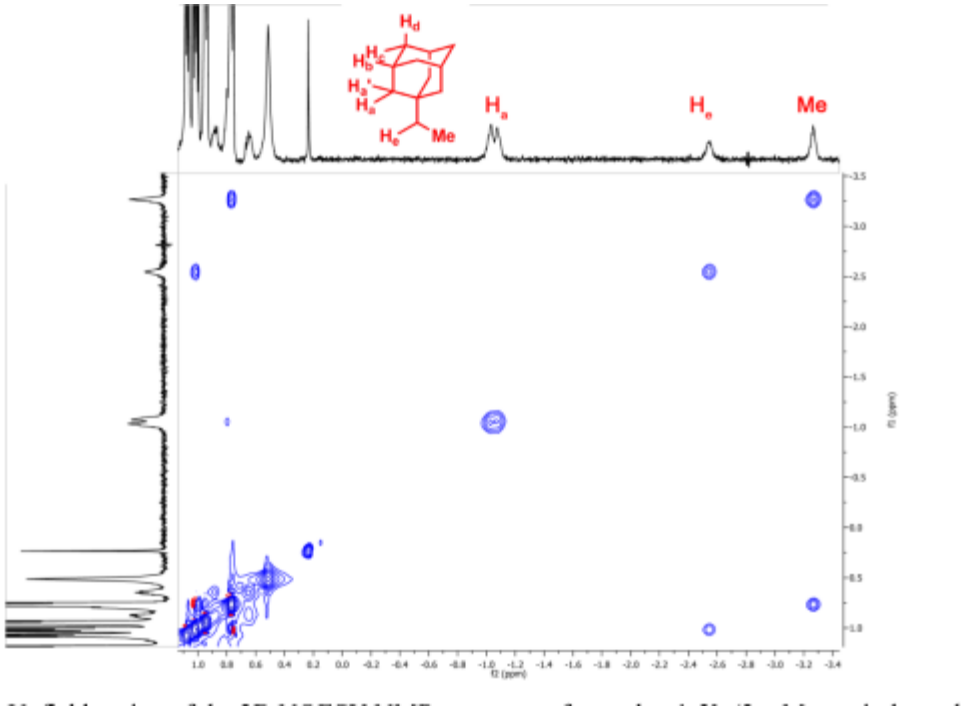




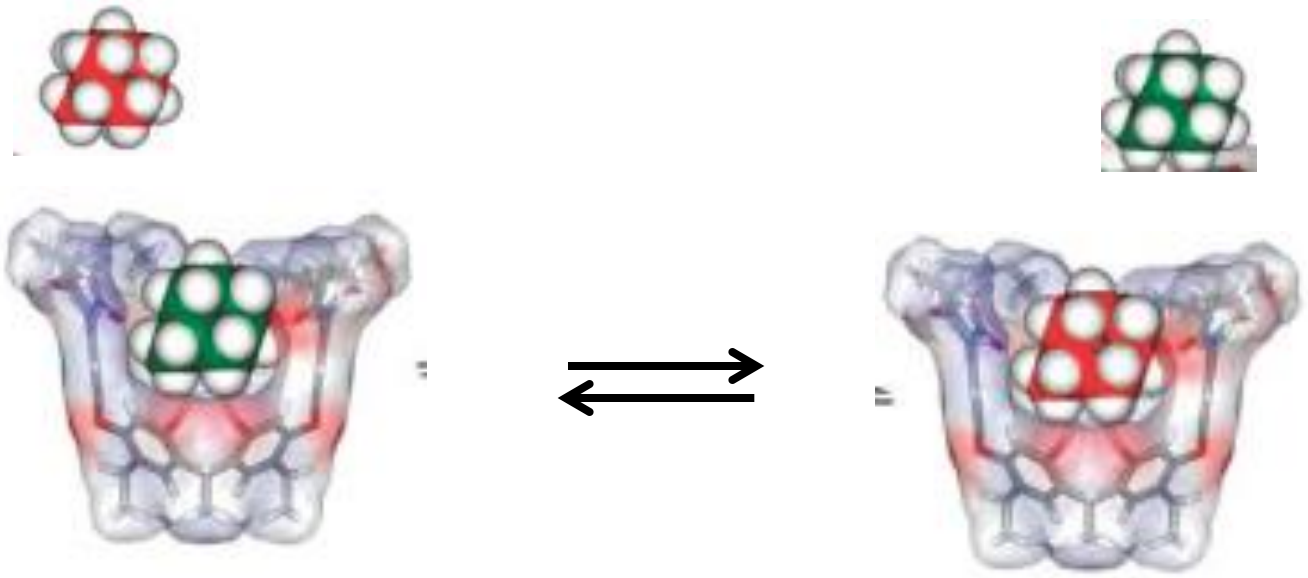


Stabilità migliaio di kcal/mol

2D NOESY accoppiamenti di vicinanza spaziale tra cavitando e bound guest

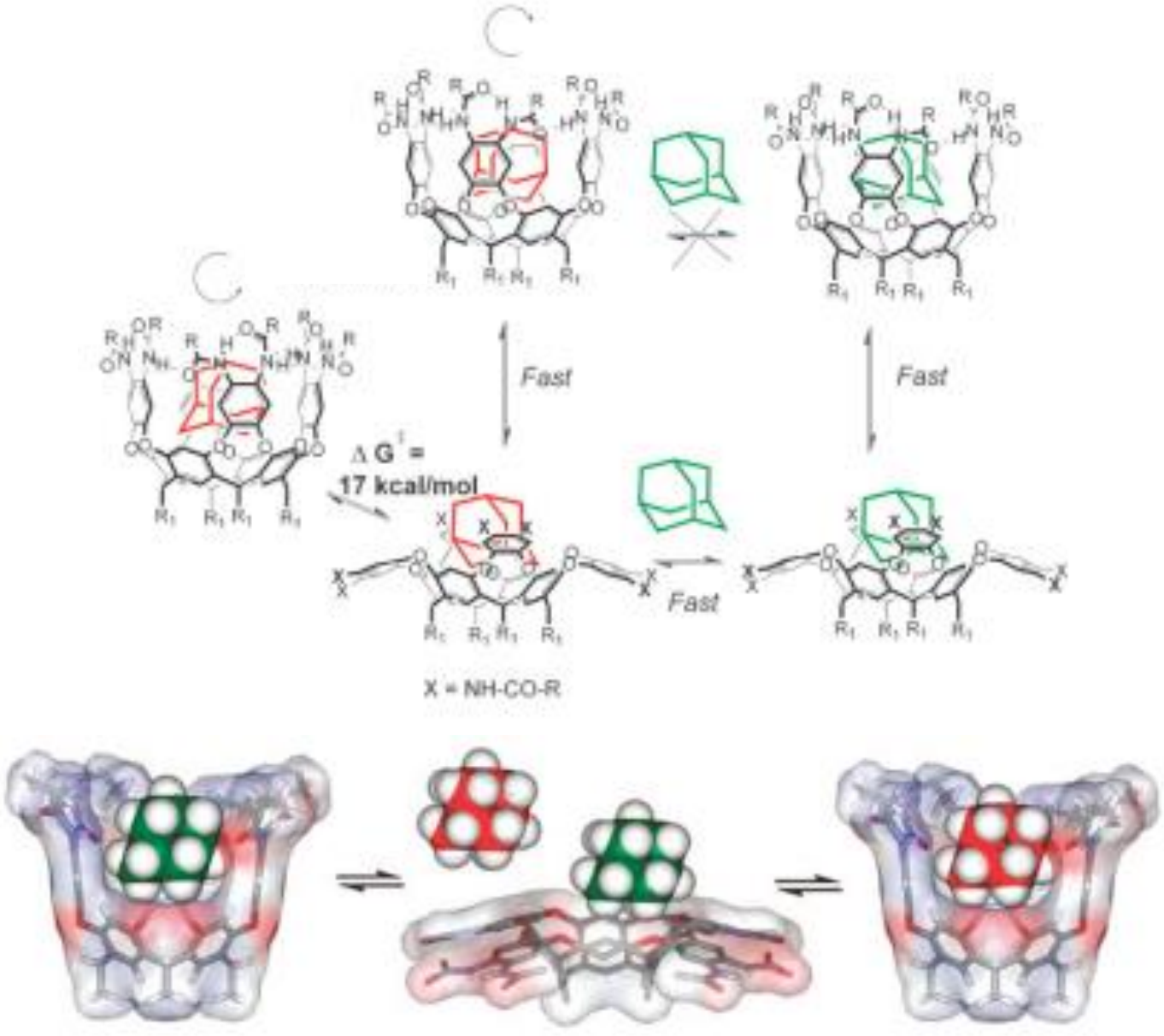


In eccesso di guest: segnali NMR distinti per free and bound guest + evidenza di scambio da 2D EXSY

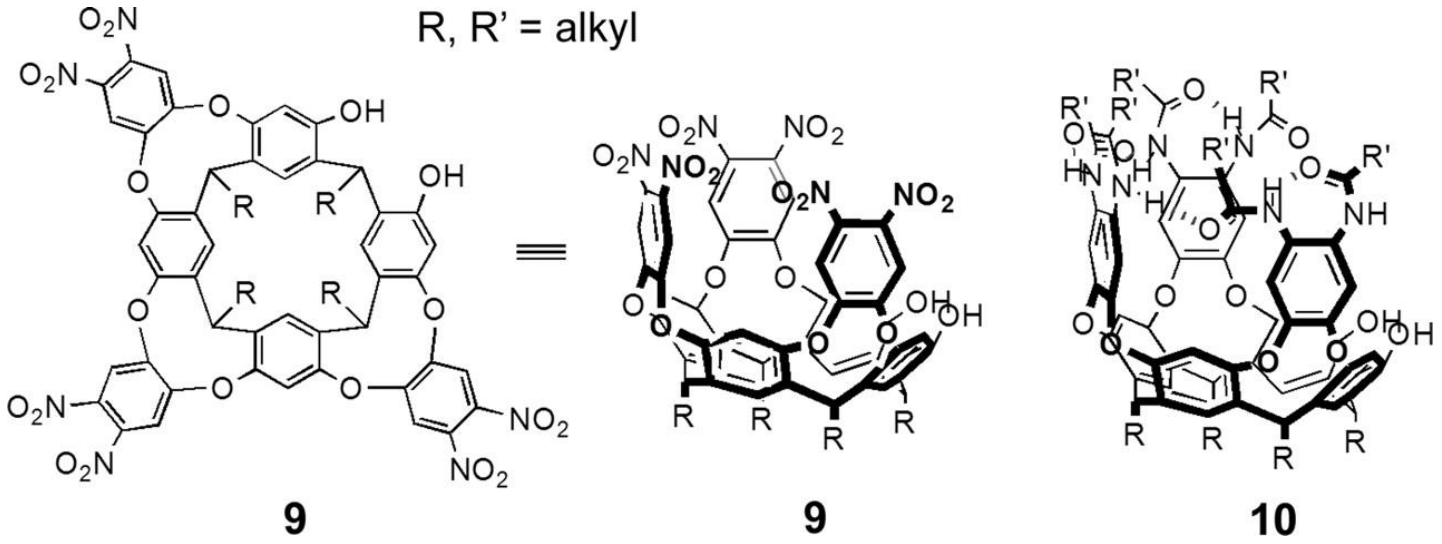


Scambio lento nella scala dei tempi NMR!!

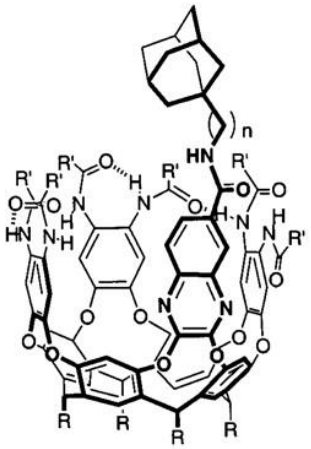
Misura della cinetica di scambio (VT NMR):
barriera cinetica di scambio di *ca.* 17 kcal mol^{-1}



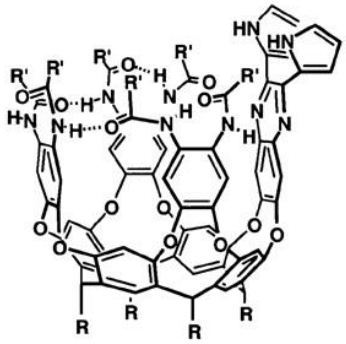
Cavitandi funzionali?



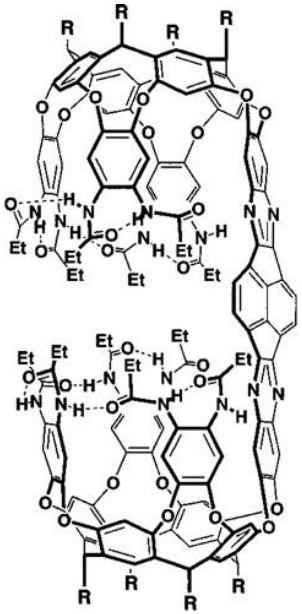
From the hexanitro precursor **9**, encountered as side-product in the preparation of the octanitro derivative, reduction and acylation to obtain hexamide **10**, followed by addition of the fourth wall and reduction to the diamine affords the common precursor to monofunctionalized cavitands.



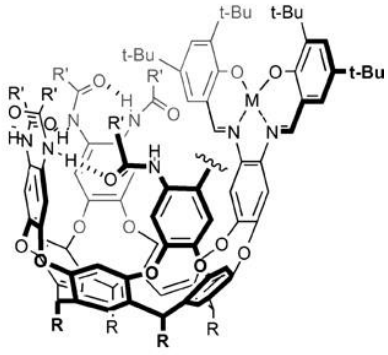
11



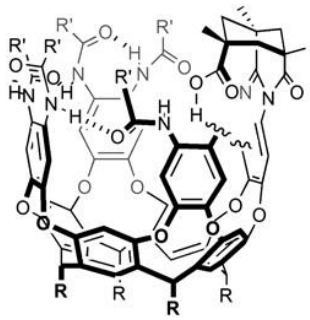
13



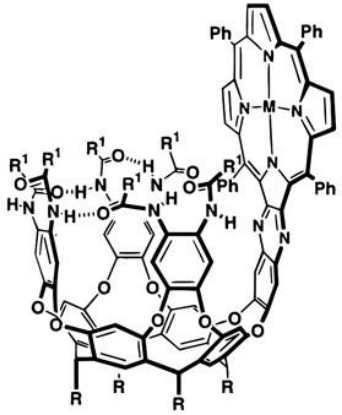
15



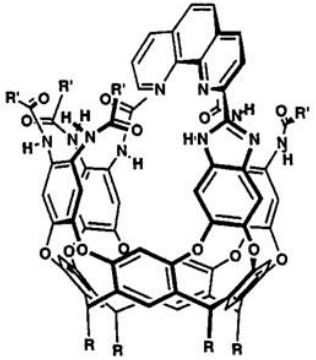
17



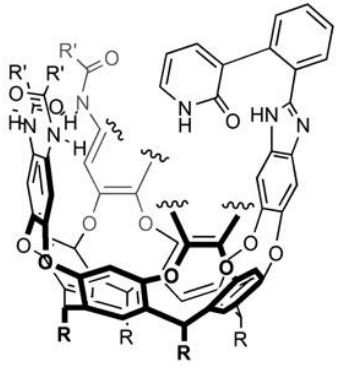
12



14



16



18

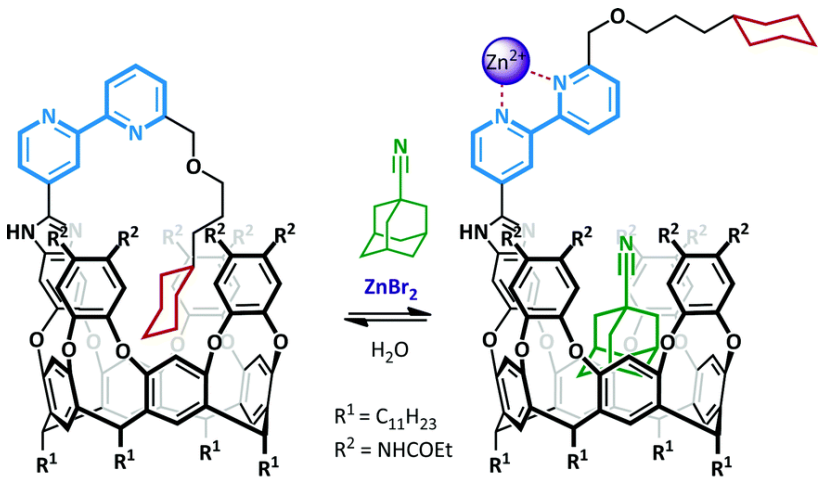
Self-Hosting Cavitand

DOI: 10.1002/anie.200906753

The Ouroborand: A Cavitand with a Coordination-Driven Switching Device**

*Fabien Durola and Julius Rebek, Jr.**

Angew. Chem. Int. Ed. **2010**, *49*, 3189–3191



closed-**11** *occupied*-**11**

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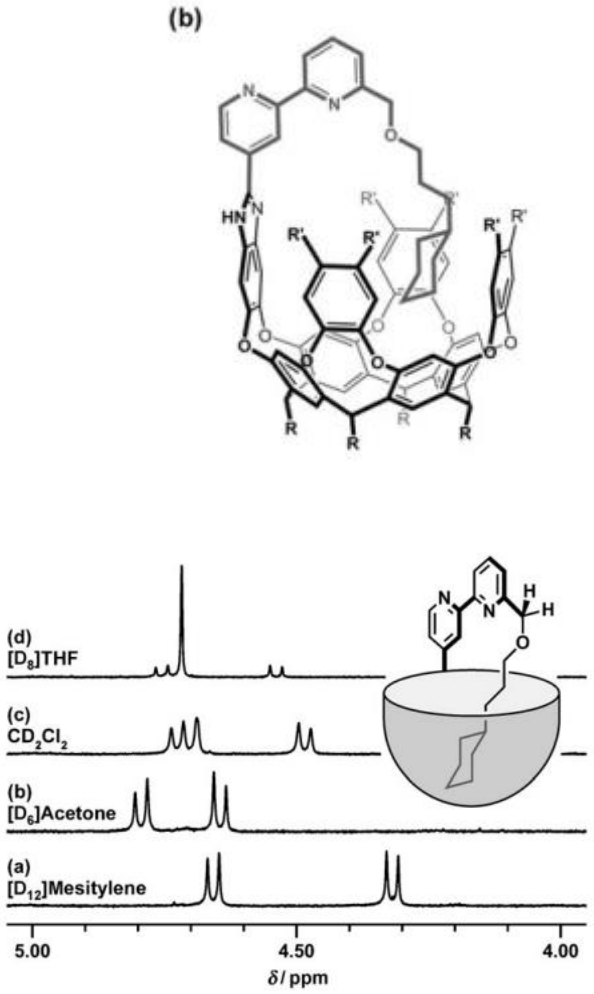
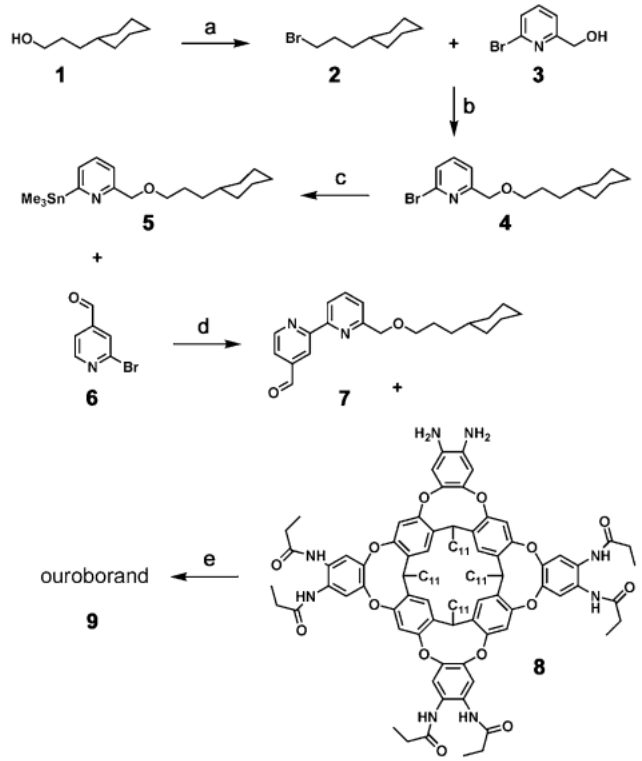
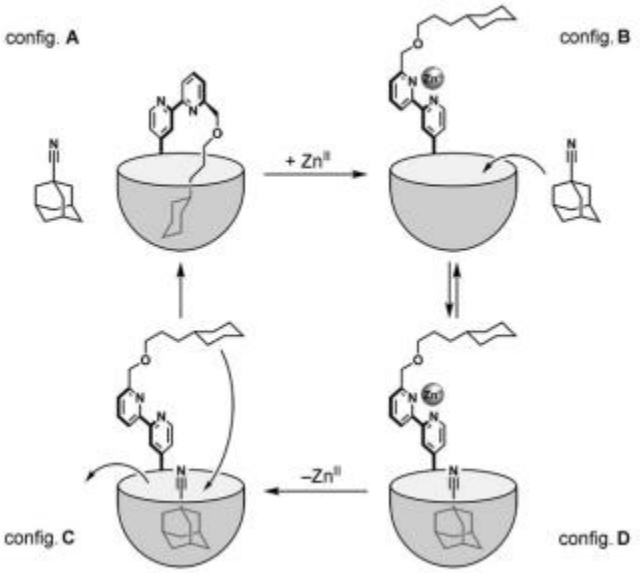
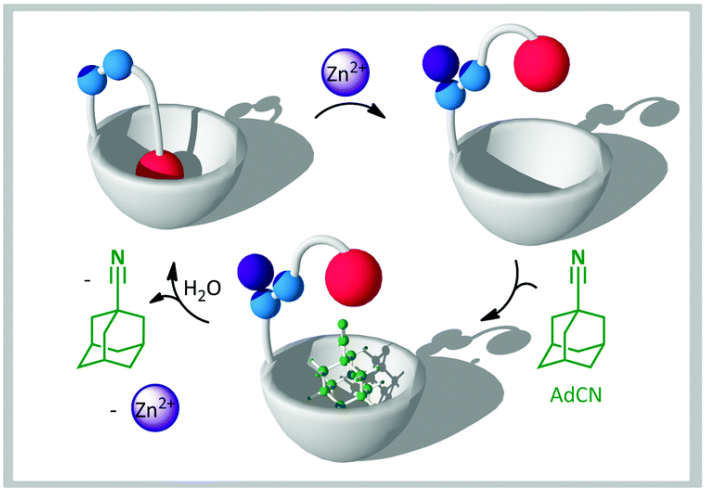
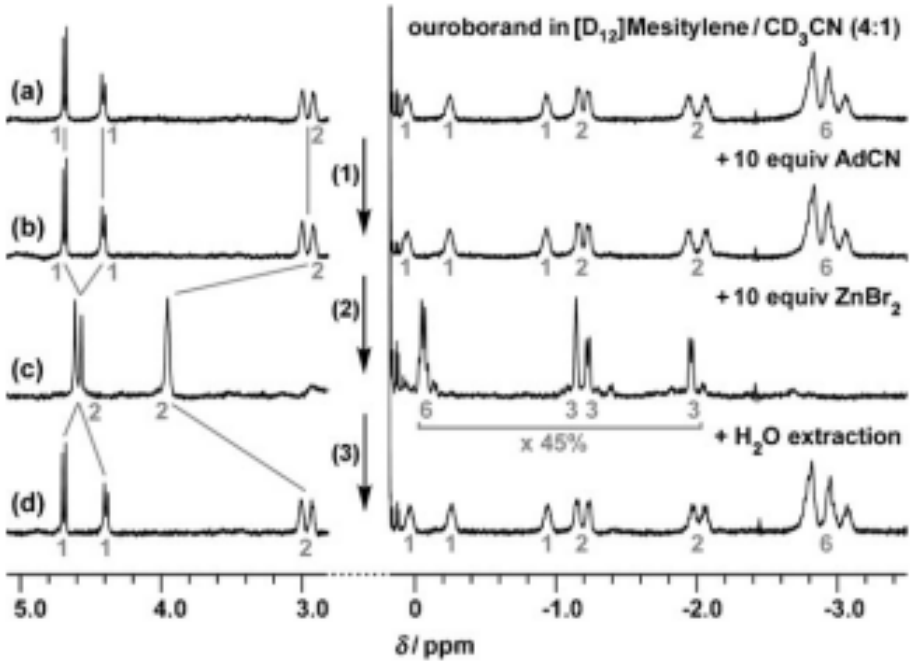




Scheme 3. Synthesis of the ouroborand. a) PBr_3, 0 °C 15 min, RT 2 h, 100 °C 1.5 h, 100%; b) NaH, THF, RT 2 h, 75 °C 16 h, 26%; c) BuLi, toluene, −20 °C, −78 °C 2 h, Me_3SnCl, −78 °C 1 h, RT, 55%; d) [Pd-(PPh_3)$_4$], toluene, 110 °C 48 h, 75%; e) dioxane, RT 30 min, 100 °C 16 h, 67%.


config. A
config. B
+ Zn^{II}
config. C
config. D
–Zn^{II}


Zn^{2+}
N
H$_2$O
AdCN
Zn^{2+}

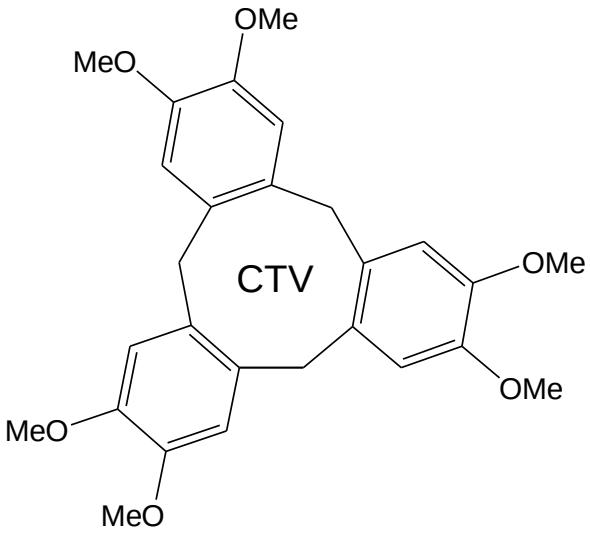

ouroborand in [D$_{12}$]Mesitylene / CD$_3$CN (4:1)
(a)
(b)
(c)
(d)
(1)
(2)
(3)
+ 10 equiv AdCN
+ 10 equiv ZnBr$_2$
+ H$_2$O extraction
x 45%
5.0
4.0
3.0
0
-1.0
-2.0
-3.0
δ / ppm

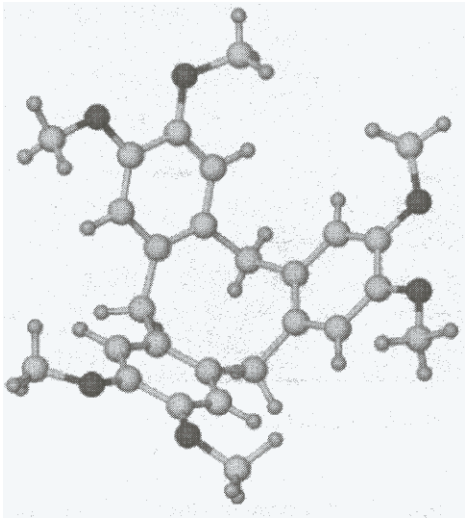
Recettori per molecole neutre

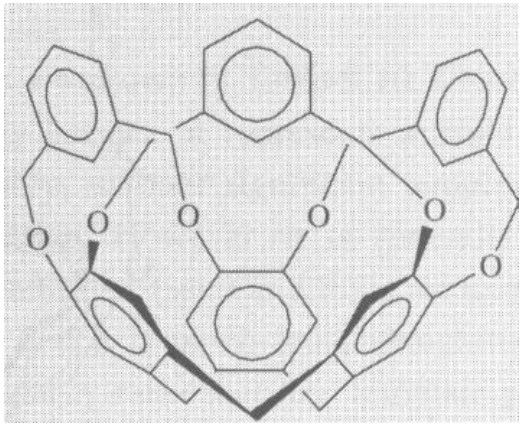
Interazioni CH-π pre organizzazione (cavità profonde e rigide)

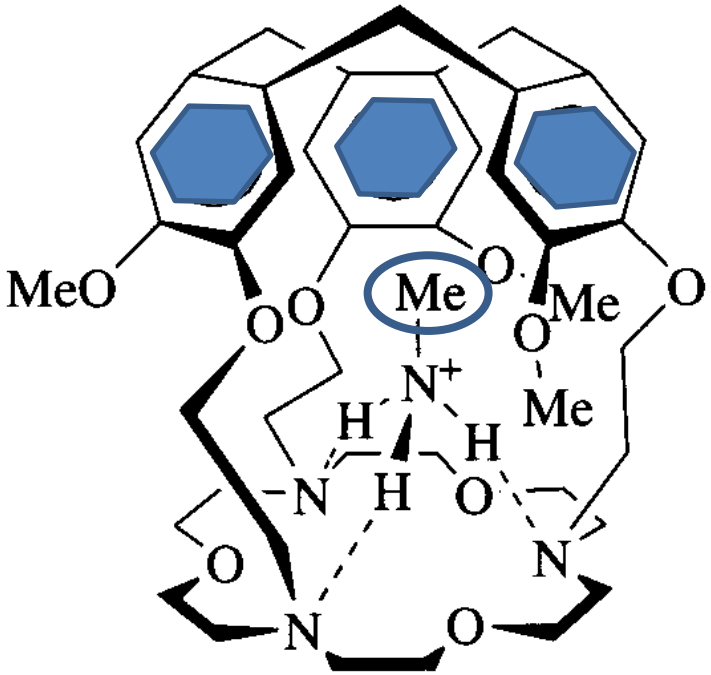
Ciclotriveratrilene CTV

condensazione 1,2-dimetossi benzene e formaldeide, H_2O ac.









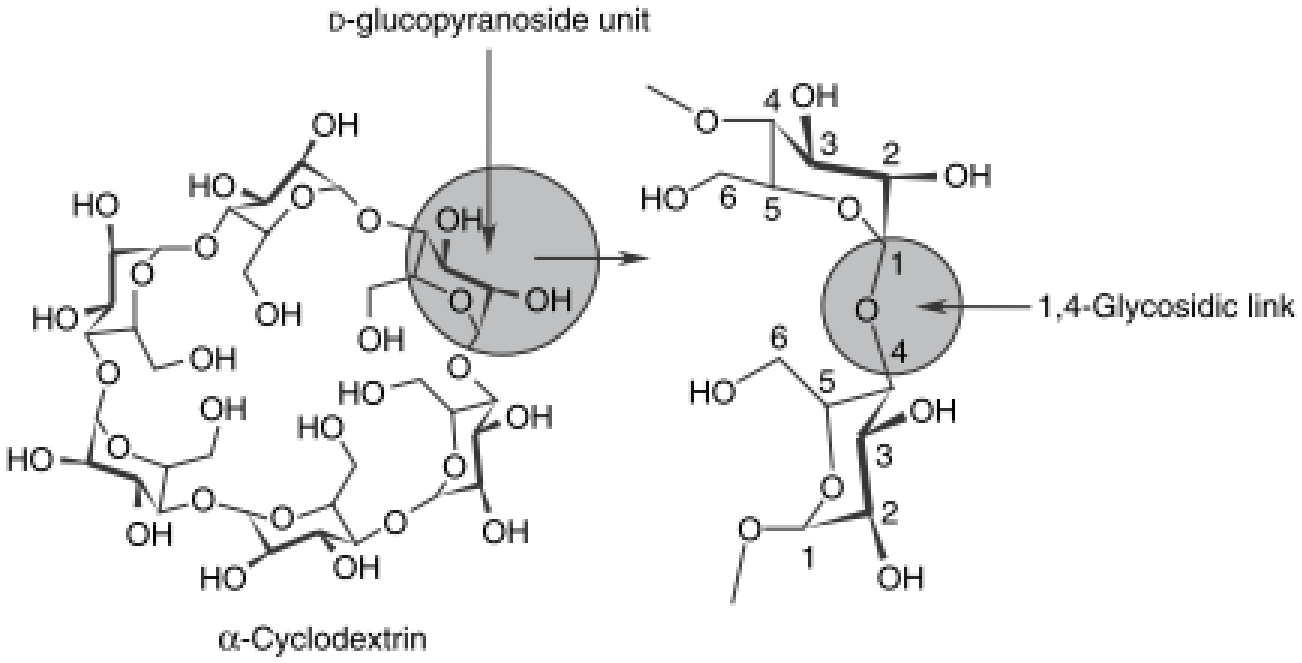
ciclotriveratrilene

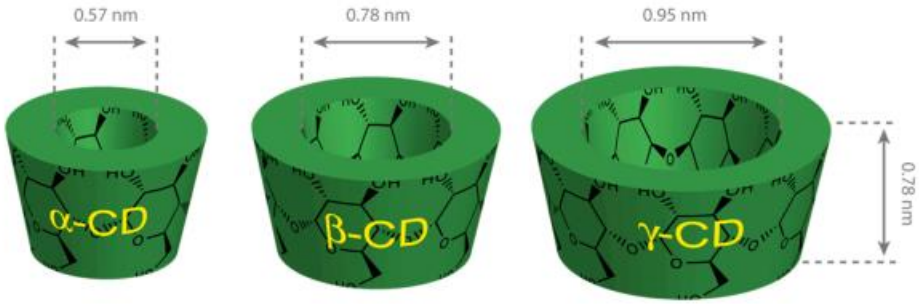
corando

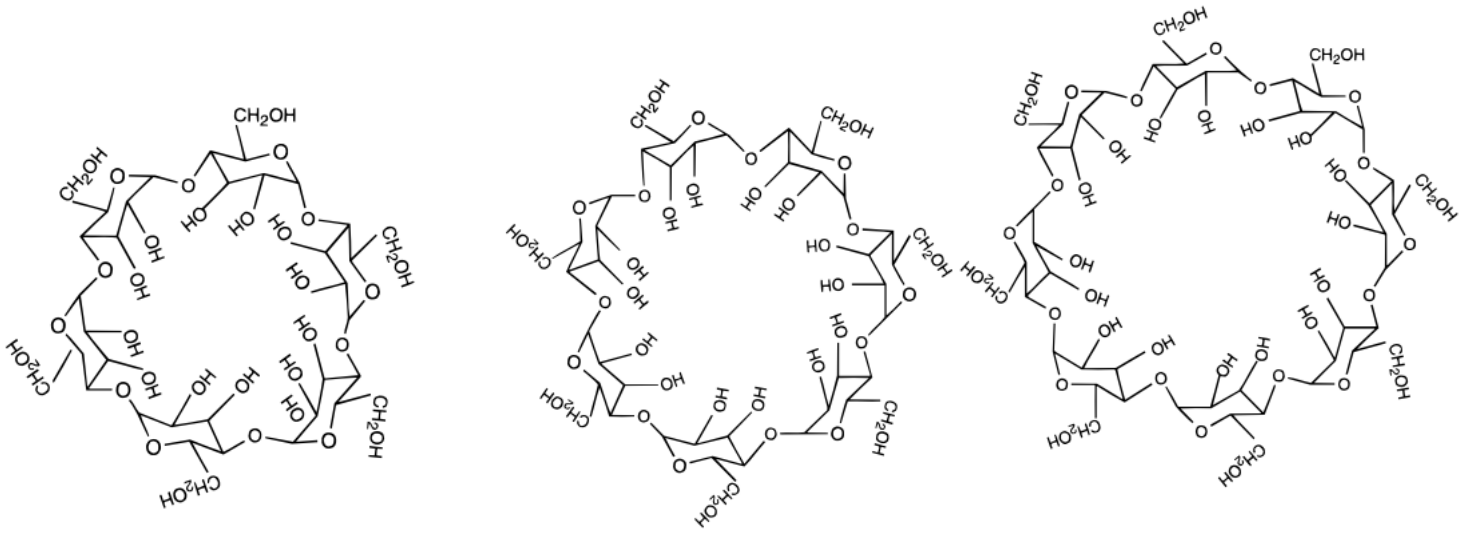
Recettori per molecole neutre

Effetto idrofobico esterno polare (e/o carico) tasca idrofobica

Ciclodestrine – unità D-glucopiranosidiche (legami 1,4-glicosidici)

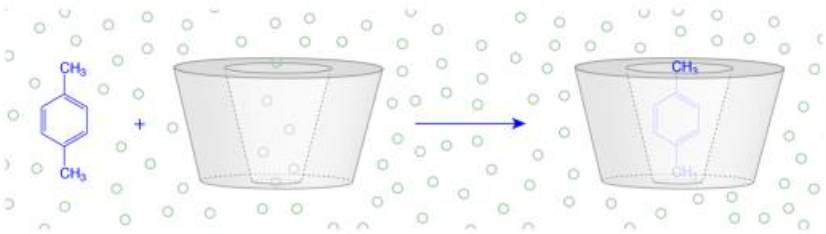



0.57 nm
0.78 nm
0.95 nm
α-CD
β-CD
γ-CD
0.78 nm

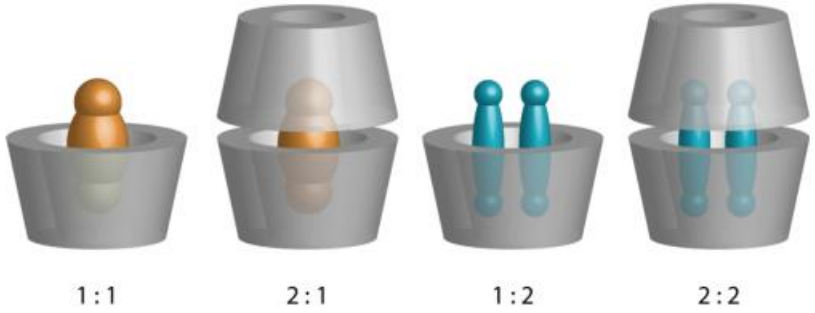


Solubilità (H_2O): α 145g/L β 18.5 g/L γ 232 g/L

Size-fit, effetto idrofobico, vdW, dipolo-dipolo, legami a idrogeno..



Complessi 1/1 o con varie stechiometrie



Derivatizz tramite gruppi OH:
alkyl/hydroxyalkyl/carboxyalkyl/ester/thiol/tosyl/…

non toxic…termostabili..airstable…

Production 1000 tons/year

Settori applicativi:

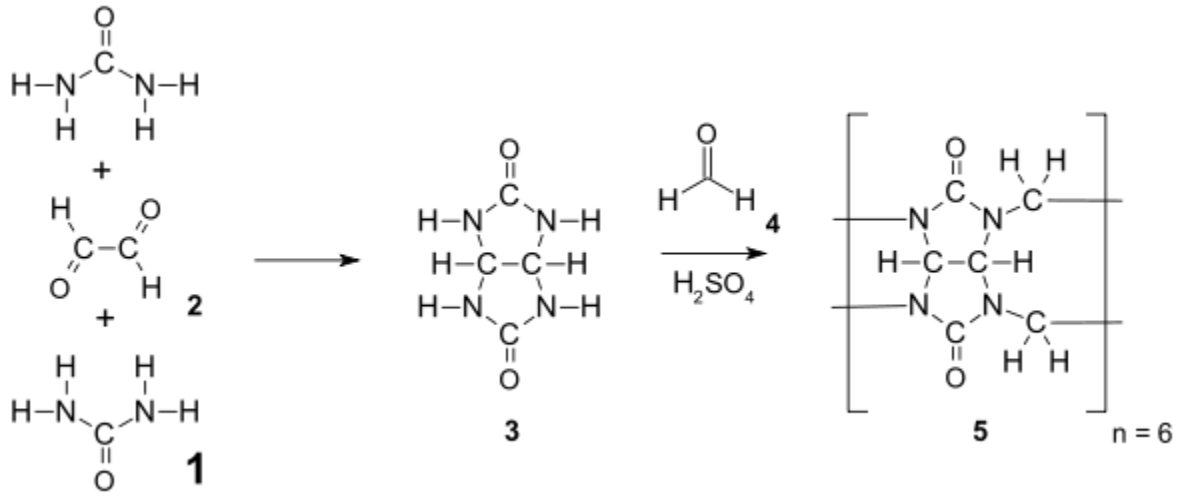
Farmaceutico: stabilità (luce aria). Biodisponibilità, formulazione, somministrazione..
Alimentare: aromi, spezie, emulsioni, colesterolo, vitamine
Cosmetico: lozioni solari
Analitici: grafting su supporti polimerici x cromatografia (HPLC chirale)

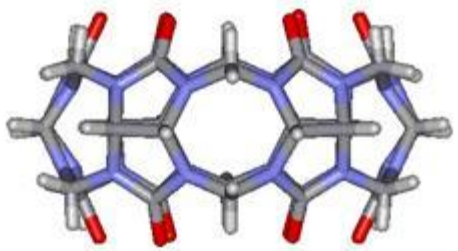
Cyclodextrins News

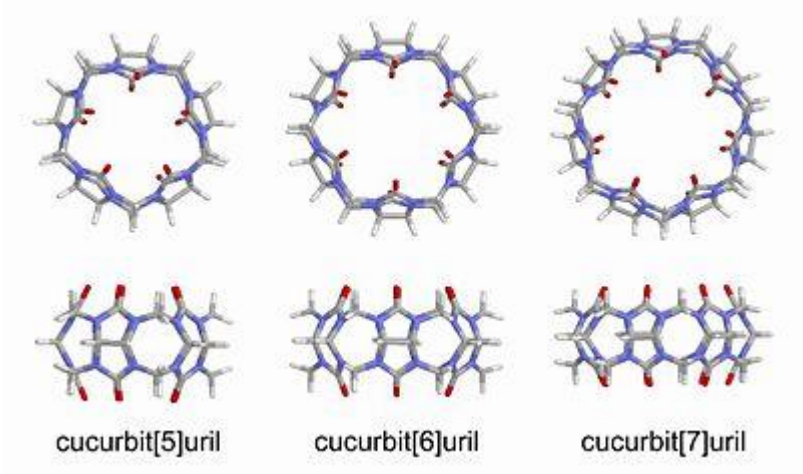
Table 1. Recap of the Main Results of Freudenberg on Schardinger Dextrins

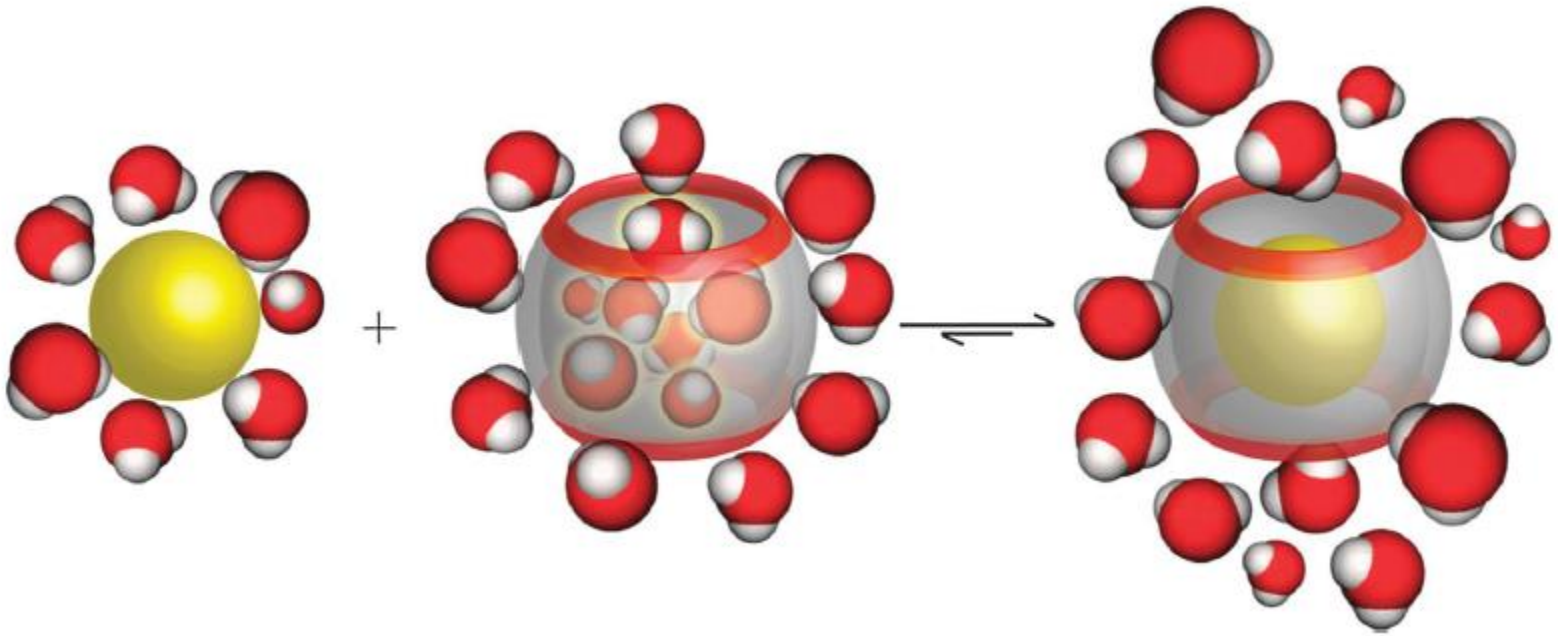
year	result
1922	tosylated dextrins
1930	Schardinger dextrins: laboratory curiosities and/or unwanted byproducts of starch degradation
	Schardinger dextrins: chain molecules intermediate between maltose and starch
1935	the dextrins were lined with a hydrocarbon interior
	synthesis of Schardinger dextrins with high purity
	determination of molecular weights (five for α-dextrin and six for β-dextrin)
	solubility differences of the dextrins
	chemical modification of dextrins (acetylation, methylation, saponification reactions)
1936	studies on the nature of the glycosidic bonds
	hypothesis on the cyclic nature
1938	cyclic chemical structure of dextrins
	hydrophobicity of the inner surface of the dextrins
	ability to form inclusion complexes
	Foundation of the Research Institute for the Chemistry of Wood and Polysaccharides
1939	description of the mechanism of action for *Bacillus macerans*
1943	cyclic structure composed of maltose units bound together by $\alpha(1\rightarrow 4)$ glycosidic linkages
1947	the first scheme for the isolation of pure fractions
1948	discovery of γ-dextrin
	Freudenberg and Cramer demonstrated their conclusions on cyclic structure using optical activity data
	the first indication of the existence of dextrins comprising more than 8 glycosyl units
1950	structure of γ-dextrin
	involvement of hydrophobic forces in the formation of the complexes
	possible existence of dextrins with 9 or 10 units of glucose
1953	first patent concerning applications in pharmaceutical formulations

Cucurbiturili– unità glicolurile (legami metilenici)









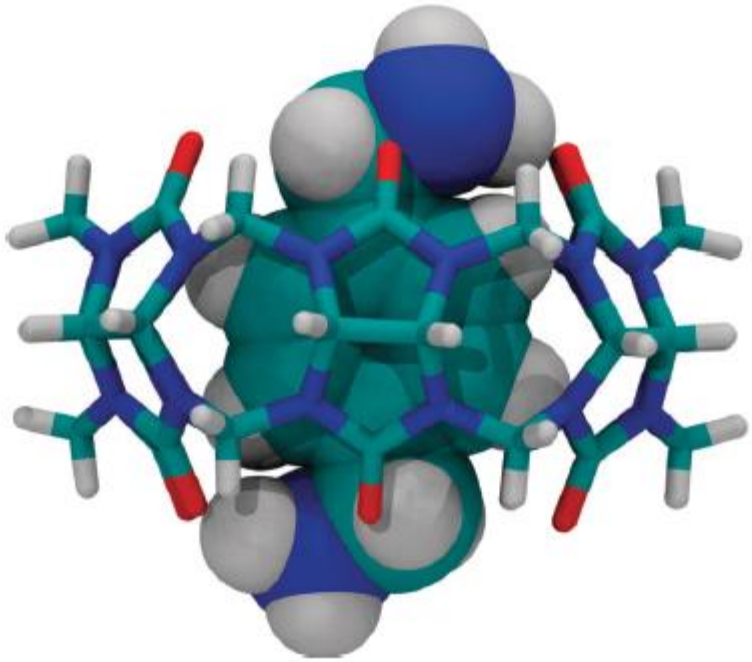


Fig. 13 X-ray structure of the *p*-xylylenediammonium ion encapsulated by CB6, the first X-ray diffraction structure of a CB*n* complex.[127]

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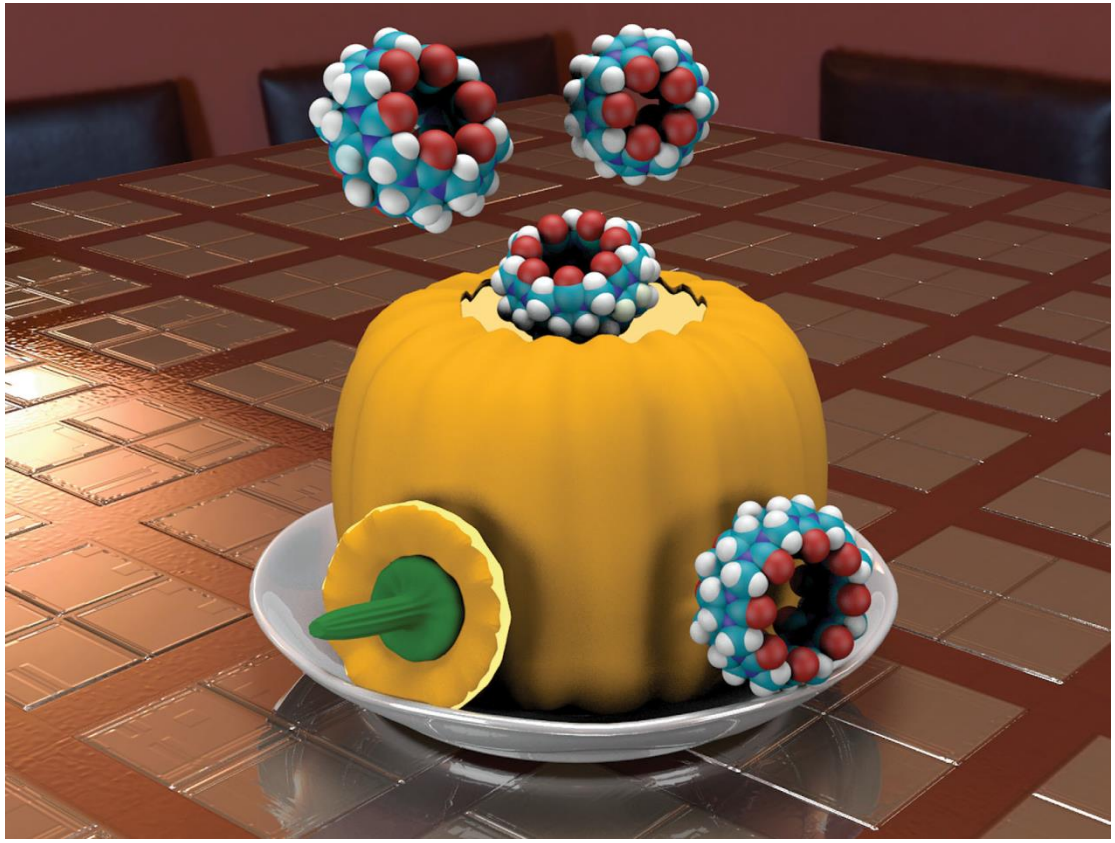
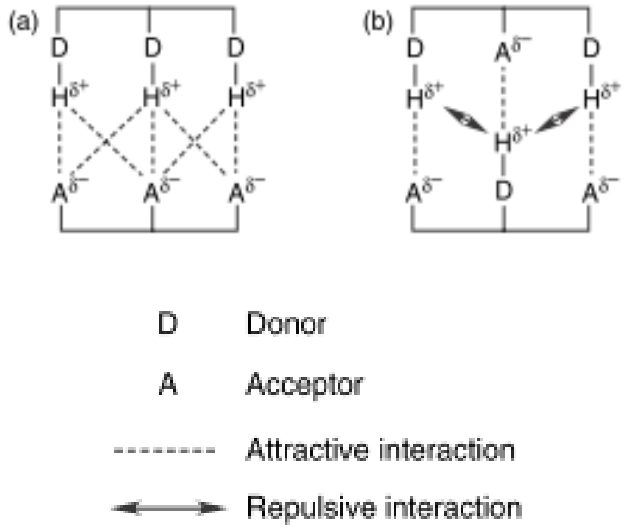
Cucurbiturils: from synthesis to high-affinity binding and catalysis

Khaleel I. Assaf and Werner M. Nau*



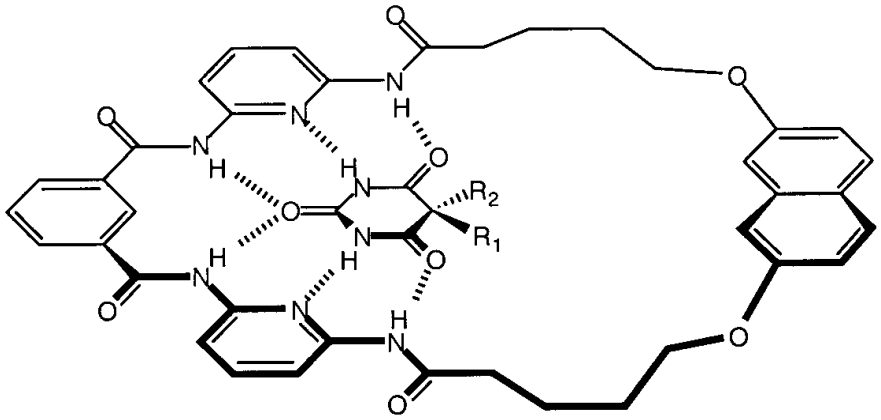
Recettori per molecole neutre

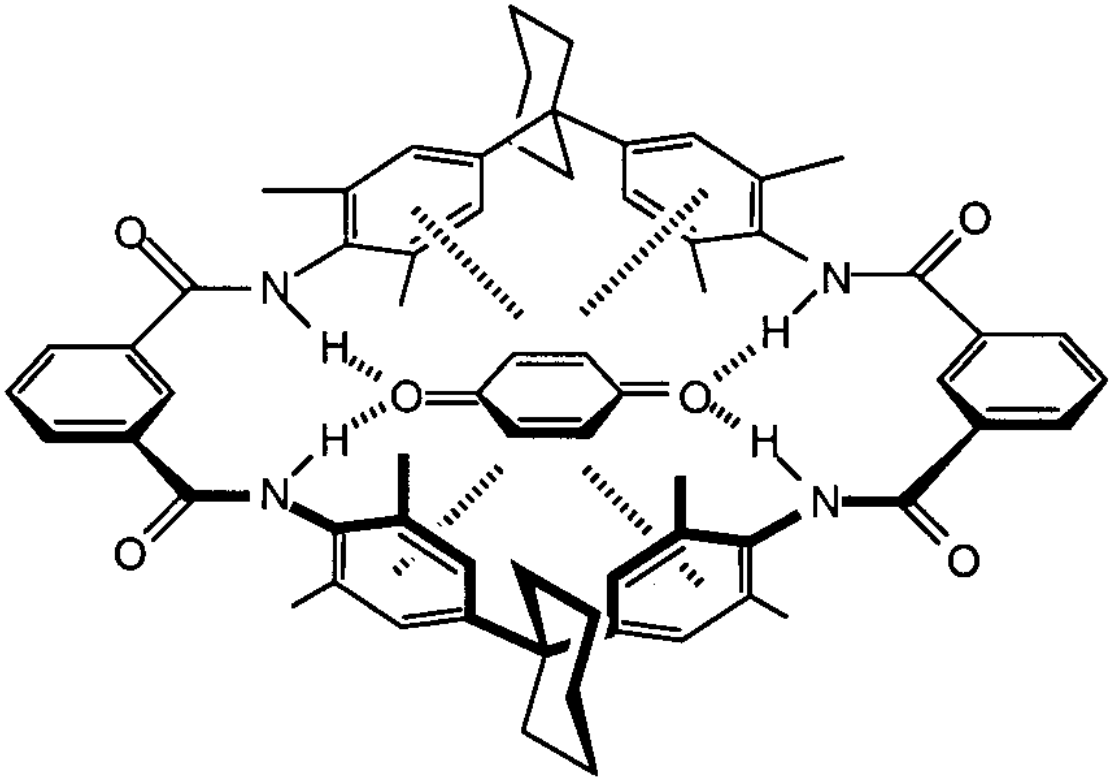
Legami idrogeno siti D A multipli



Recettori per molecole neutre

Legami idrogeno preorganizzazione e complementarietà (direzionale)





Receptor for benzoquinone which alters the electronic properties of the guest.