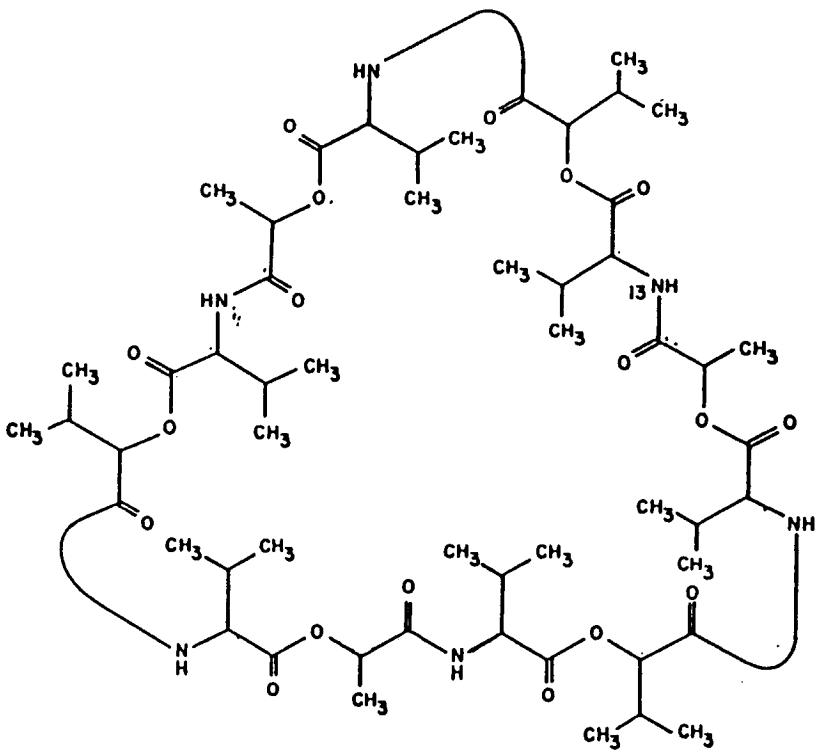
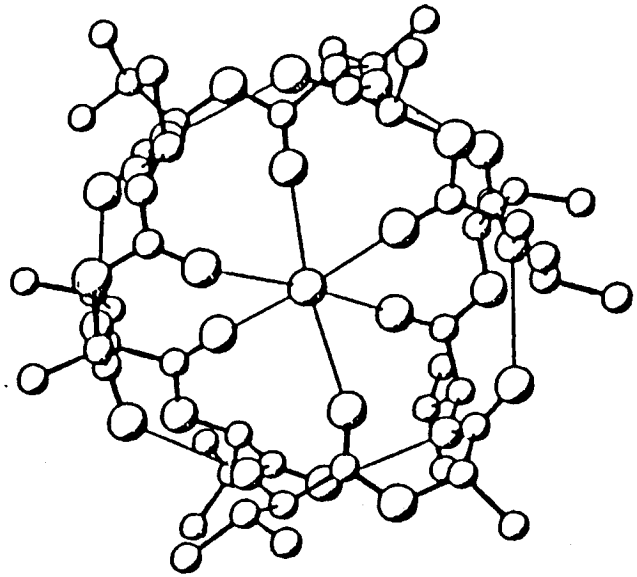
DESIGN AND SYNTHESIS OF ARTIFICIAL RECEPTORS BASED ON CALIXARENES
IASOC V. (1992)

- Introduction
- Metal Ion Recognition by Calixarene Ligands
  - Calix[4]arene esters and amides
  - Calix[4]arene siderophores
  - Calixcrowns and Calixspherands
- Flexible and Rigid Ionophores Based on Calix[6]arenes

R. Ungaro, A. Pochini in "Calixarenes a Versatile Class of Macrocyclic Compounds" J. Vicens, V. Böhmer (Eds), Kluwer, Dordrecht, 1990, pp. 127-147;
R. Ungaro, A. Pochini in "Frontier in Supramolecular Organic Chemistry and Photochemistry". H.J. Schneider, H. Dürr (Eds), VCH, Veinheim 1991 pp. 57-81;
G.D. Andreetti et. al. in Inclusion Compounds, vol.4, J.L. Atwood, J.E. Davies and D.D. Mc. Nicol (Eds). Oxford University Press. 1991 pp. 64-125;
A. Arduini et al. Supramolecular Chem., in press;
A. Arduini et al. "Supramolecular Chemistry", V. Balzani and L. De Cola (Eds.), Kluwer Academic Publ., Dordrecht, 1992, pp. 31-50.

VALINOMYCIN and its K^+(1:1) COMPLEX

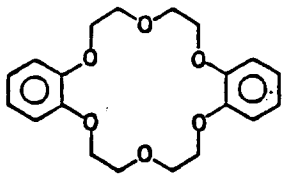
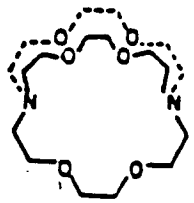
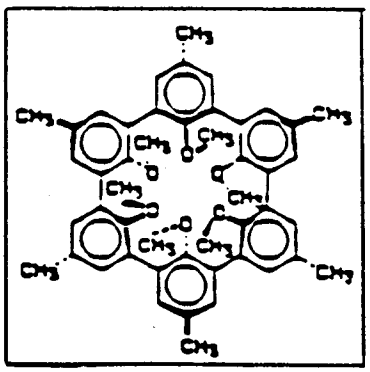




K. Neupart-Laves, M. Dobler, Helv. Chim. Acta, **58**, 432 (1975)

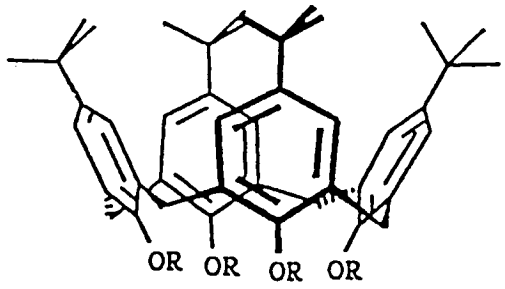
PREORGANIZATION AND RATES OF COMPLEXATION - DECOMPLEXATION

$$H + G \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{COMPLEX} \qquad K_a = \frac{k_1}{k_{-1}}$$

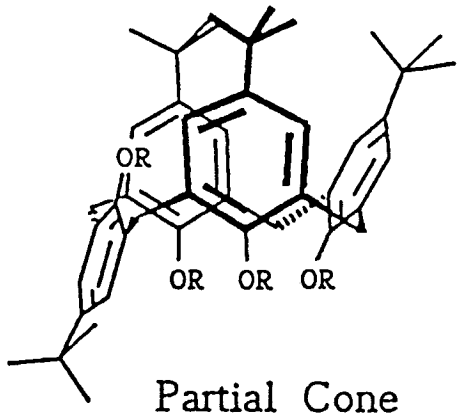
HOST	CATION/SOLVENT	T = 25°C
 DIBENZO-18-CROWN-6	Na^+/MeOH	$K_a = 2.28 \times 10^4$ M^{-1} $k_1 = 3.2 \times 10^8$ $M^{-1}\ s^{-1}$ $k_{-1} = 1.4 \times 10^4$ s^{-1} *E. Schori and J. Jagur - Grodzinski (1973)*
 CRYPTAND (2,2,2)	Na^+/MeOH	$K_a = 0.94 \times 10^8$ M^{-1} $k_1 = 2.7 \times 10^8$ $M^{-1}\ s^{-1}$ $k_{-1} = 2.87$ s^{-1} *B.G. Cox and H. Schneider (1978)*
 SPHERAND	$Na^+/CHCl_3$	$K_a = 1.2 \times 10^{14}$ M^{-1} $k_1 = 4.1 \times 10^5$ $M^{-1}\ s^{-1}$ $k_{-1} = 3.4 \times 10^{-9}$ s^{-1} *D.J. Cram and G.M. Lein (1985)*

D.J. Cram. Angew. Chem. Int. Ed. Engl., 25, 1039 (1986)

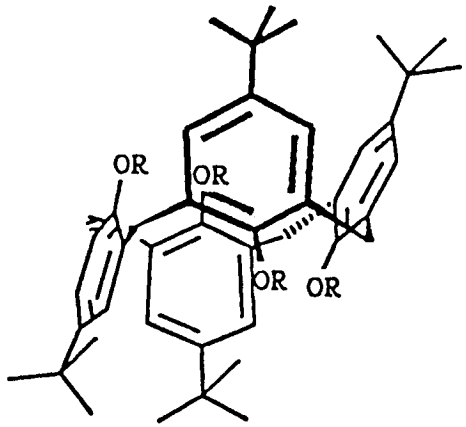
Conformations of calix[4]arene tetra-ethers



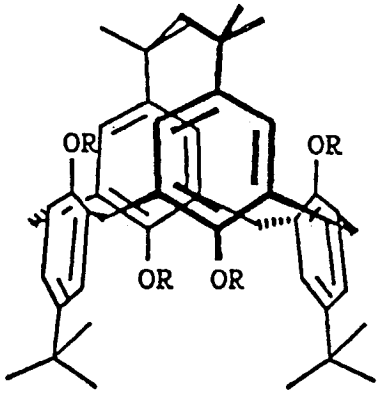
Cone



Partial Cone



1,2-Alternate

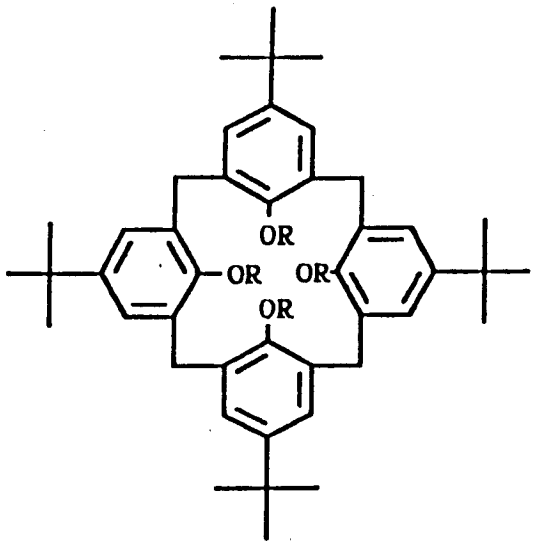


1,3-Alternate

C.D. Gutsche, Calixarenes, Monograph in Supramolecular Chemistry, Stoddart J.F. (Ed.) Royal Society of Chemistry, Cambridge 1989

Molecular mechanics energies of the conformations

of tetra-alkylated calix[4]arenes (kcal mol^{-1})

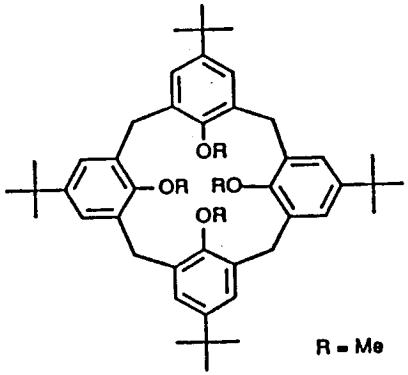


R	PACO	CONE	1,2-ALT.	1,3-ALT.
CH_3	64.80	70.81	68.60	66.55
C_2H_5	76.02	96.60	84.75	62.49

L. Groenen et. al. J. Am. Chem. Soc., **113**, 2385-2392 (1991)

600 MHz ^{1}H NMR Spectrum of tetra-methoxy-p-tert-butylcalix[4]arene

T = -30°C



+ cone

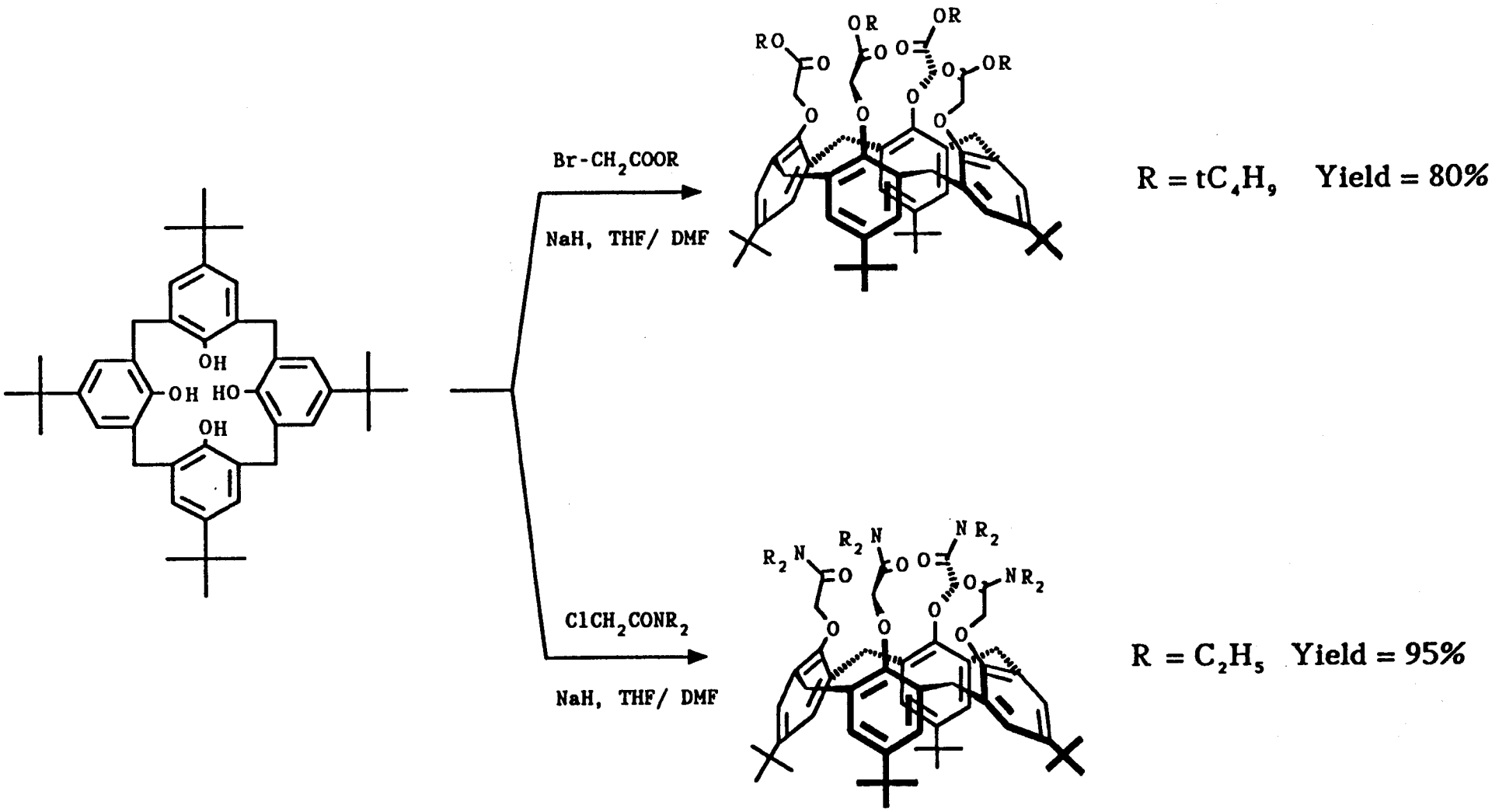
□ partial cone

◊ 1,2-alternate

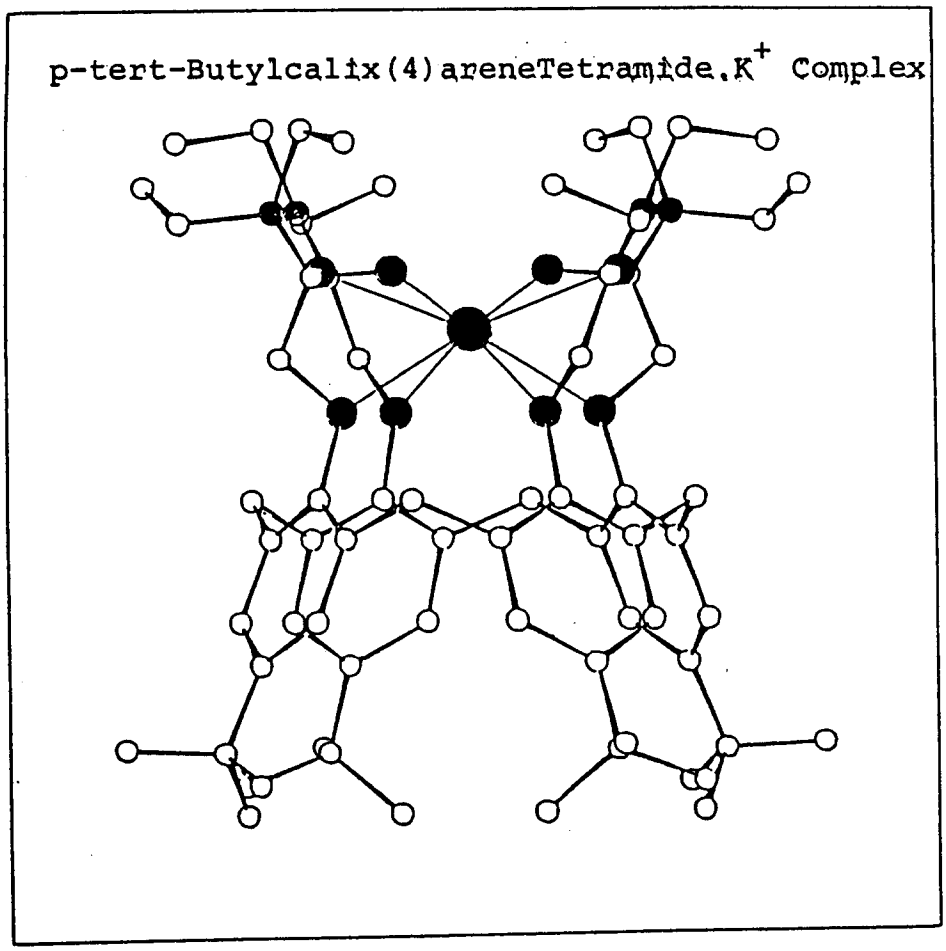
△ 1,3-alternate

L. Groenen et. al. J. Am. Chem. Soc., **113**, 2385-2392 (1991)

Ligands from calix[4]arenes in the fixed cone conformation



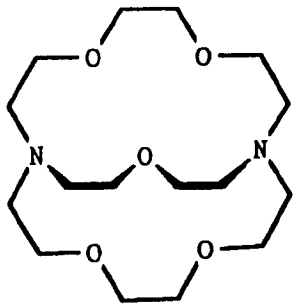
R. Ungaro et al., J.Chem.Soc., Chem.Commun., 981-982 (1984); Tetrahedron, **42**, 2089-2100 (1986); J.Inclusion Phenom., **6**, 119-134 (1988).



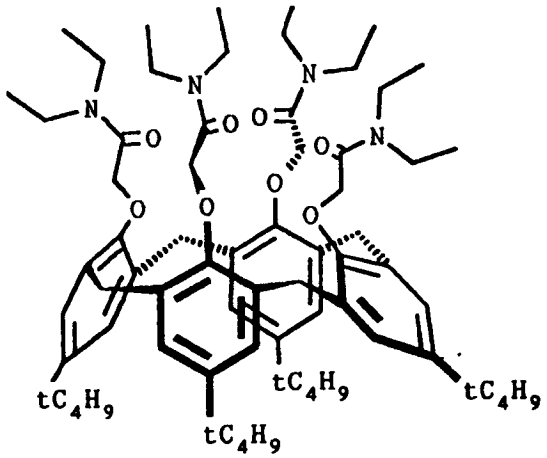
R. Ungaro et al., J.Inclusion Phenom., 6, 119-134 (1988).

Stability Constants (log β) for Selected Complexes of Cryptand 221 (1)

and Tetramide Ligand (2) in MeOH



1



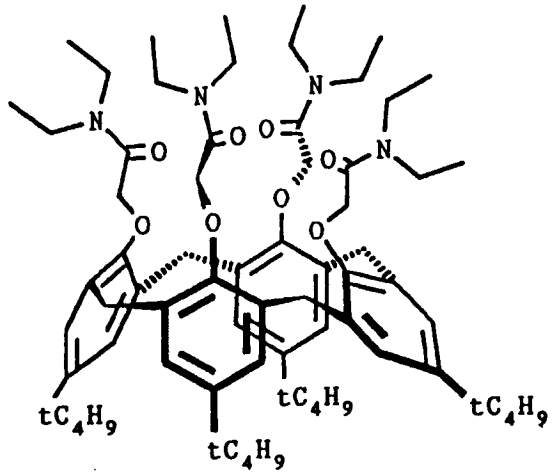
2

	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
1[a]	5.4	8.6	8.5	6.7	4.3	4.2	9.3	10.7
2[b]	3.9	7.9	5.8	3.8	2.4	1.2	>9	7.2

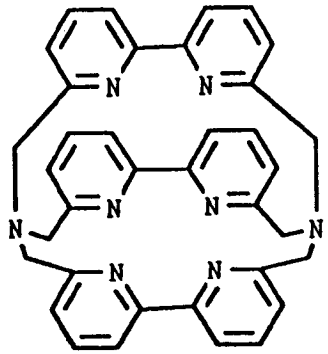
a) B. Cox et al. J. Am. Chem. Soc. 1981, 103, 1384

b) F. Arnaud et al. New J. Chem. 1991, 15, 33

Encapsulation of Lanthanide Ions: Luminescence Probes



1



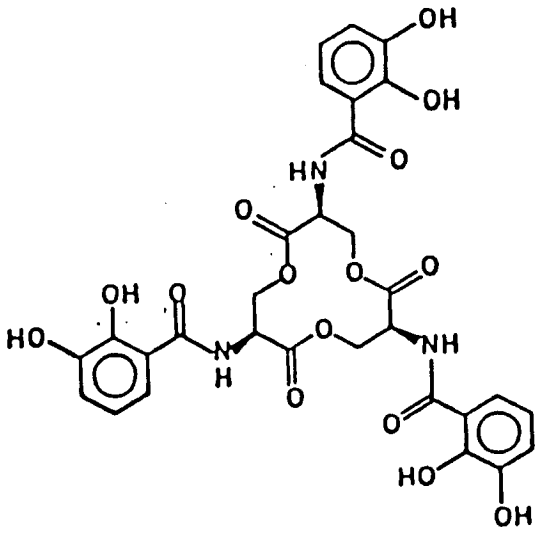
2

Complex	Absorption		Emission		
	λ_{max} [nm]	ϵ_{max} [$M^{-1} \cdot cm^{-1}$]	λ_{max} [nm]	$\tau_{H_2O}^{300K}$ [ms]	ϕ
$[Eu \subset 1]^{3+}$	270	1500	614	0.65	10^{-4}
$[Tb \subset 1]^{3+}$	270	1500	545	1.50	0.20
[a]$[Eu \subset 2]^{3+}$	304	25000	615	0.34	0.02
[a]$[Tb \subset 2]^{3+}$	304	29000	542	0.33	0.03

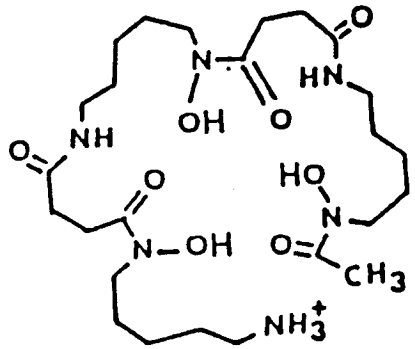
[a] B. Alpha et al., Angew.Chem. Int. Ed. Eng., 26, 1266 (1987).

N. Sabbatini et. al. J. Chem. Soc. Chem. Commun., 878-879 (1990)

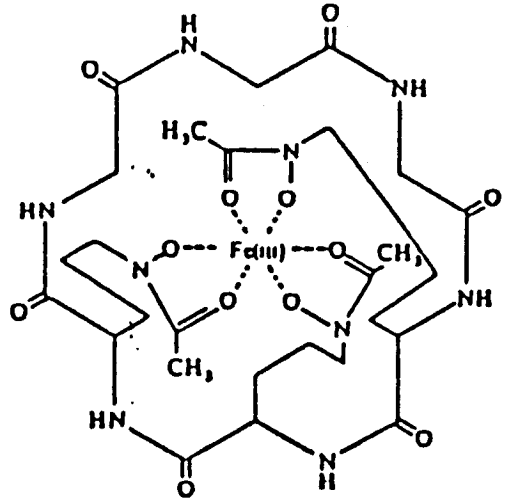
NATURAL SIDEROPHORES



Enterobactin



Desferrioxamine B



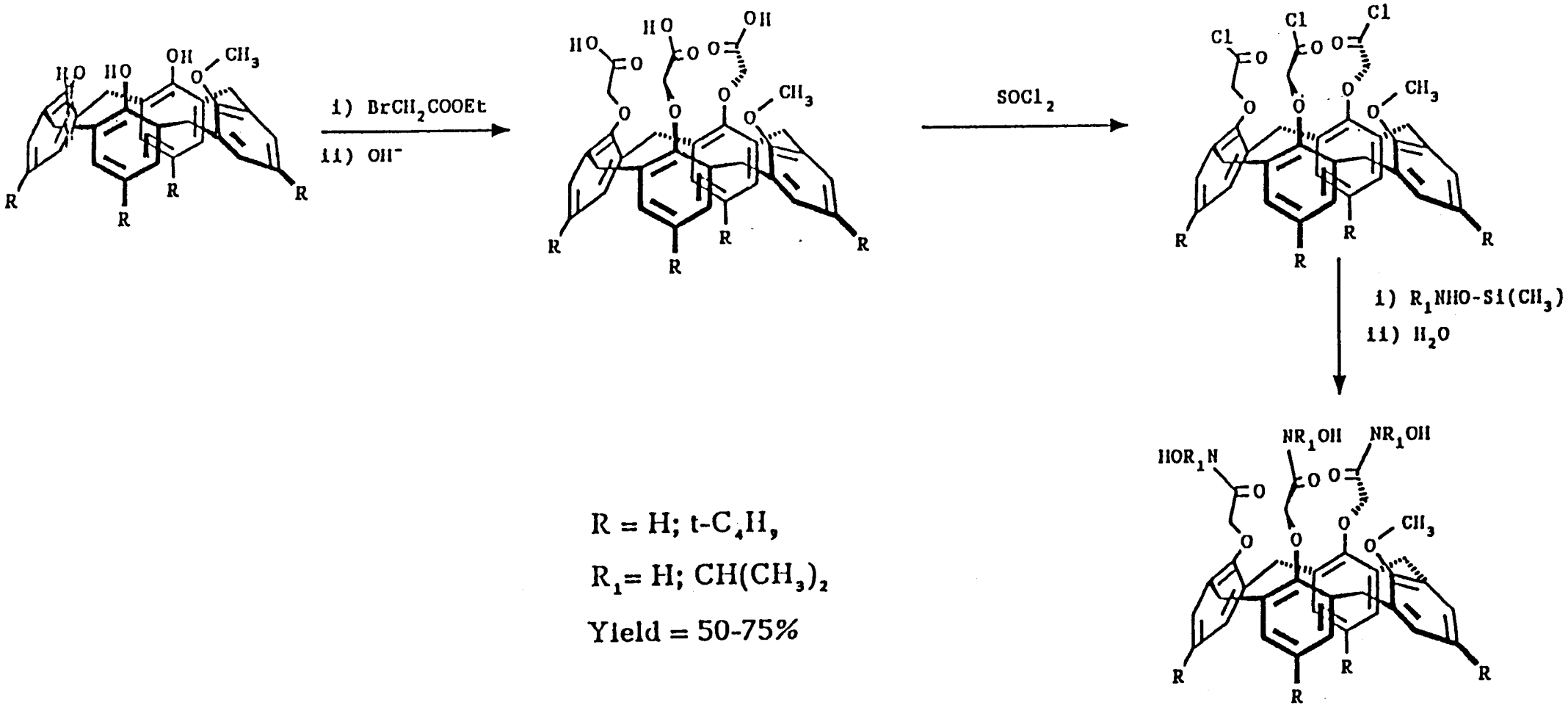
Ferrichrome

log β 110 52.0

30.1

29.1

Synthesis of tri-hydroxamate siderophores



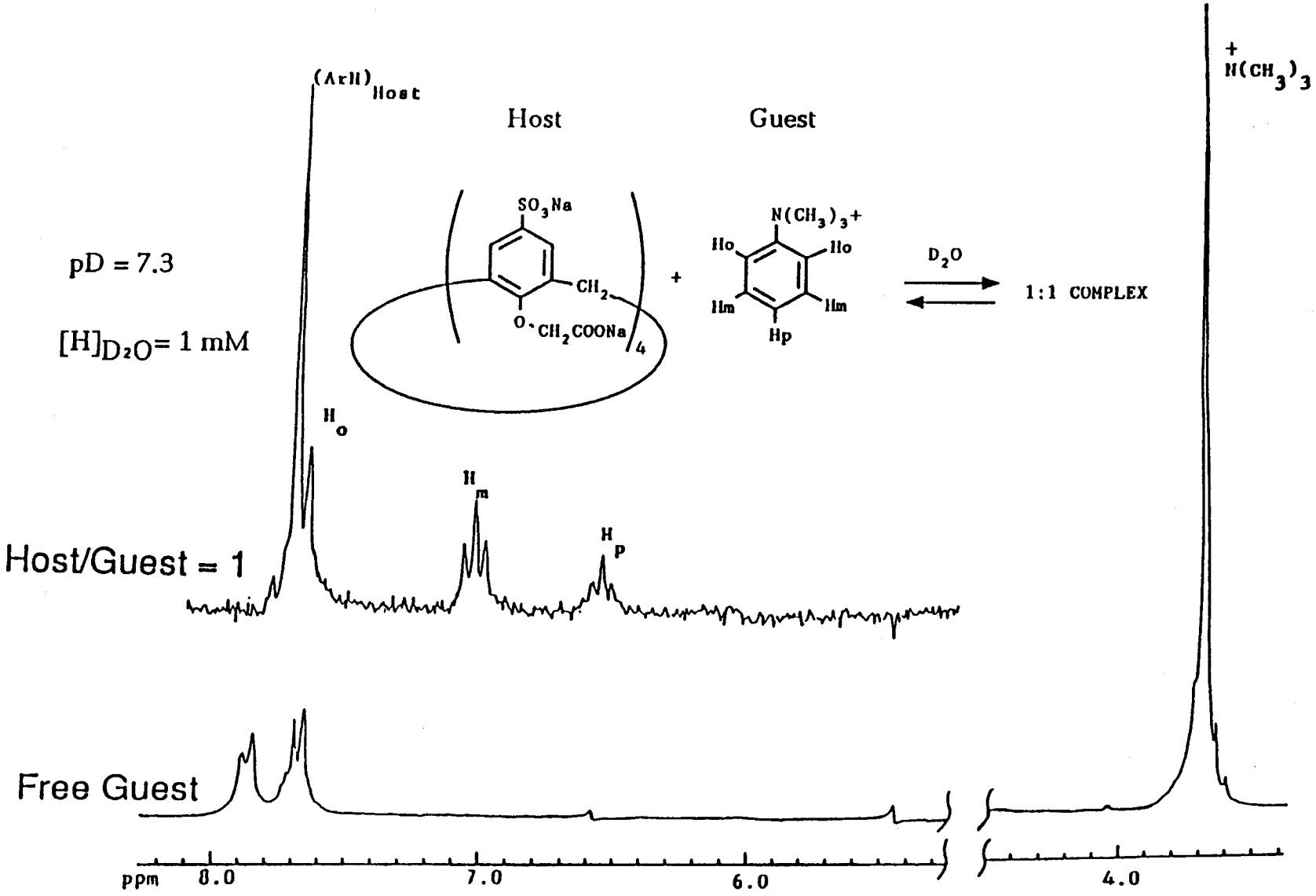
R = H; t-C_4H_9,

R_1= H; $CH(CH_3)_2$

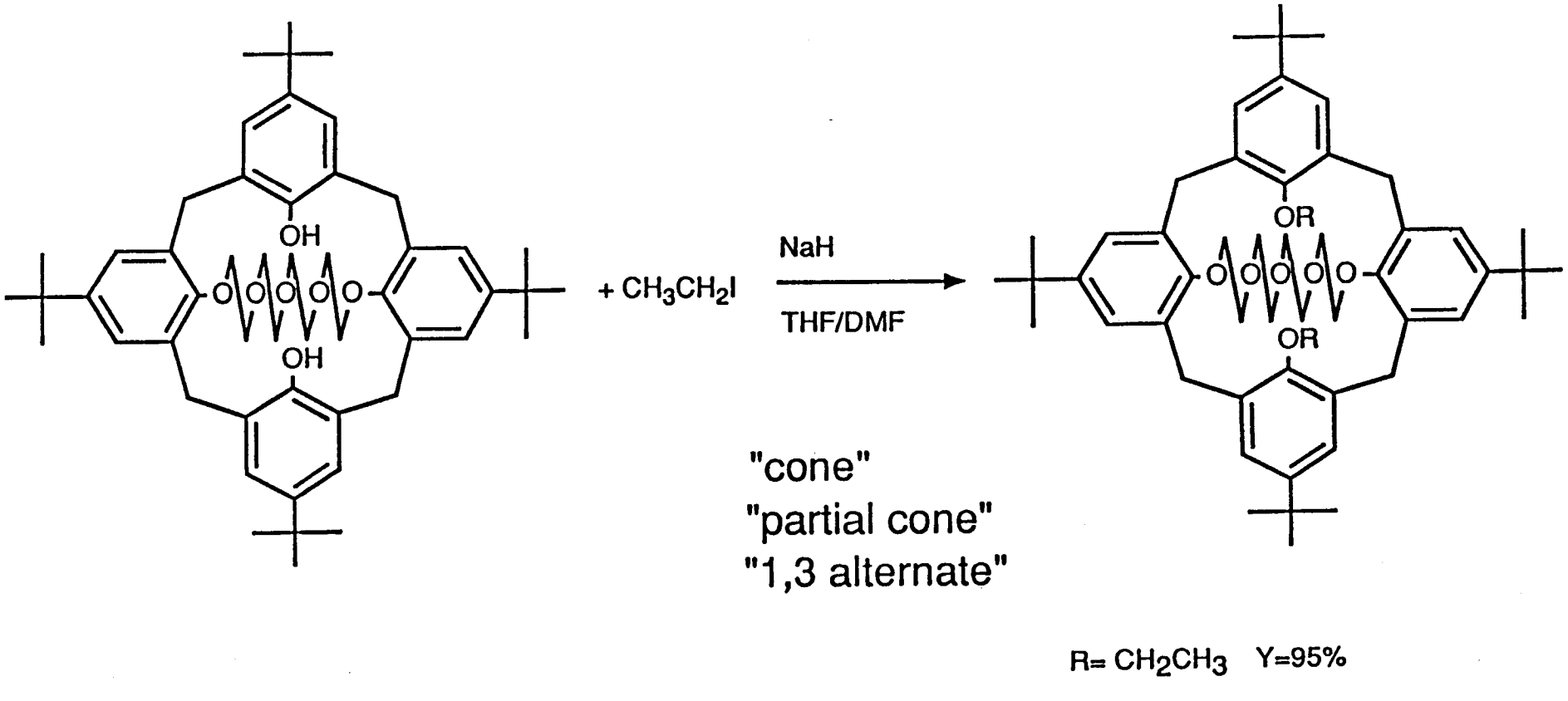
Yield = 50-75%

A. Arduini et. al. Supramolecular Chem, in press.

Inclusion of Organic Cations in Water Soluble Calix[4]arenes Fixed in the Cone Conformation

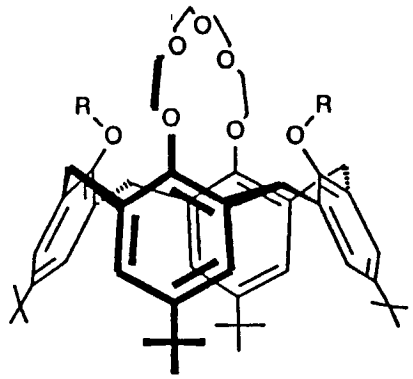
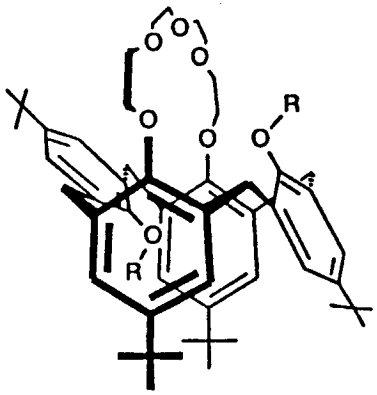
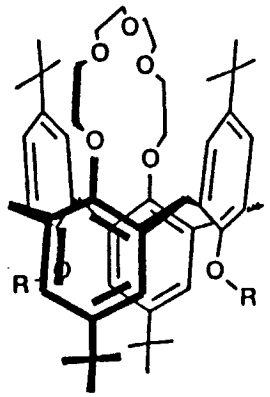


A. Arduini et. al. in Supramolecular Chemistry, V. Balzani and L. De Cola (Eds.) Kluwer Academic Publ., 1992 pp. 31-50



E. Ghidini et. al. J. Am. Chem. Soc. **112**, 6979-6985 (1990)

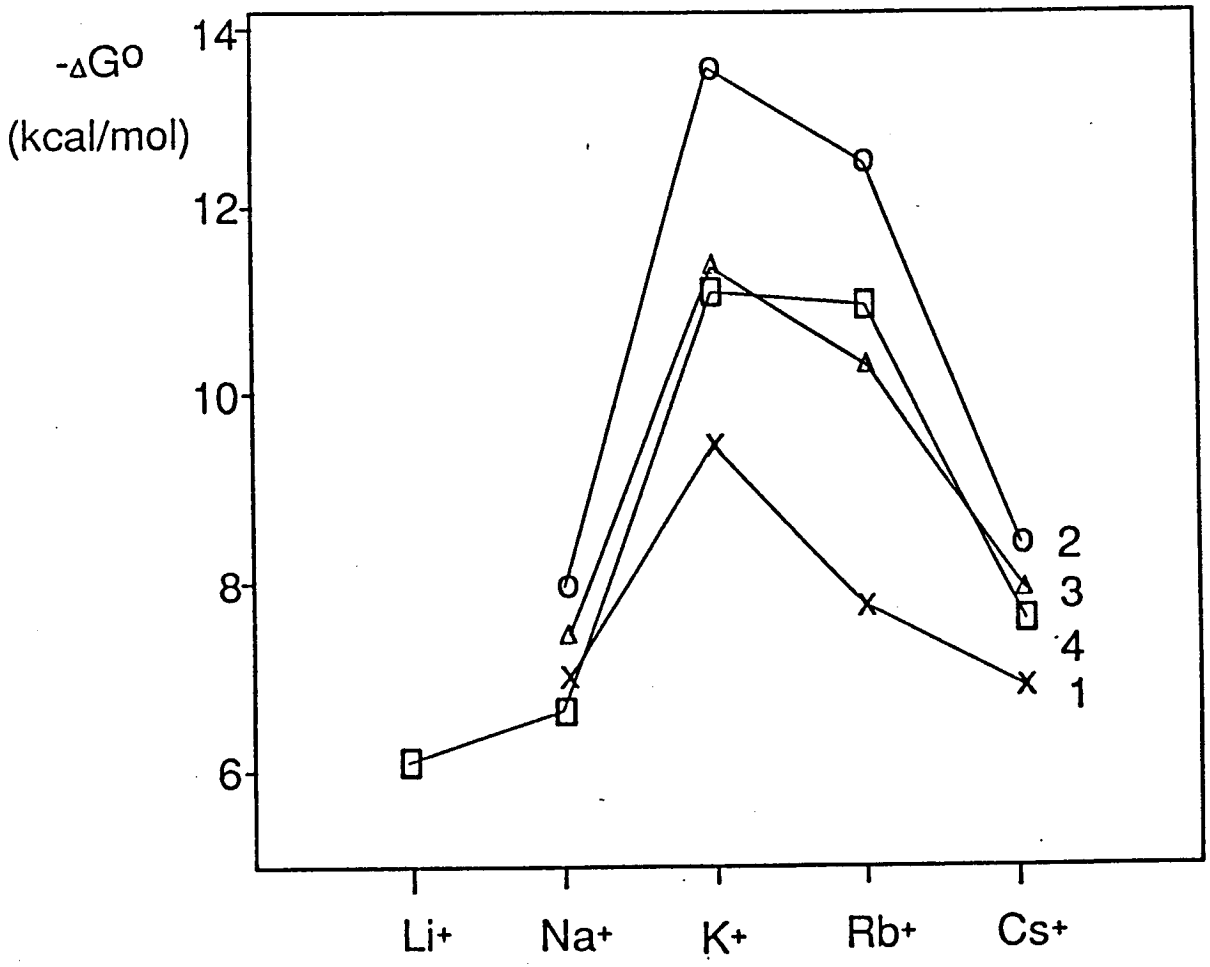
Isolated yield (%) of stereoisomers

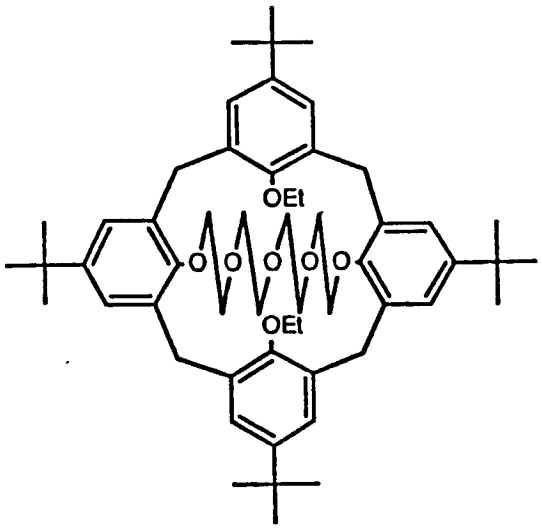
			
R = CH_3	75	-	-
R = CH_2CH_3	53	28	13
R = CH_2Bz	66	15	-
R = $(CH_2)_2CH_3$	42	28	-
R = $CH(CH_3)_2$	10	73	-

E. Ghidini et. al. J. Am. Chem. Soc. **112**, 6979-6985 (1990)

Binding free energies ($-\Delta G^o$) of alkali picrate complexes

($CDCl_3$, 22°C)





1 = cone (x)

2 = partial cone (o)

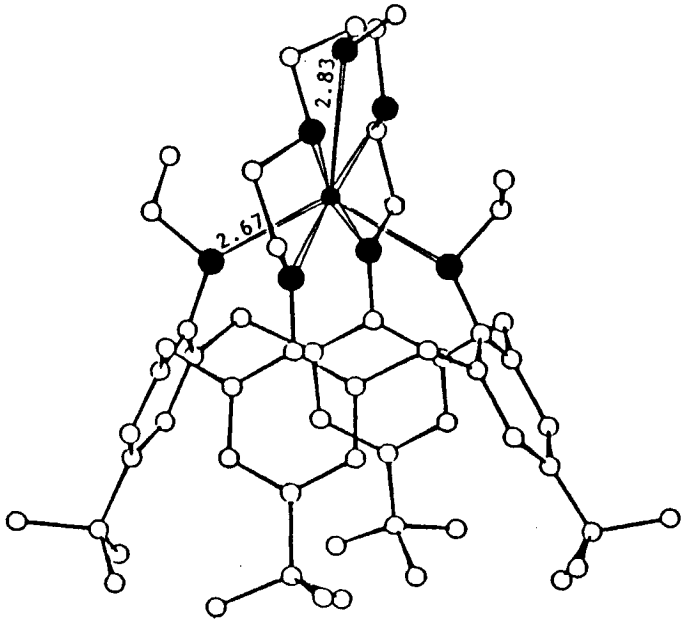
3 = 1,3 alternate (Δ)

4 = R = CH_3 (□)

E. Ghidini et. al. J. Am. Chem. Soc. **112**, 6979-6985 (1990)

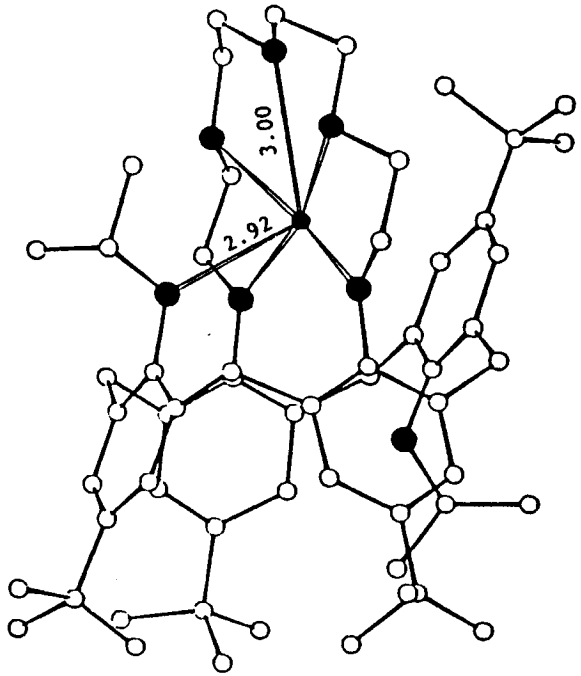
K^+ Complexes

diethyl-cone



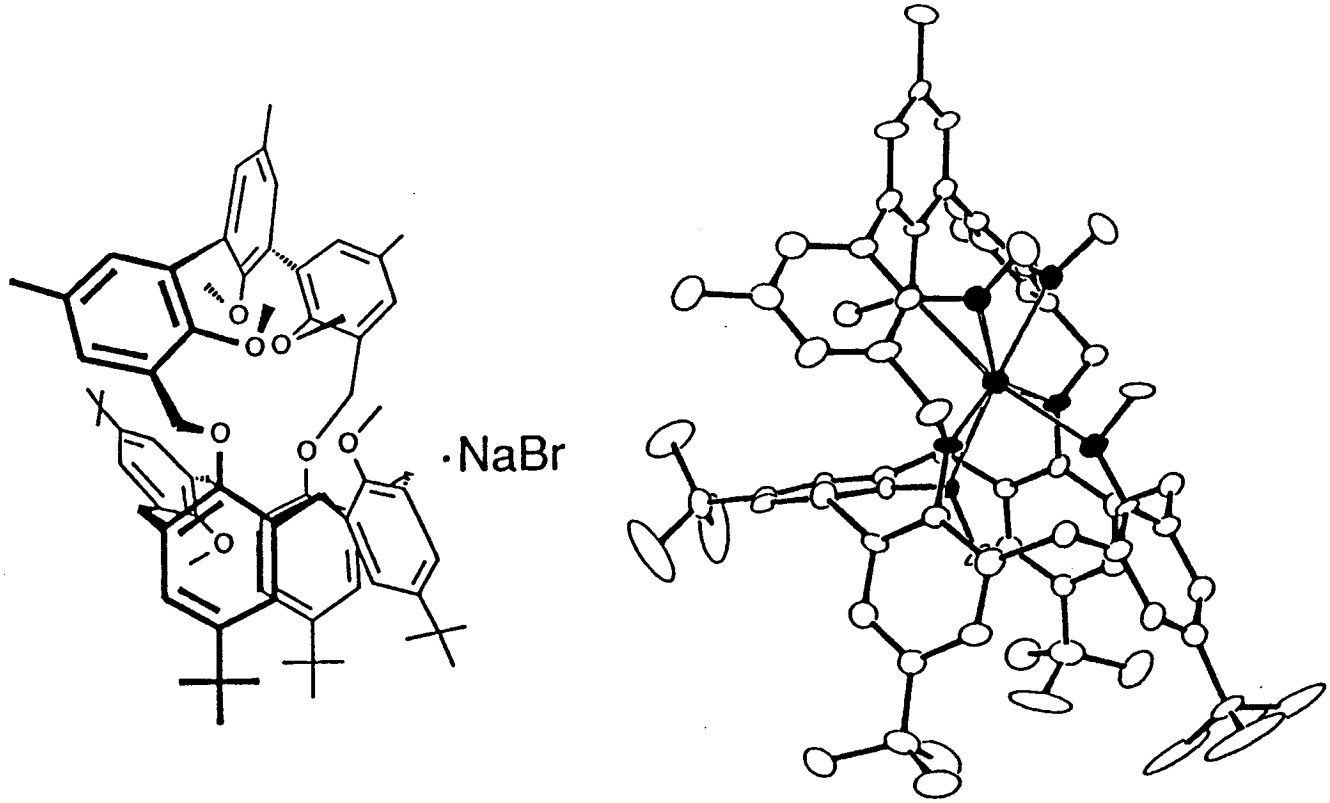
$-\Delta G^{\circ}$(kcal mol^{-1}) in $CDCl_3$ = 9.6

diisopropyl - partial cone



$-\Delta G^{\circ}$(kcal mol^{-1}) in $CDCl_3$ = 12.6

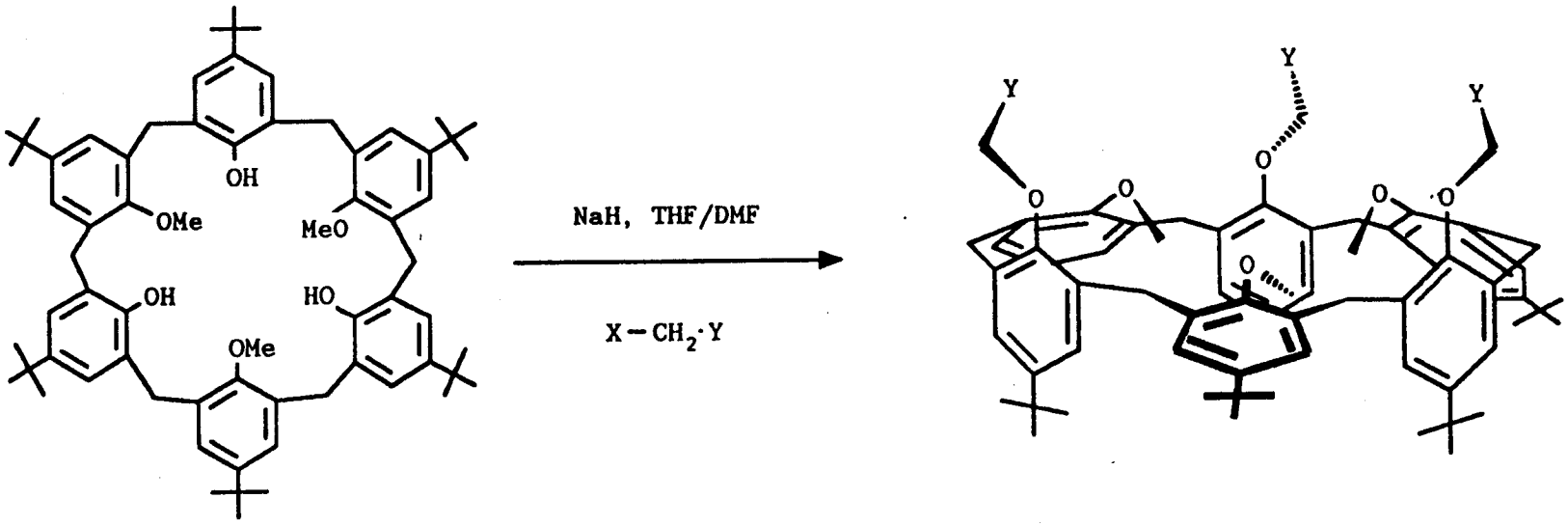
E. Ghidini et. al. J. Am. Chem. Soc. **112**, 6979-6985 (1990)



Calixspherand · NaBr complex

A.S Dijkstra et. al. J. Am. Chem. Soc., **111**, 7567-7575 (1989)

p-tert-Butylcalix[6]arene Derivatives in the Fixed Cone Conformation



X = Cl ; Y = $CON(C_2H_5)_2$ Yield = 75%

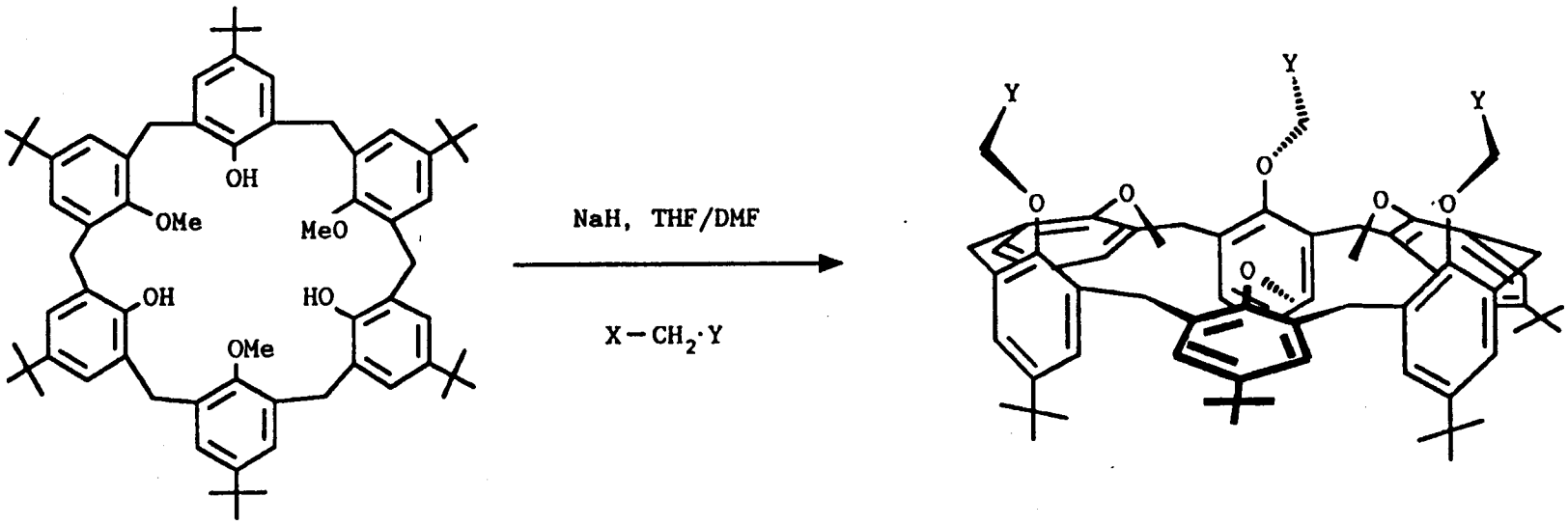
X = Br ; Y = $COOtC_4H_9$ Yield = 80%

X = Br ; Y = Ph Yield = 80%

A. Casnati et. al. J. Chem. Soc. Chem. Commun. 1413-1414 (1991)

A. Casnati et. al. Israel J. Chem., 1992 in press

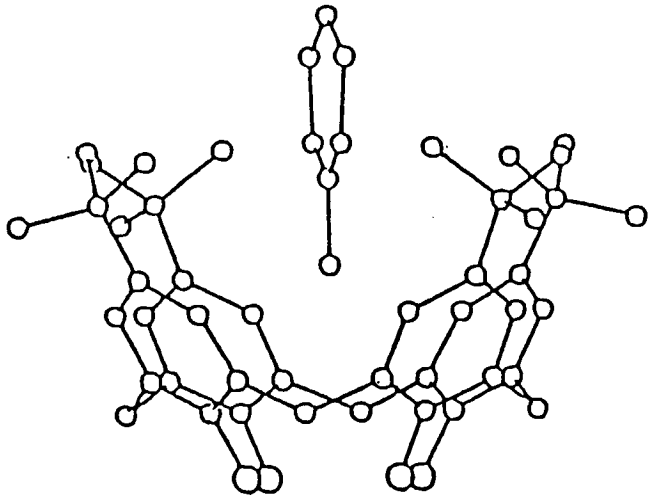
p-tert-Butylcalix[6]arene Derivatives in the Fixed Cone Conformation



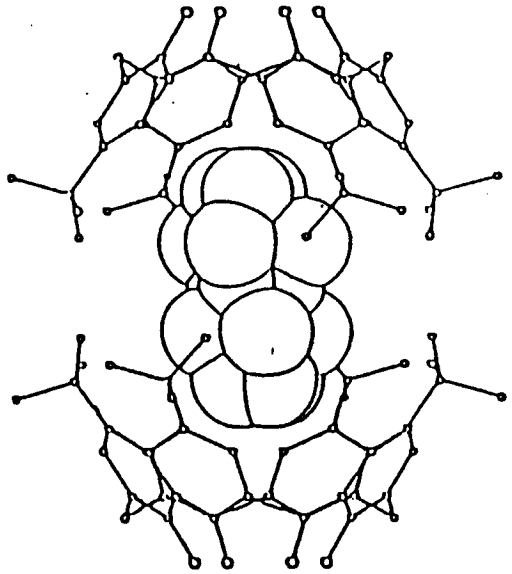
X = Cl ;	Y = $CON(C_2H_5)_2$	Yield = 75%
X = Br ;	Y = $COOtC_4H_9$	Yield = 80%
X = Br ;	Y = Ph	Yield = 80%

A. Casnati et. al. J. Chem. Soc. Chem. Commun. 1413-1414 (1991)

A. Casnati et. al. Israel J. Chem., 1992 in press



p-TertButylCalix[4]Arene / Toluene 1:1

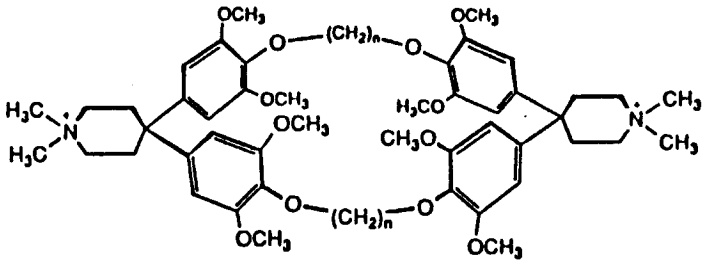


p-TertButylCalix[4]Arene / Anisole 2:1

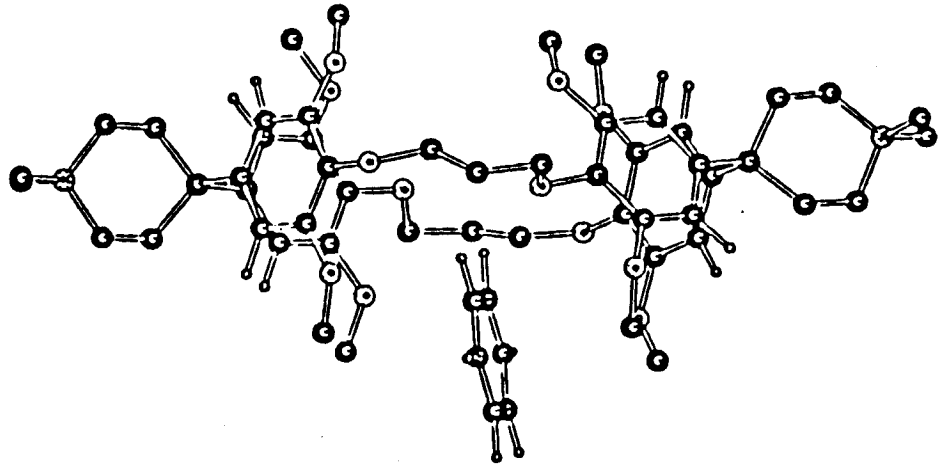
G.D. Andreetti, R. Ungaro, A. Pochini, J.Chem.Soc., Chem.Commun., 1005-1006 (1979).

M.Coruzzi et al., J. Chem. Soc. Perkin Trans. 2, 1133-1141 (1982).

Monte Carlo Calculated Structure for the Complex of Host 1 and Benzene

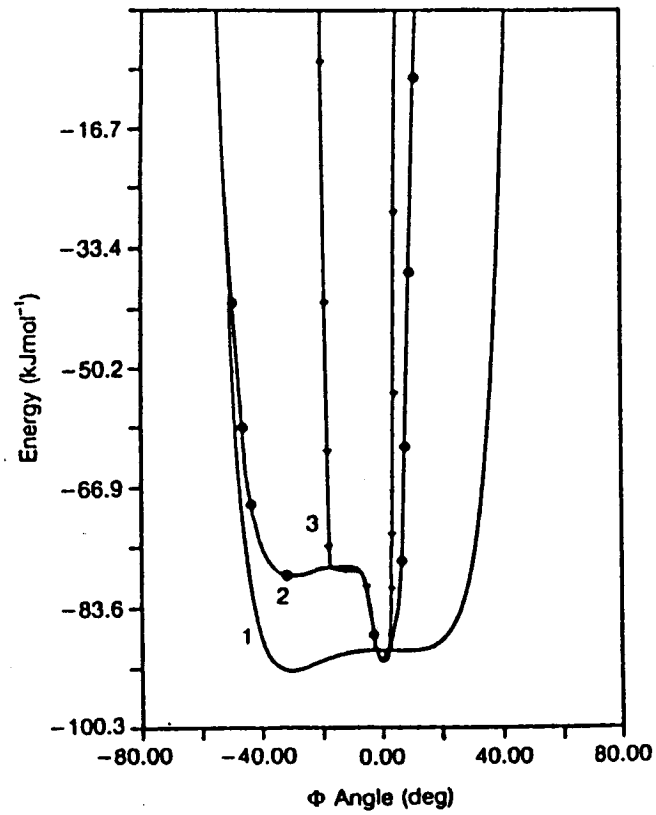


1 n = 3



W.L. Jorgensen, T.B. Nguien, in "Supramolecular Chemistry ", V. Balzani, L. De Cola (Eds.), Kluwer, 1992, pp. 383-394.

Looking for $CH_3 \cdots \pi$ Attractive Interactions
Theoretical Models



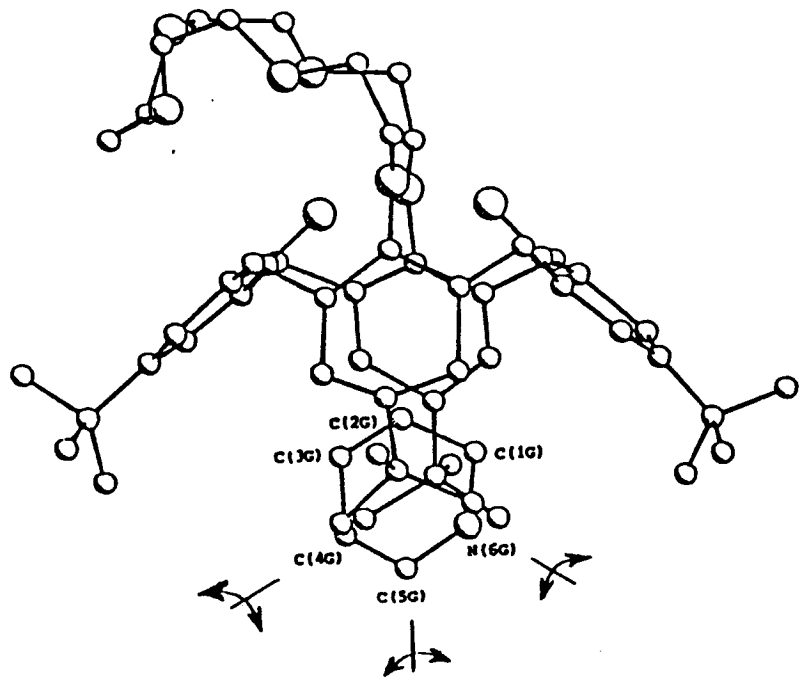
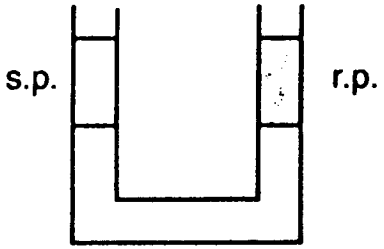


Fig. 3.26 Total potential energy of the system. (1) $U = U_{vdw} + U_{el}$ calculated as a function of rotations around the C(1G)-C(4G) or C(2G)-C(5G) or C(3G)-N(6G) axes. (2) $U = U_{vdw} + U_{el} + U_{CH\cdots N}$ calculated as a function of rotations around the C(1G)-C(4G) or C(2G)-C(5G) axes. (3) $U = U_{vdw} + U_{el} + U_{CH\cdots N} + U_{CH_3\cdots\pi}$ contributions calculated as a function of rotations around the C(1G)-C(4G) and C(2G)-C(5G) axes.

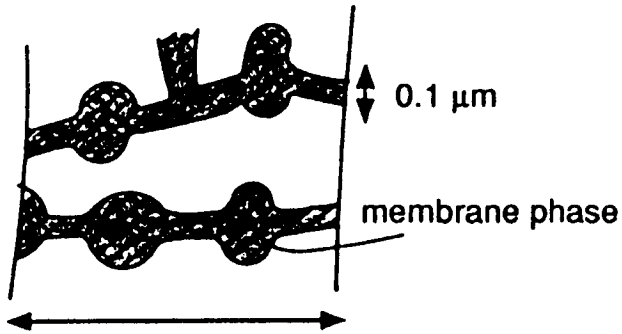
G.D. Andreetti et. al. J. Inclusion. Phenom. 6, 523-528 (1988)

U-tube system



$CHCl_3$/Carrier

Liquid Immobilized Membranes



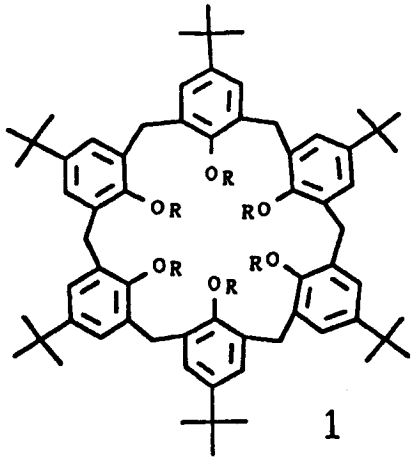
$d_0 = 100\ \mu m$

Accurel^R /NPOE/Carrier

NPOE = o-nitrophenyl octyl ether

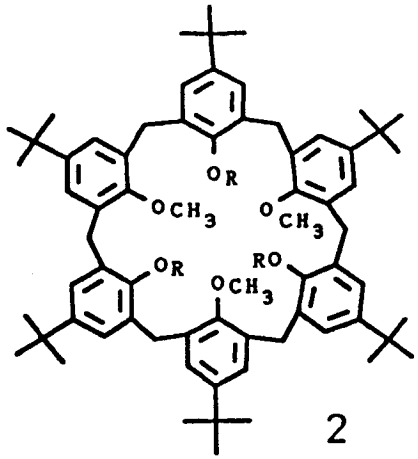
$$J = \frac{D_m}{d_0}\ [complex]_m$$

Transport of Guanidinium, Sodium and Potassium Cations through a Supported Liquid Membrane (Accurel^{R}/NPOE)



1

$R\text{-}CH_2CON(C_2H_5)_2$



2

Ligand	Gu^{+} [a]	Na^{+} [a]	K^{+} [a]
1	25.9	18.4	17.7
2	5.3	0.7	1.3
blank [b]	0.9	0.3	0.5

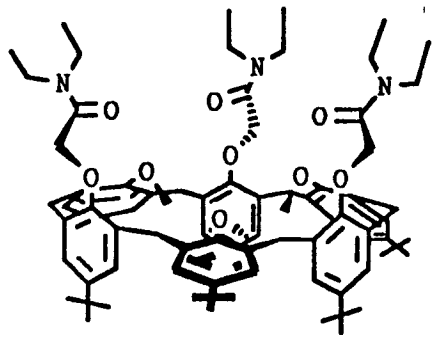
[a] Fluxes J in 10^{-8} mol $cm^{-2}h^{-1}$; $[thiocyanates]_{s.p.}$ = 0.1M.; $[carrier]_m$ = 10^{-2}M; T=298K

[b] Fluxes in absence of carrier

A. Casnati et. al. Israel J. Chem., 1992 in press

Carrier Mediated Transport of Cation and Amino Acid Ethyl Ester Picrates through Liquid Membranes (U-tube system)

Carrier



Picrate	Flux (10^{-6}mol·h^{-1}·cm^{-2})
Na^+	No Transport
K^+	No Transport
NH_4^+	No Transport
L-Alanine	No Transport
L-Arginine	0.295

$[Picrate]_{H2O} = 10^{-2}M$; $[carrier]_{CHCl3} = 10^{-3}M$