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New tailored hosts: From molecular recognition to mechanical bonds

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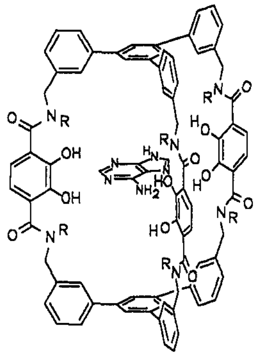
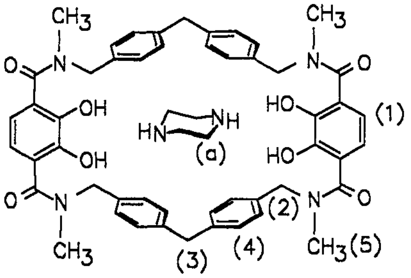
Abstract - Recent developments in the areas of "*all*-homocalixarenes", "tweezers" and "catenanes" are reported.

A. *all*-HOMOCALIXARENES: NEW CARBOCYCLIC HOSTS

Combining host/guest chemistry and cyclophane chemistry we investigated endofunctionalized macro*bi*cyclic (**I**) [1] and macro*mono*cyclic (**II**) [2] host molecules. Concerning these cavity-containing macrocyclic phanes we were successful in complexing basic guests as shown in **I** and **II** as well as acidic guests by molecular cavities containing bipyridine moieties [3].

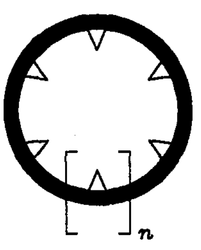


I (+ guest)



II (+ guest)

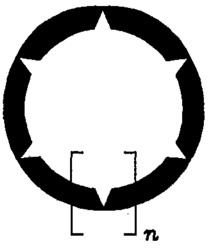
Triggered by these findings and by the need of tailored sensor materials we now designed a new type of endoacidic cavities **IIIa** formed by a large ring *carbon* skeleton and their endobasic analogs **IIIb**:



Δ ≙ OH-groups

(endoacidic; hydrogen bond donor)

IIIa



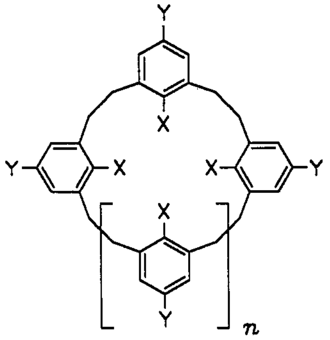
∇ ≙ N

(endobasic; hydrogen bond acceptor)

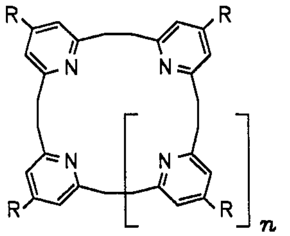
IIIb

In contrast to **I** and **II** *carbon-carbon bonds* are formed here in the decisive cyclization step. The stable carbon skeleton of **III** allows to modify the funtional groups even by rigorous procedures.

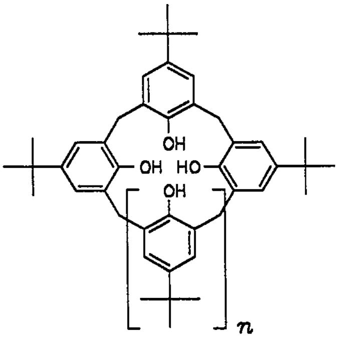
This new host type was achieved by the synthesis of [2_n]metacyclophanes of the following general type **IV** (endoacidic) and **V** (endobasic) - which we call for reasons of simplicitiy "homocalixarenes" - because in favour of flexibility all of their bridges contain one additional CH_2-group compared to calixarenes (VI). In this way unfavourable rigid conformers (perhaps unable to enclose guests) are just as avoided as mixtures of stable conformers which have to be characterized and separated.



IV



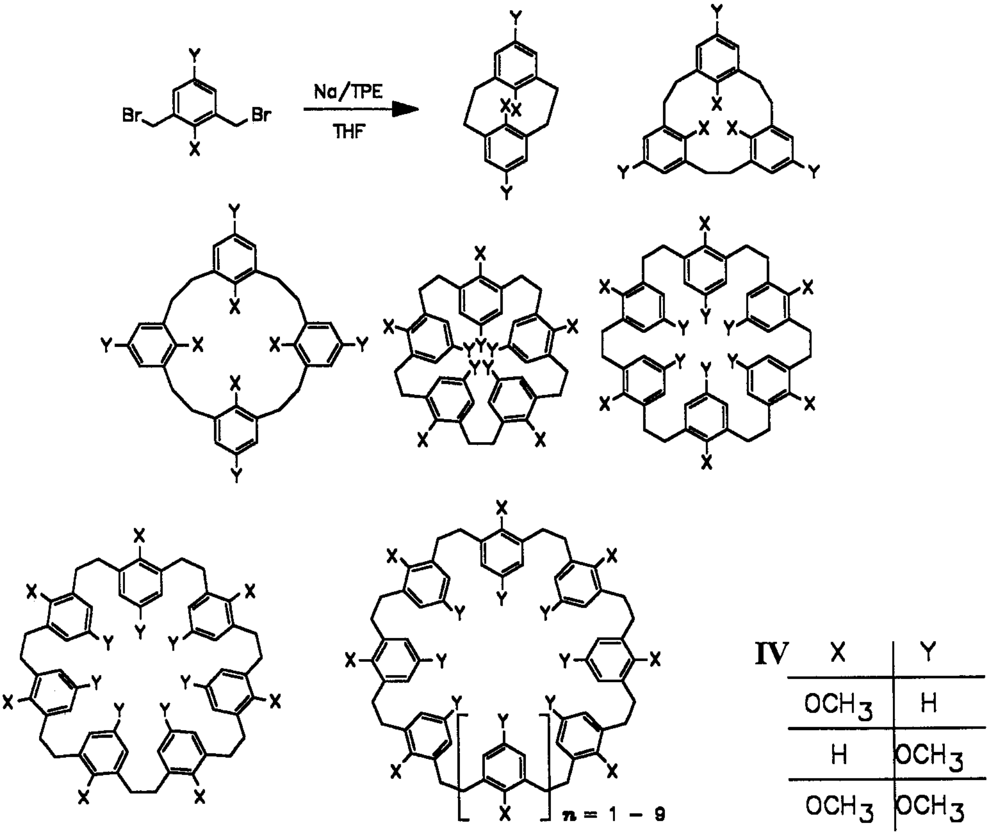
V



VI

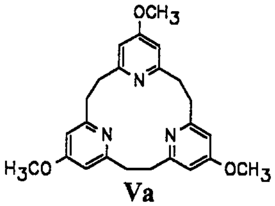
The aromatic structural units ensure the necessary rigidity of the host molecules, they form an anchor skeleton for functional groups and they bear the various coordination sites for a cooperative binding of guests. Apart from this the cavity size is eligible by varying the number of aromatic units which can be synthetically controlled by intra- and extraannular groups X, Y.

The *all*-homocalixarenes are prepared by *Müller-Röscheisen*-cyclization which yields in one step a complete spectrum of various cyclooligomers of both large ring types IV and V. A series of representatives have been isolated and characterized by physical methods including x-ray-analyses.

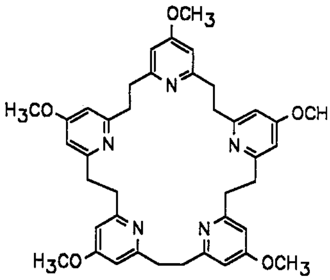


IV	X	Y
	OCH_3	H
	H	OCH_3
	OCH_3	OCH_3

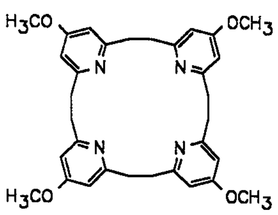
For complexation of several kinds of guests it proved possible to endow the homocalixarenes with endoacidic or alternatively with various endobasic functional groups. Moreover, an influence on the binding strength of the hosts towards their guests can be exerted by fitting them with OR-groups in the 4-position which obviously enhances the donor-capacity, nucleophilicity and basicity of the pyridine nitrogen atoms in **Va-d**.



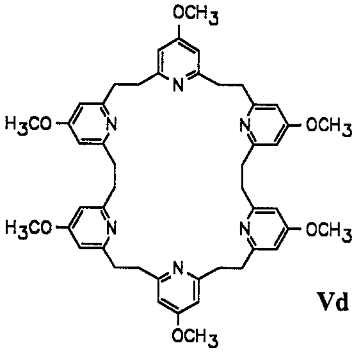
Va



Vb



Vc

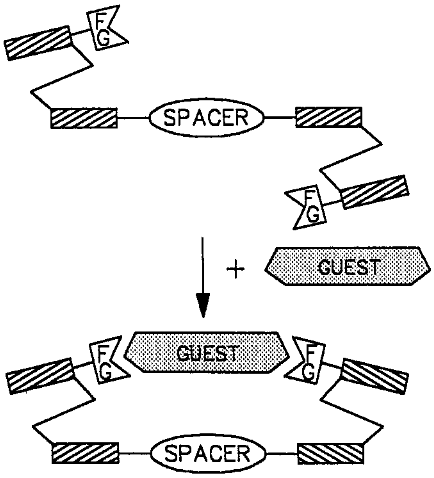


Vd

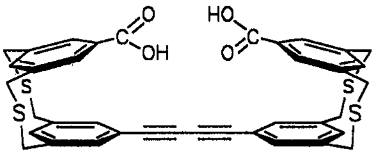
In addition the new architecture allows to fix lipophilic groups at various positions. A big advantage of these homocalixarenes is their good solubility in lipophilic solvents. They are therefore attractive as synthetic receptor molecules. Guests that could be bound selectively with these new carbocyclic hosts comprise so far metal cations, diamines and nucleic bases [4-6].

B. MOLECULAR TWEEZERS

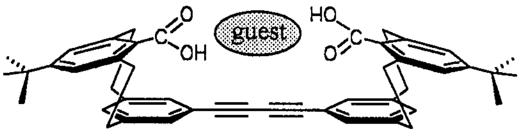
New molecular tweezers of the following general type fitted with well preorganized functional groups have been prepared [7]:



The connection of two appropriate rigid cyclophane units separated by a spacer yields a molecular niche into which two convergent carboxy groups project. Host/guest-studies with the new molecular tweezers **VII–VIII** show high association constants towards diamines, purine and pyrimidine nucleic bases as guests [7]:



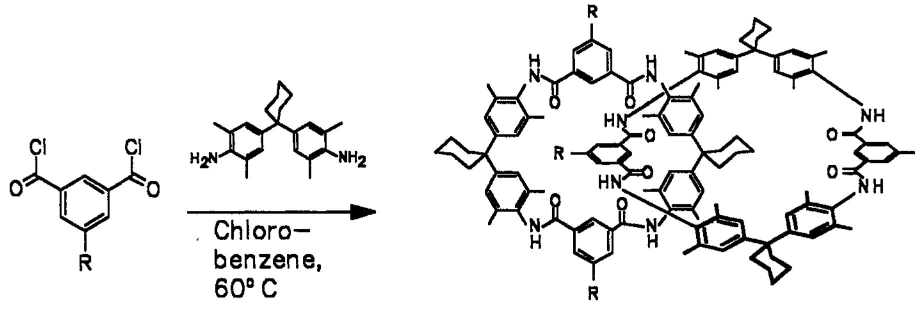
VII



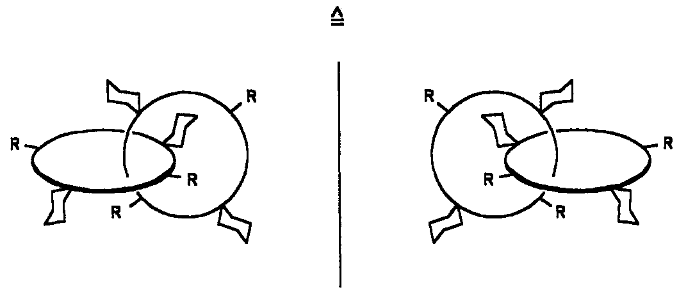
VIII

C. CATENANES

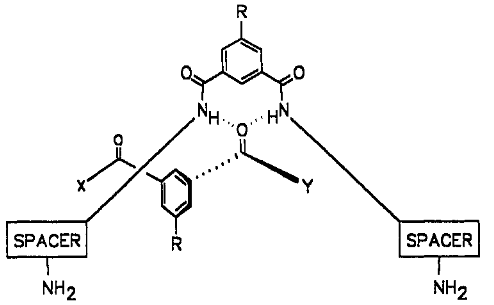
A new catenane type **IX** [8] was discovered in a one step one pot synthesis starting from simple compounds. As a consequence of the relatively fixed conformation the fourfold functionalized catenane **IX** should exist in enantiomeric forms:



IX



The template assistance in the catenane forming reaction may be due to "orthogonalization" of the intermediates by C(O)···H-N-hydrogen bonds:



IX: X,Y = Cl, NHR
R = OCH_3

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[6] We thank Prof. Dr. K. Gloe, Dr. O. Heitzsch and Dr. H. Stephan for careful extraction studies and DECHEMA e. V. (BMFT-project NT 2057 4) for financial assistance.

B: [7] R. Güther, M. Nieger, F. Vögtle, *Angew. Chem. 105*,(1993), in press.

C: [8] F. Vögtle, S. Meier, R. Hoss, *Angew.Chem. 104*, 1628 (1992); *Angew. Chem. Int. Ed. Engl. 31*, 1619 (1992); cf. C. A. Hunter, *J. Am. Chem. Soc. 114*, 5303-5311 (1992).