CAVITANDS. (REVIEW)

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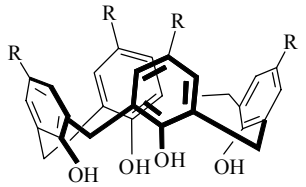
The syntheses, reactivity and complexing properties of cavitands are reviewed.

Keywords: calixarenes, cavity, complexation, host-guest systems, inclusion, resorcinarenes.

Cavitands are derivatives of resorcinarenes, which are compounds related to the calixarene family. Calixarenes **1** [1-6], resorcinarenes **2** [7-12], cavitands **3** [13-16], and cyclotriveratrylenes **4** [17-19] are promising as host molecules in supramolecular chemistry.



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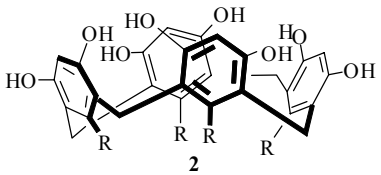

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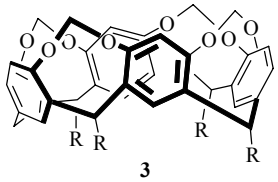

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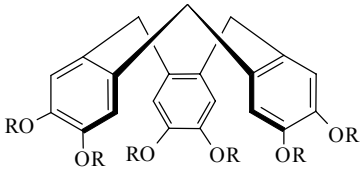

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In the present paper selected examples of cavitands are described in view of their syntheses, reactivity, and complexing properties. References of works that appeared during the years 1998-2000 are cited.

1. SIMPLE CAVITANDS

Cavitands are bowl-shaped macrocycles of a rigid structure, readily obtained by bridging the hydroxyl groups of neighboring aromatic rings of resorcinarenes; they are of interest in host-guest chemistry serving as receptors [20-22]. The large cavities of these species allow using them as hydrogen-bonded networks [23].

In the synthesis of cavitands bromochloromethane often serves as bridging reagent; in this way resorcinarenes **5** can be converted into cavitands **6** [24].

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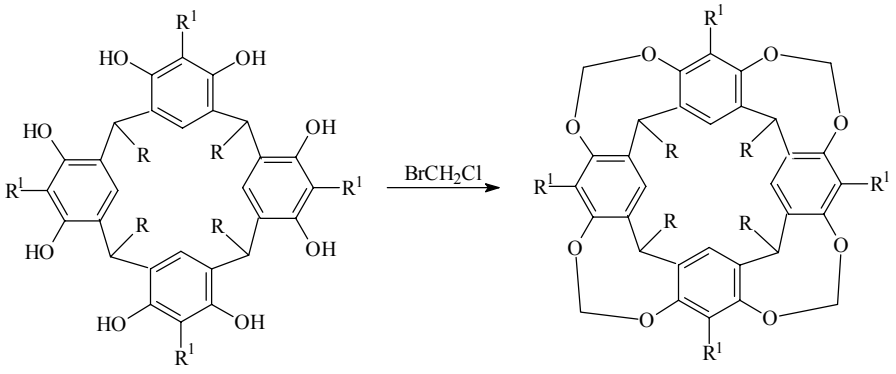
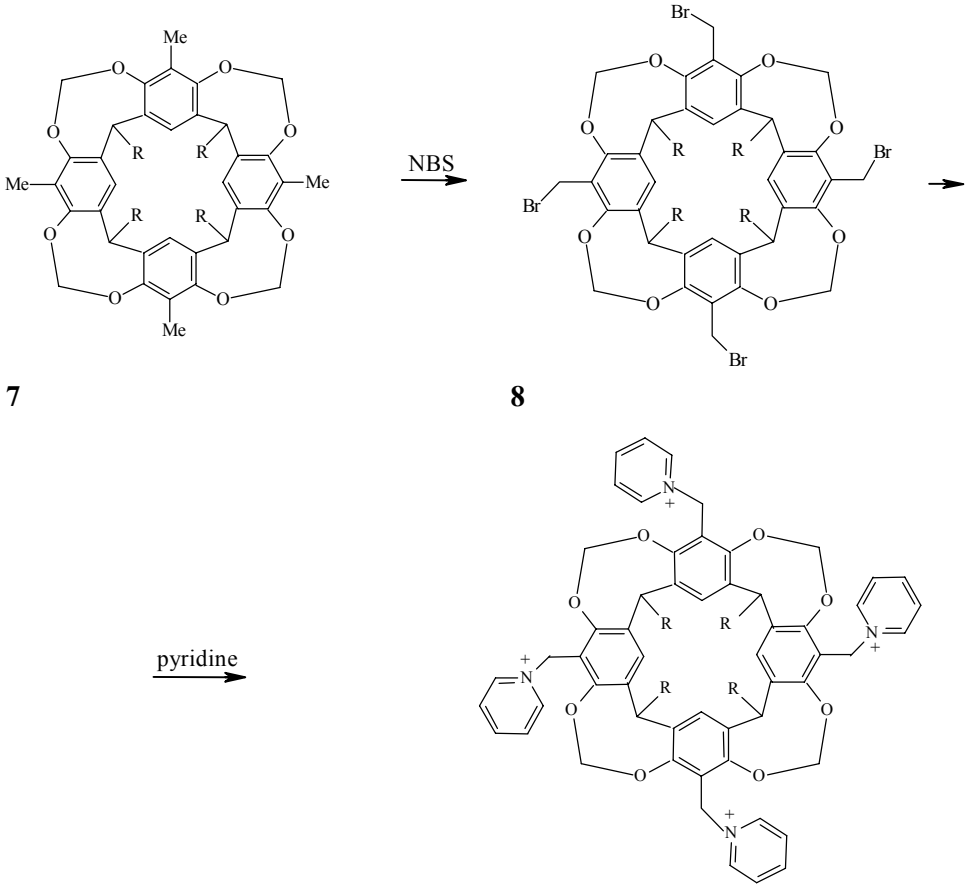


5 **6**

R = alkyl, aryl; R^1 = H, OH, Me

The reaction of compounds **7** with NBS affords bromomethylcavitands **8**, which react with pyridine to give cationic species **9a-c**. Cavitands **9** are water-soluble over a broad pH range. Methylcavitand **9a** forms with *p*-cresol and *p*-toluenesulfonate 1:1 host-guest complexes [24].

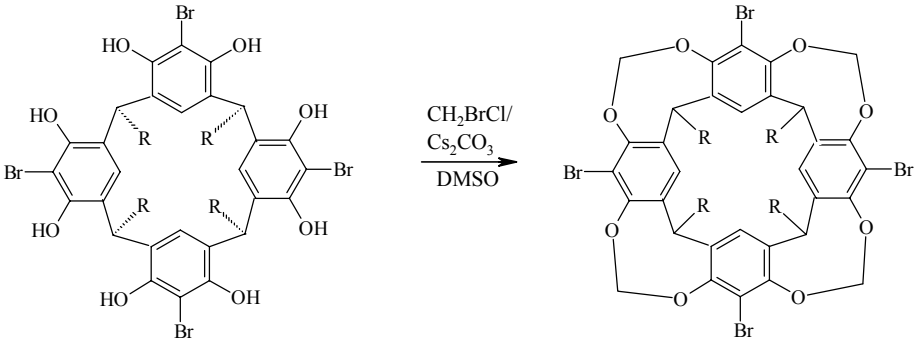


7 **8**

9

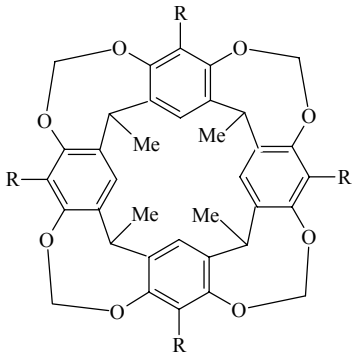
7-9 a R = Me, **b** R = C_5H_{11}, **c** R = $C_{11}H_{23}$

The temperature of the bridging of resorcinarenes **10a-c** with the use of bromochloromethane is limited by its low boiling point (68°C). It was observed that the heating of the reaction mixture at 88°C in a sealed tube improves the synthesis of cavitands **11a-c**; the reaction time is shorter and yields are higher [25].



10, 11 a R = Me, **b** R = C_5H_{11}, **c** R = CH_2CH_2Ph

Compounds **12a-c** are examples of water-soluble cavitands; among them **12a** shows complexing ability toward Cs^+ ion [26].

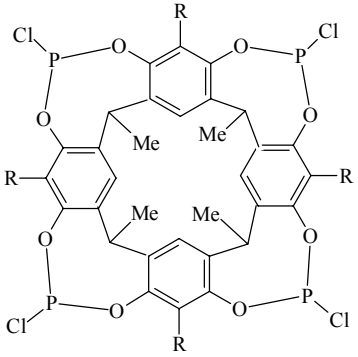


12a-c

12 a R = OH; **b** R = CH_2COOH; **c** $CH_2N[(CH_2)_2OH]_2$

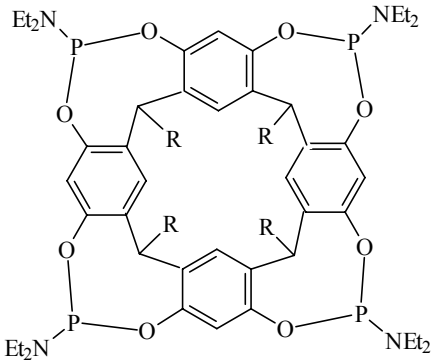
2. PHOSPHORUS-BRIDGED CAVITANDS

In the study of phosphorus-bridged cavitands [27], the X-ray crystal structure determination of **13b** was made. The molecule has a cone conformation with chlorine atoms directed inwards [28].



13a,**b a** R = H, **b** R = Br

Cavitands **14a,b** have been synthesized from appropriate resorcin[4]arenes by treatment with hexaethylphosphorous triamide [29, 30].

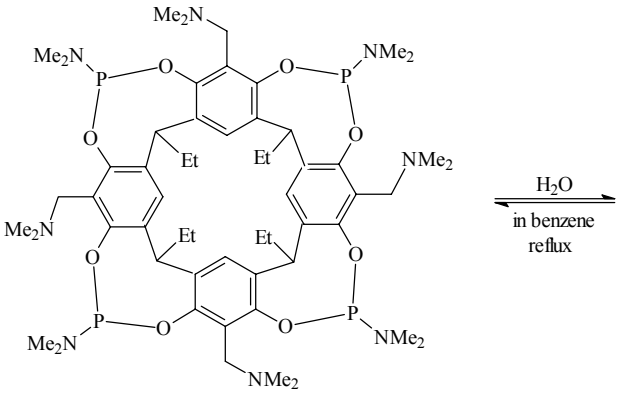


14a,**b**

14 a R = *n*-Pr, **b** R = *n*-C_6H_{13}

It was observed that **14b** forms 1:2 complexes with amines such as Et_2NH, Et_3N, and $H_2NCH_2CH_2OH$ [30].

The cleavage of endocyclic P–O bonds of cavitand **15** in aqueous solution affords compound **16**, and heating of **16** in benzene with azeotropic distillation of water gives back **15** [31].



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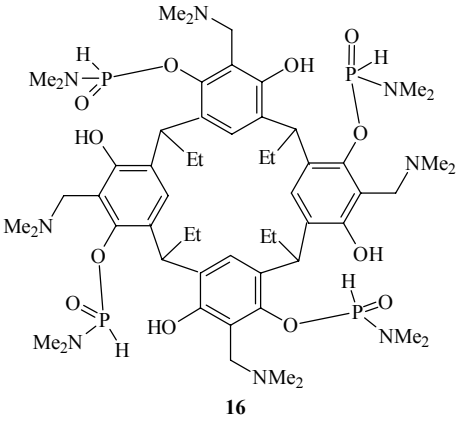

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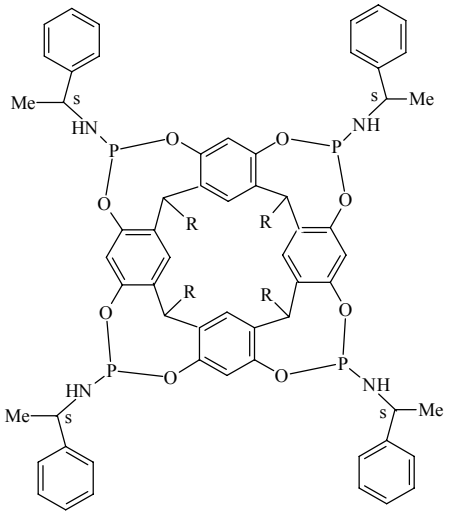
Chiral phosphorus-bridged cavitand **17** has been used for the pH-dependent enantioselection of amino acids in Langmuir monolayers [32-36].

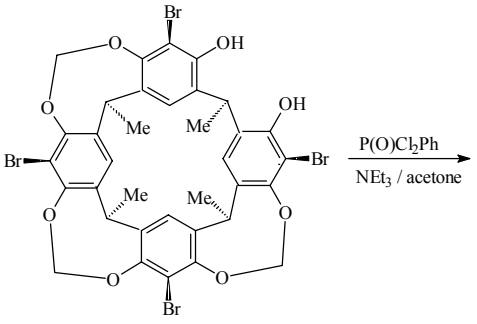


17 R = $C_{11}H_{23}$

Enantiomeric recognition of amino acids depends on the pH of the subphase. Two pairs of amino acids, *D*- and *L*-valine and *D*- and *L*-tryptophan, could be recognized with the use of the Langmuir technique [32].

Partially phosphonated (containing one or two P=O groups) and fully phosphonated (containing four P=O groups) cavitands derived from resorcin[4]arenes have been synthesized and their configurations determined with the use of ^{1}H and ^{31}P NMR spectra and ^{13}C relaxation times [37].

The introduction of one phenylphosphonic moiety on tribridged resorcinarene **18** leads to both possible diastereomers **19a** (P=O group outward the cavity, *o*-isomer) and **19b** (P=O group inward the cavity, *i*-isomer).



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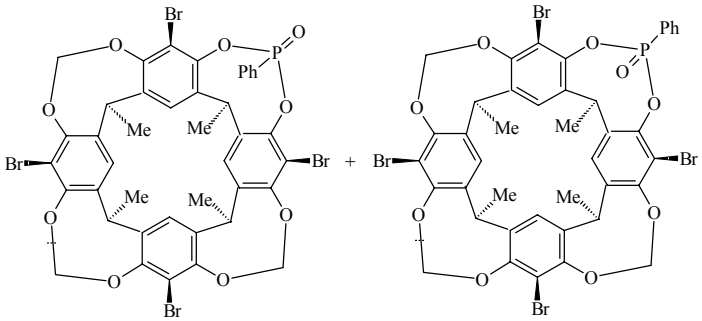
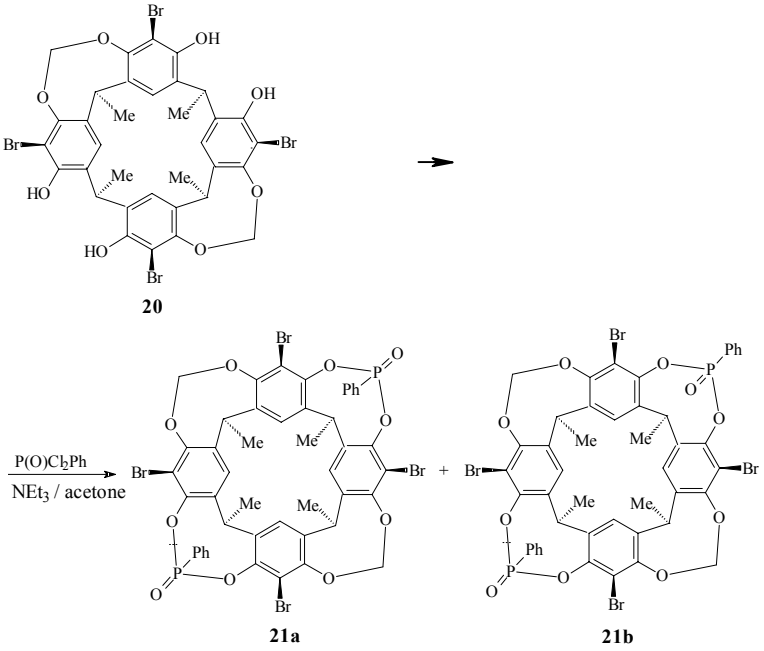


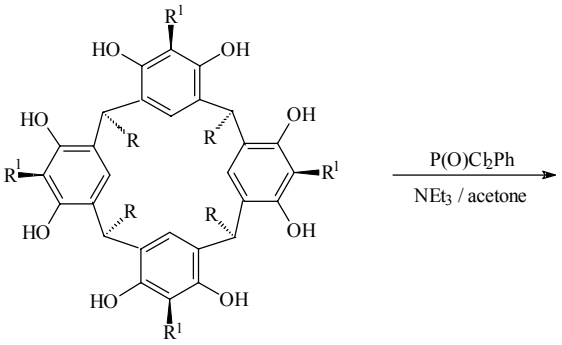
19a **19b**

The introduction of two distal phenylphosphonic groups on methylene-dibridged resorcinarene **20** gives rise to two of three possible diastereomers: **21a** (outward, outward) and **21b** (inward, outward); no (inward, inward) isomer was formed.

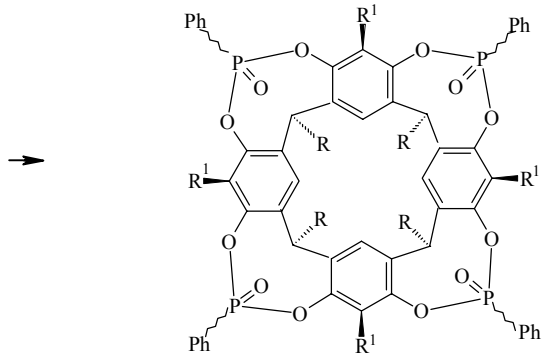


20 **21a** **21b**

The bridging reactions of resorcinarenes **22a-d** give cavitands **23a-d**.

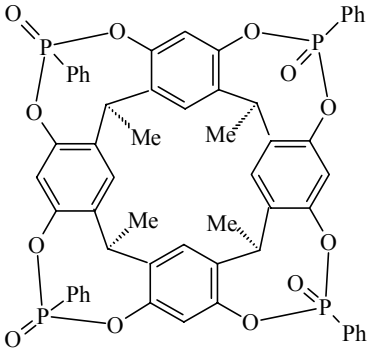


22 a R = Me, R^1 = H; **b** R = R^1 = Me, **c** R = Me, R^1 = Br, **d** R = C_6H_{13}, R^1 = Br

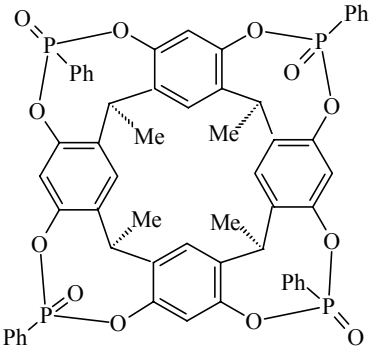


23 a R = Me, R^1 = H; **b** R = R^1 = Me, **c** R = Me, R^1 = Br, **d** R = C_6H_{13}, R^1 = Br

The reaction of resorcinarene **22a** with phenylphosphonyl dichloride affords two diastereomers **23a'** and **23a''** out of the six possible ones [37].



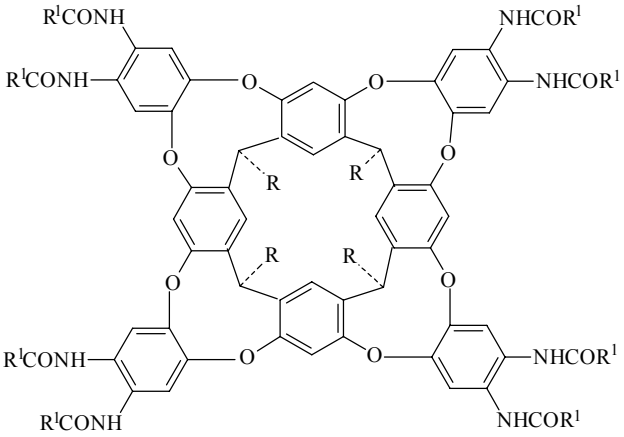
23a'



23a"

3. FUNCTIONALIZED CAVITANDS

Cavitands **24** fold into a deep cavity by means of intramolecular hydrogen bonds. This self-folding of **24** is reversibly controlled by solvent and temperature [38].



24

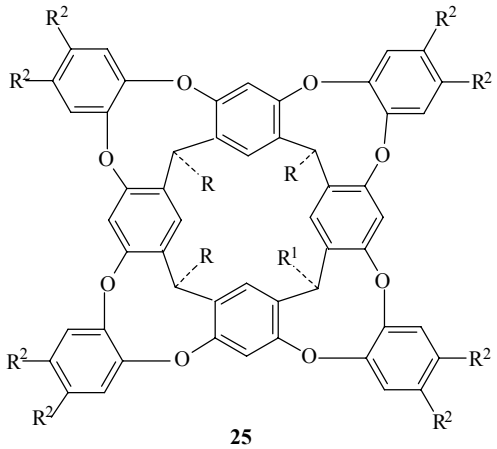
$R = C_9H_{19}, C_{11}H_{23}$

$R^1 = CH_2Cl, C_6H_{13}$, cyclohexyl

It was observed that cavitands **24** form complexes with cyclohexane derivatives, lactams, and 1-substituted adamantanes [38]. These species are promising as ^{1}H NMR supramolecular shift reagents due to the exchange between free and complexed guest [38].

Compound **25** is an example of self-folding cavitands interesting as polymeric capsules and promising in applications as solid supports [39].

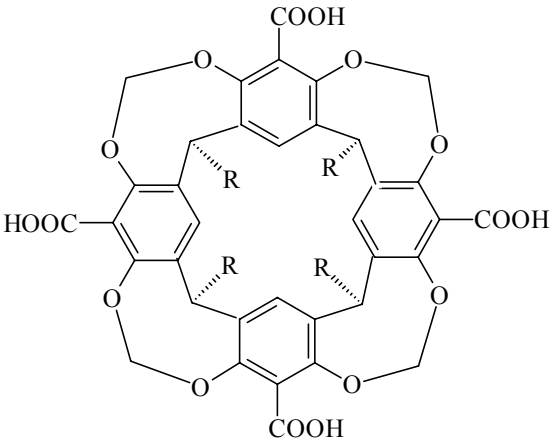
The recrystallization of cavitand **26** from *p*-xylene and DMF leads to its self-assembly into a wave-ladder type of one-dimensional hydrogen-bonded network [40]. In this way the highly porous three-dimensional packing structure consisting of huge chambers is formed. Each chamber is filled with one molecule of *p*-xylene and five DMF molecules. Single crystals are composed of **26**: *p*-xylene: DMF = 1:1:5. The *p*-xylene molecule is accommodated in the cavity of **26** *via* CH···O and CH-π interactions [41].



25

R = *n*-$C_{10}H_{21}$, R^1 = $(CH_2)_9OH$, R^2 = NHC(O)*n*-C_7H_{15}

The carboxy groups of **26** form intramolecular hydrogen bonds. Two of five DMF molecules form hydrogen bonds with alternate carboxy groups of **26**, and the other three DMF molecules are highly disordered and are included in the void space of the crystal lattice [40].

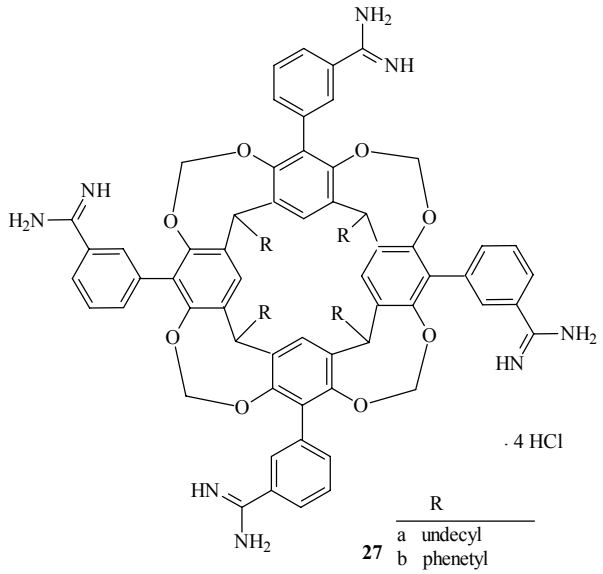


R = $(CH_2)_2Ph$

26

Cavitands **27a-c** have been obtained and their complexation ability toward dicarboxylates and phosphates has been studied [42].

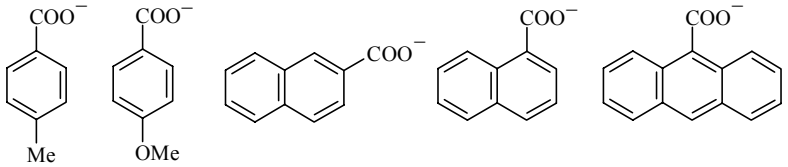
Compounds **27a,b** show limited solubility in protic solvents; **27c**, however, is readily soluble in protic medium, and its complexation properties for isophthalates and nucleotides have been investigated by ^{1}H NMR titrations and Job's method of continuous variation. Cavitand **27c** forms with nucleotides stable 1:1 host-guest complexes. The association constants increase with the guest charge in the order c-AMP<AMP<ADP<ATP [42].



	R
a	undecyl
b	phenetyl
c	$(CH_2)_3(OCH_2CH_2)_3OMe$

27

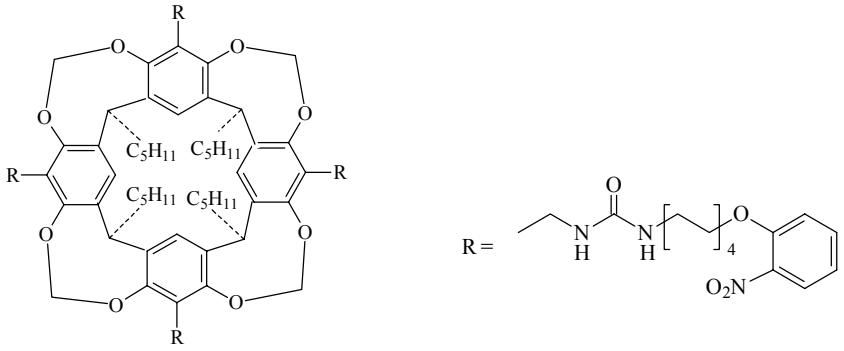
In the investigations concerning supramolecular chemistry it was found that self-assembly processes may generate new recognition sites [43, 44]. The reaction of cavitand **28** with the Pd complex **29** gives the water-soluble compound **30** which forms with a guest the inclusion system **31** [45]. The four pyridyl groups of the cavitand **28** have been intramolecularly assembled with Pd(II) ions affording the receptor **30**. This assembly of flexible ligands around the coordination sphere of the Pd ion results in the formation of a hydrophobic binding site able to incorporate aromatic guests in aqueous solution (Scheme 1). Aromatic carboxylates **32**-**36** have been used as guests [45].



32 **33** **34** **35** **36**

^{1}H NMR analysis has shown the 1:1 stoichiometry of the complexes. The highest association constants have been found for **32** and **33**, indicating that the presence of methyl groups enables deep inclusion into the host cavity. It was established that **30** forms complexes with anionic guests by cooperation of hydrophobic and electrostatic interactions [45].

Cavitand **37** containing four N-(*o*-nitrophenoxy-*n*-octyl)ureide groups forms 1:1 complexes with chloride, bromide, and iodide anions available from tetra-*n*-butylammonium halides [46-48].



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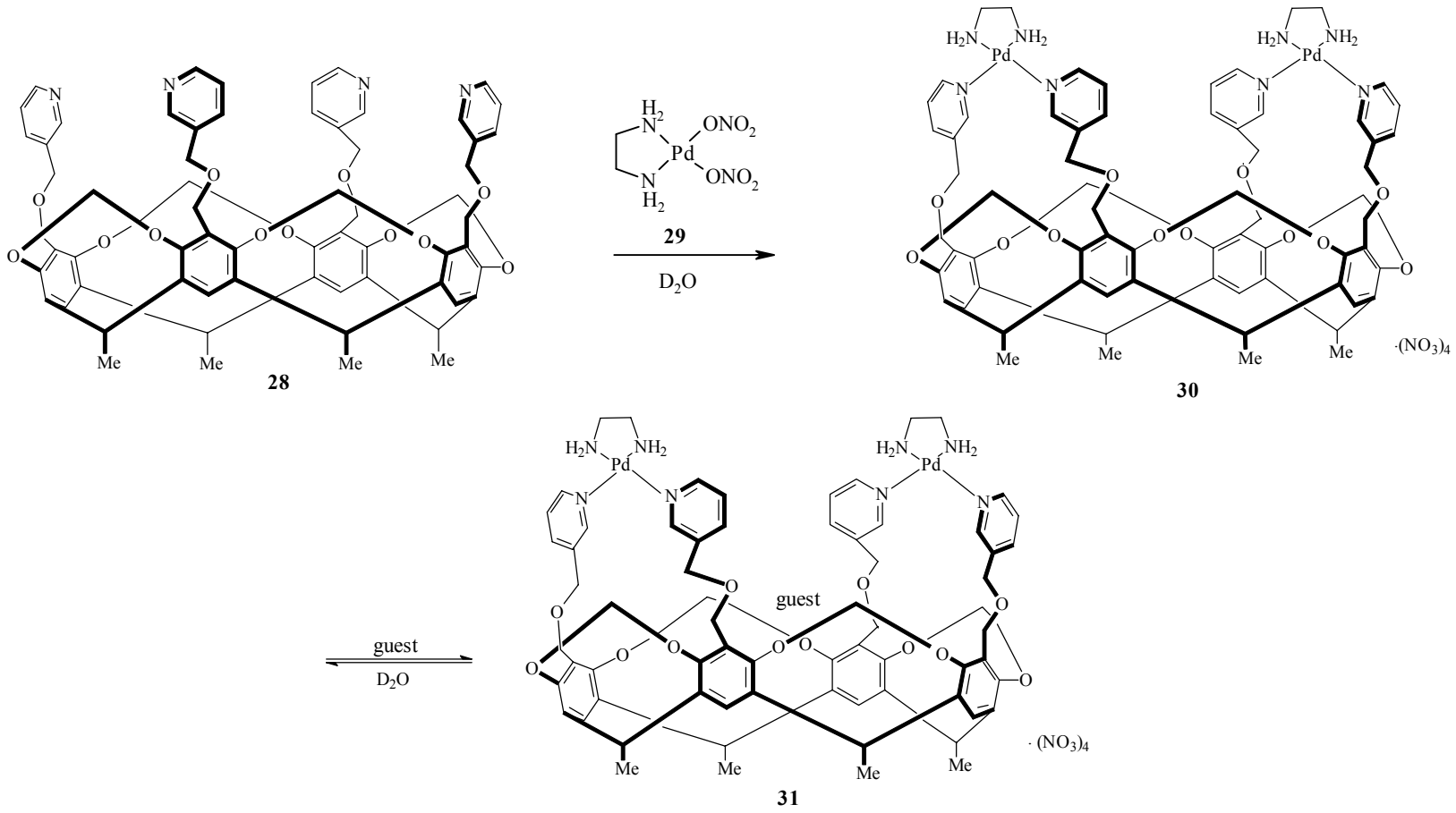
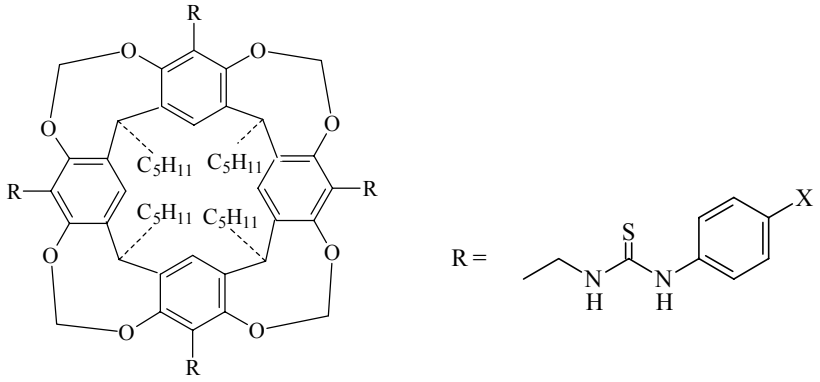
Scheme 1



The association constants are high, with a small preference for the complexation of chloride over bromide and iodide ions. The binding occurs within the cavity, and the association in chloroform takes place *via* hydrogen bonding by the urea moieties. It was found by IR analysis that, upon binding, the intramolecular array of hydrogen bonds is disturbed, thus enabling the encapsulation of the halide anion [46].

Cavitands **38a**,**b**, bearing four thioureide moieties, form complexes with Cl^-, Br^-, and I^- anions [47-49], similarly as in the case of ureide-substituted cavitands [46].

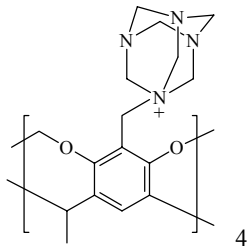


38a,**b** R = **a** X = H; **b** X = F

The association occurs *via* hydrogen bonding between thioureide groups and halide guest. It should be pointed out that in the case of the ureidecavitand a circular array of hydrogen bonds exists; here, however, the intramolecular hydrogen bonding does not extend through the whole molecule but leaves free one thioureide unit.

The complexation of halide ions by **38a,b** is stronger than in the case of their oxo analogues, this being due to the higher acidity of the thioureide group as compared to ureide unit [49].

In the study of anion recognition, not so extensively investigated as cation recognition [50], the complexation of the water-soluble cavitand **39** with aromatic carboxylates **40-48** in water has been reported [51]. The cooperation of electrostatic and hydrophobic interactions results here in strong complex formation [51, 52]. Job ^{1}H NMR titration has shown the 1:1 stoichiometry for the complexes formed. The highest association constant has been observed for **46** used as a guest.



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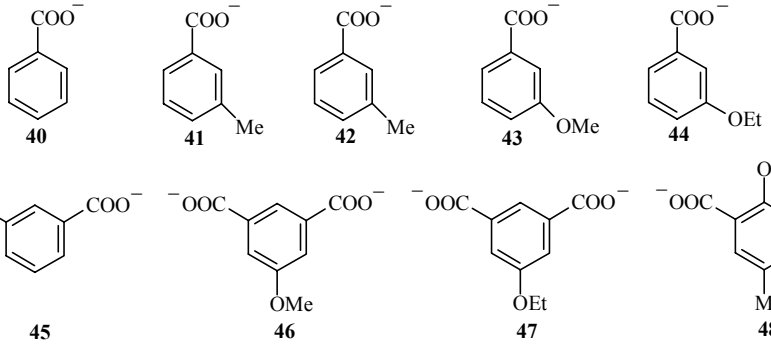
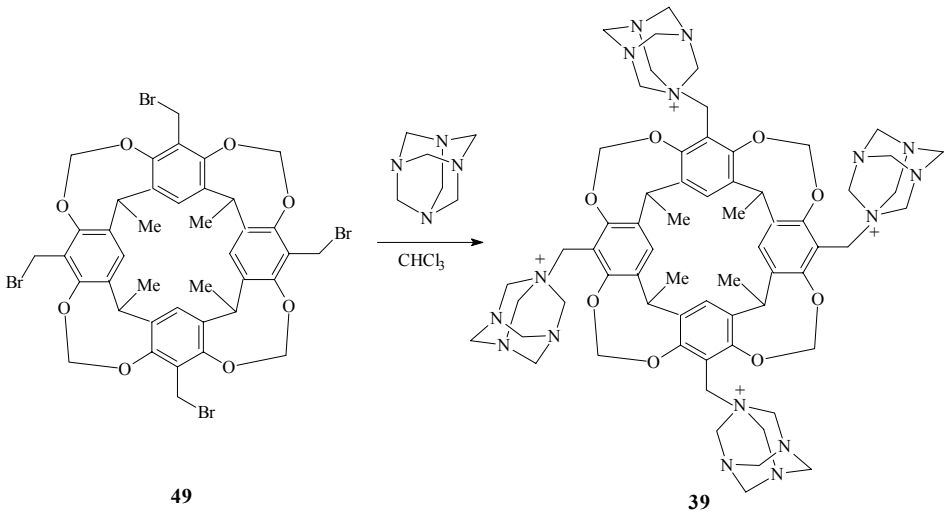


40 **41** **42** **43** **44**

45 **46** **47** **48**

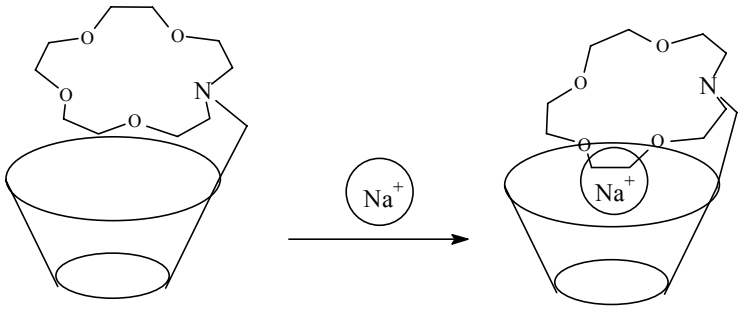
The cavitand **39** has been obtained from bromomethylcavitand **49** in the reaction with hexamethylenetetramine [51].



49 **39**

Mono- and bis-chloromethylation of the cavitand **50** leads to compounds **51** and **52** which by treatment with aza-15-crown-5 afford azacrown modified cavitands **53** and **54**, respectively [53] (Scheme 2).

In the induced fit type complexation of Na^+ ion by cavitand **53** in $CHCl_3$ solution, the presence of the azacrown unit increases the Na^+ binding ability; azacrown serves as an arm to catch the Na^+ ion and to introduce it into the cavity of **53** [53], as shown below.



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4. DEEP CAVITANDS

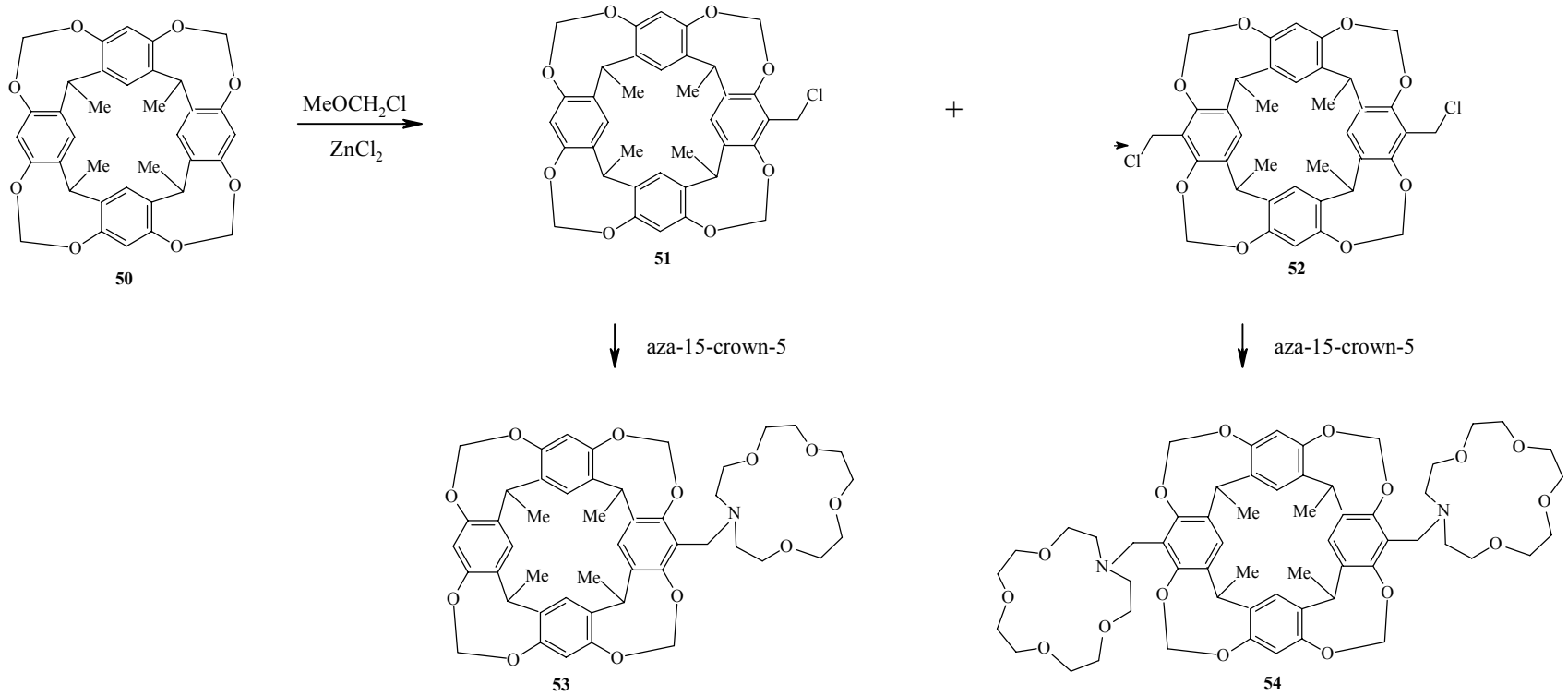
In the study of deep cavitands of nanomeric dimensions [54] and of extended calixarene-resorcinarene-based surfaces [55], compounds **55** and **56** have been obtained [56].

The synthesis begins with the reaction of resorcinarene **57** with 1,2-difluoro-4,5-dinitrobenzene, leading to the octanitrocavitand **58** which was submitted to reduction followed by treatment with diethyl 2,3-dioxosuccinate or acenaphthenequinone yielding **55** or **56** [56, 57] (Scheme 3).

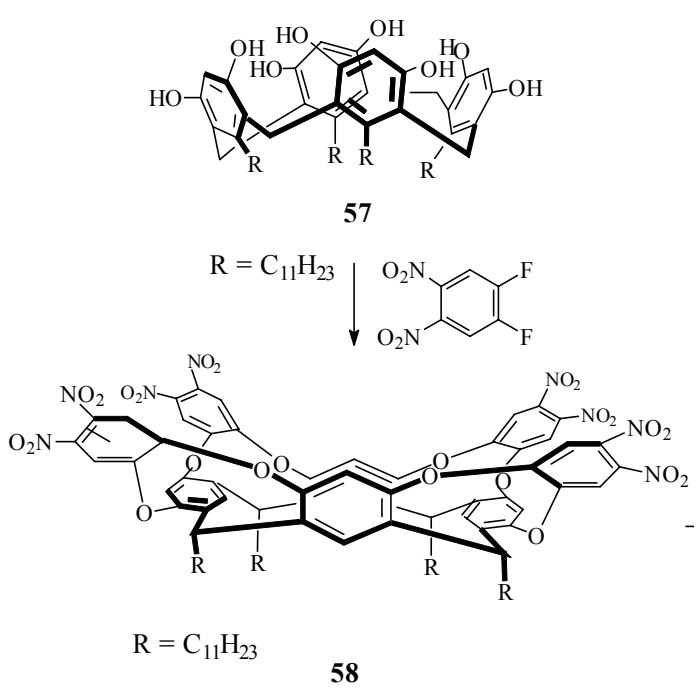
The ester groups in **55** may be hydrolyzed or converted into amide groups to give derivatives **59** and **60** , respectively (Scheme 4).

^{1}H NMR analysis indicates that **55** and **56** are conformationally flexible, as shown below (Scheme 5).

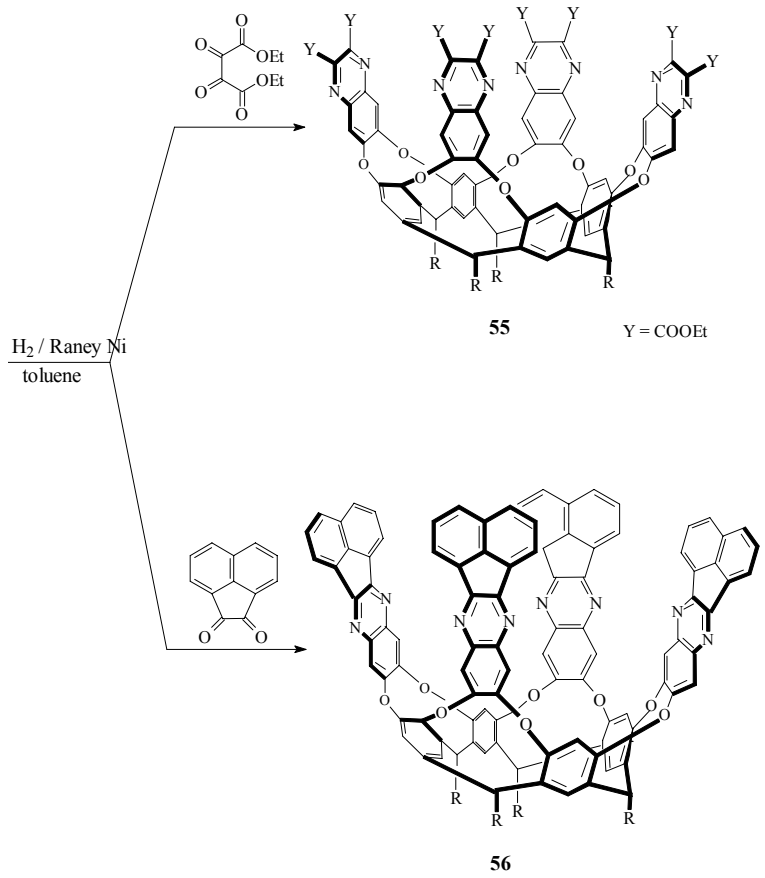
Scheme 2



Scheme 3

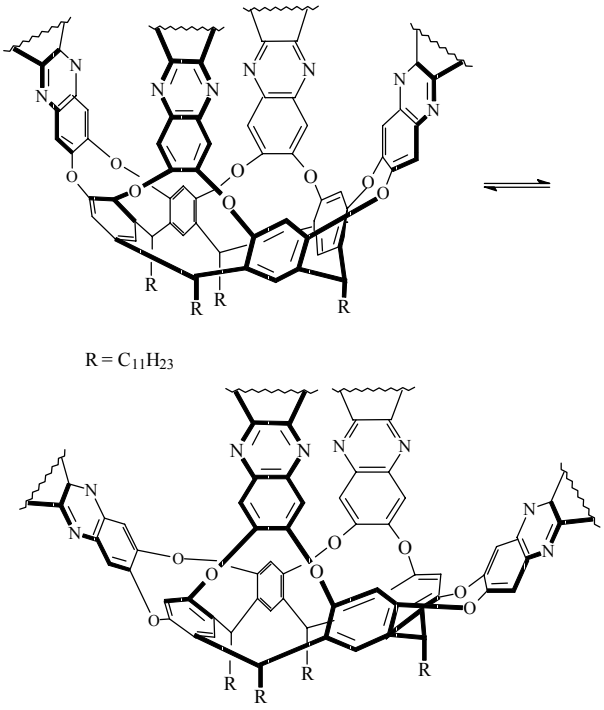


57, **58** R = $C_{11}H_{21}$



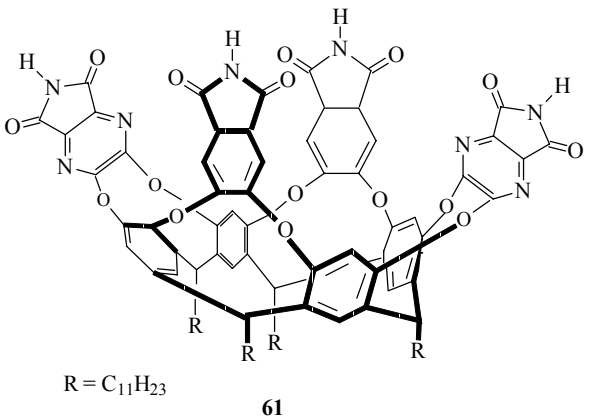
Scheme 4

Scheme 5



The dimensions of cavities are large, 11 Å deep for **55** and 14 Å deep for **56**. Cavitand **55** may accommodate three molecules of benzene or four molecules of chloroform, while **56** may encapsulate four molecules of benzene or toluene and up to five molecules of $CHCl_3$. Cavitand **56** can accommodate C_{60}, but, unexpectedly, the only slightly larger C_{70} molecule cannot be incorporated; this behavior is interesting in the use of **56** as a selective reaction vessel [56].

The self-assembled cylindrical capsule **61·61** has been synthesized. The cavity of **61·61** has nanometer dimensions [58].



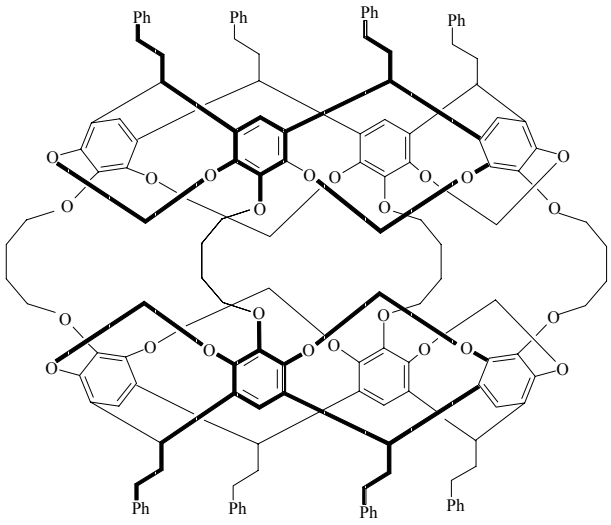
61

It was observed that **61·61** may encapsulate dibenzoyl peroxide; when encapsulated the latter loses its hemical reactivity. Dibenzoyl peroxide restores its chemical reactivity upon release from the capsule by DMF; DMF is a solvent which competes for hydrogen bonds holding the capsule together. This process of protection and release of hosted molecules is promising in the use of such capsules in catalytic processes [58].

5. CARCEPLEXES AND HEMICARCEPLEXES

Many works concern carceplexes and hemicarceplexes derived from resorcinarenes [59-61] or calixarenes [62].

The template effect in the formation of hemicarceplex **62·**guest was investigated. The bridging of two tetrol cavitands by 1,4-dibromobutane leading to hemicarceplex **62** was performed in N-formylpiperidine in the presence of a suitable guest serving as template. Among templates, a considerable preference for *para*-disubstituted benzenes has been observed [63].



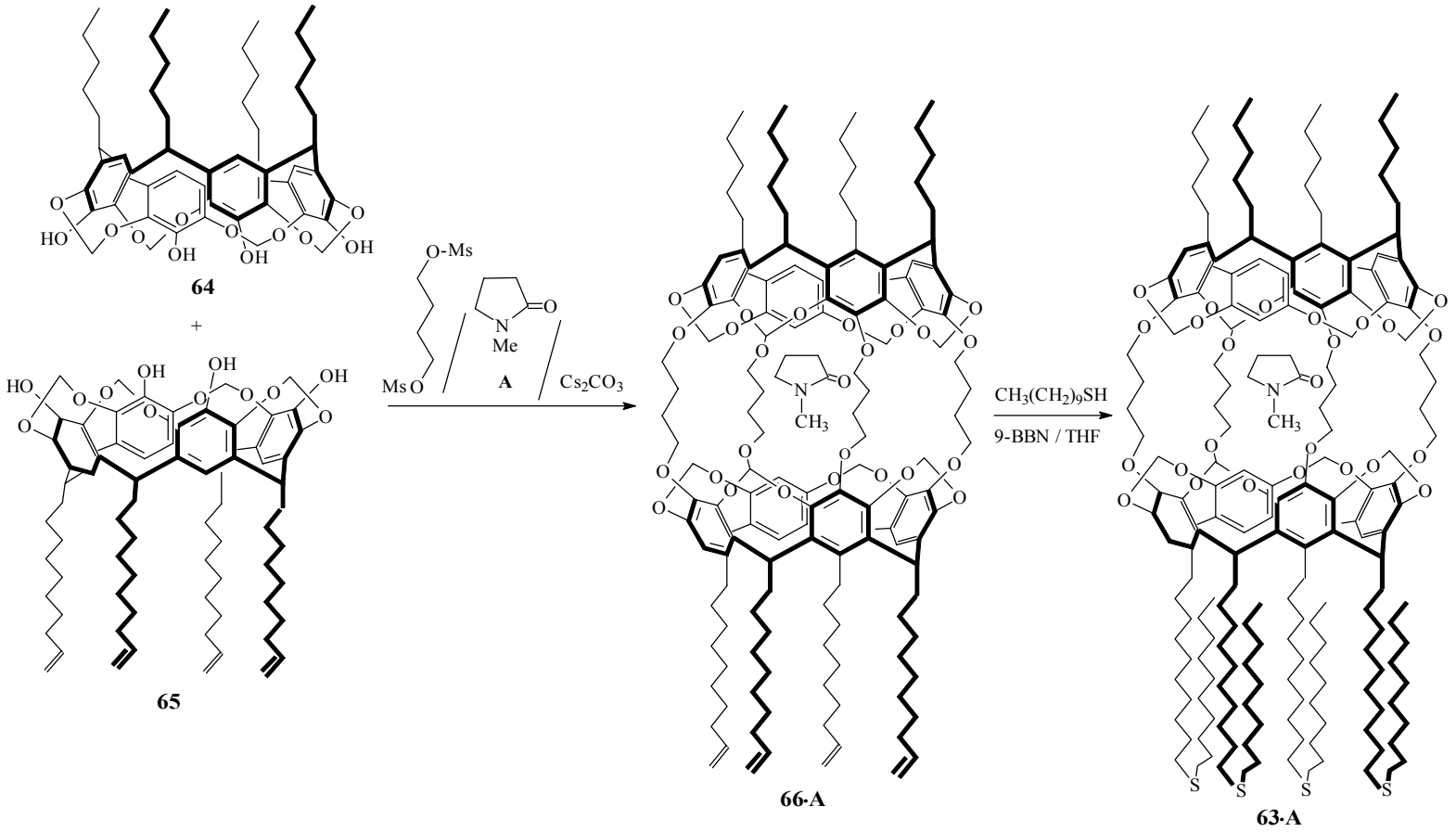
62

Sulfide-functionalized hemicarceplex **63·A**, where **A** is N-methyl(2-pyrrolidone) has been prepared [64]. The synthesis begins with the linking of two cavitands **64** and **65** by 1,4-butanediol dimesylate in the presence of **A** and Cs_2CO_3. The formed **66·A** was converted into **63·A** adsorbate by treatment with 1-decanethiol in the presence of 9-BBN (9-BBN is 9-borabicyclo[3.3.1]nonane) (Scheme 6).

Sulfide-functionalized noncentrosymmetrical hemicarceplex **63·A** in which **A** is a guest is suitable for self-assembly on gold. The adsorbates are bound to the gold surface by four anchoring dialkyl sulfide moieties. The guest can adopt different positions in the cavity; this fact results in the formation of two diastereomeric surfaces.

The synthesis of the cavitand **65** begins with the reaction of resorcinol and undecylenic aldehyde, leading to the resorcinarene **67**. The bromination of double bonds and aromatic rings of **67** followed by selective debromination regenerating the double bonds, and the subsequent bridging of the hydroxyl groups gave bromocavitand **68**. This compound was subjected to bromine-lithium exchange, followed by reaction with trimethylborate and oxidation with hydrogen peroxide, resulting in the cavitand **65** [64] (Scheme 7).

Scheme 6



Scheme 7

HO
OH
+
4
CHO
4
HO
OH
HO
OH
HO
OH
HO
OH
OH
1. Br2
2. Zn/acetone
3. ClCH2Br/DMF/K2CO3
67
Br
Br
Br
Br
O
O
O
O
O
O
O
O
O
O
1. n-BuLi
2. B(OMe)3
3. H2O2
HO
OH
OH
OH
O
O
O
O
O
O
O
O
O
68
65

CONCLUDING REMARKS

In the review only selected examples of cavitands have been presented. The rapid development of the chemistry of these compounds [65-72] is a reflection of their growing importance in theoretical studies and practical applications.

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