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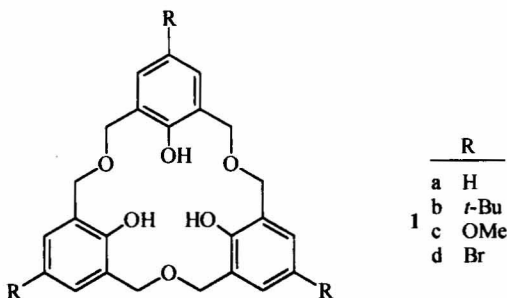
HOMOOXACALIXARENES AND RELATED COMPOUNDS

Abstract: The results of investigation of homooxacalixarenes, a new class of calixarene analogues are presented, pointing out their complexation abilities. Some examples of compounds related to homooxacalixarenes are also given.

Homooxacalixarenes belong to the calixarene family, which is a research field of an increasing interest ¹⁻⁶. The present paper is a continuation of our publications dealing with calixarenes ⁷⁻¹¹ and heteracalixarenes, i.e. analogues of calixarenes containing heteroatoms in linkages of benzene units ^{12,13}.

Homooxacalixarenes are interesting as host molecules having properties of calixarenes and crown ethers ¹⁴. They form numerous complexes, e.g. with alkali and alkaline-earth metal ions ¹⁵, quaternary ammonium ions ¹⁶ and fullerene ¹⁷.

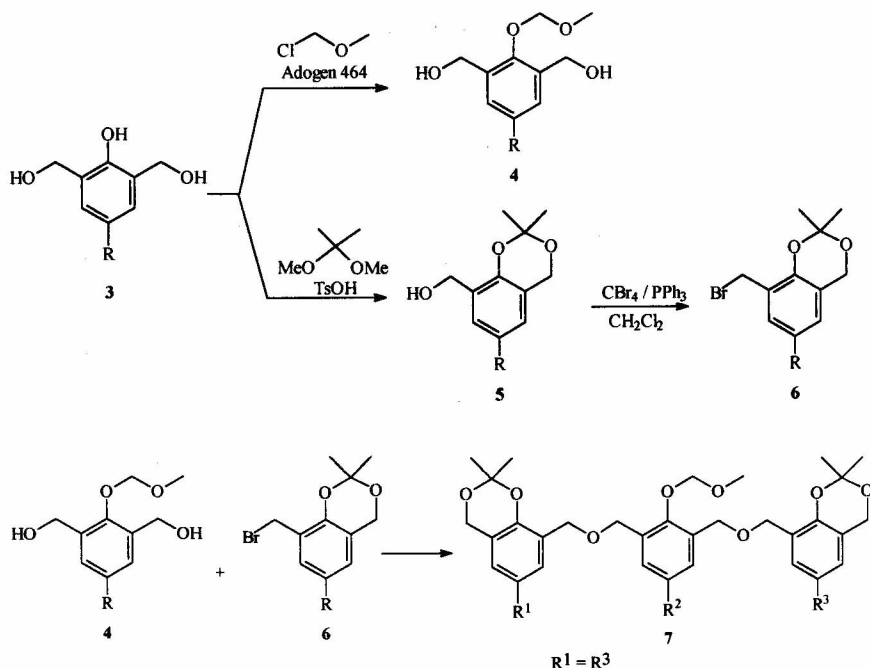
Typical examples of homooxacalixarene are hexahomotrioxacalix[3]arenes **1** ¹⁸.



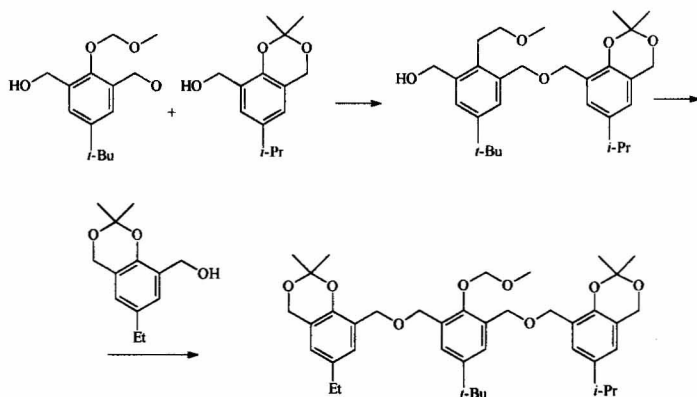
Hexahomooxacalix[3]arenes **1** have a cavity formed by an 18-membered ring. They have C_3 symmetry and may adopt only two conformations, i.e. cone and partial cone ones. The synthetic approaches to **1** involve the cyclotrimerization of 2,6-bis(hydroxymethyl)phenols ¹⁹.

Hexahomotrioxacalix[3]arenes containing different substituents at the upper rim have been synthesized, examples are **2a-h** ¹⁹. It should be mentioned, that often used cyclotrimerization of 2,6-bis(hydroxymethyl)-phenols leads to hexahomotrioxacalix[3]arenes bearing the same substituents on the upper rim.

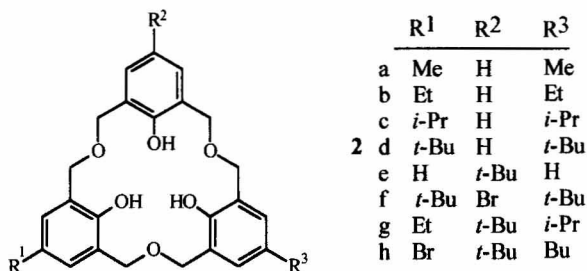
The synthesis of **2a-h** begins with the reaction of 2,6-bis(hydroxymethyl)phenols **3** with methoxymethyl chloride with the use of Adogen 464 as a phase-transfer catalyst which leads to diols **4**. On the other hand, the treatment of **3** with 2,2-dimethoxypropane in the presence of TsOH yields acetonides **5** which were brominated by $\text{CBr}_4/\text{PPh}_3$ to give benzylbromides **6**. The coupling of **4** with **6** affords linear trimers **7** having two identical substituents R^1 and R^3 .



An example of the synthesis of linear trimer bearing three different substituents is the following procedure:

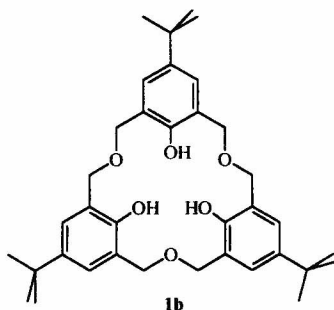


Linear trimers submitted to cyclization under acidic high dilution conditions afford **2a-h**.



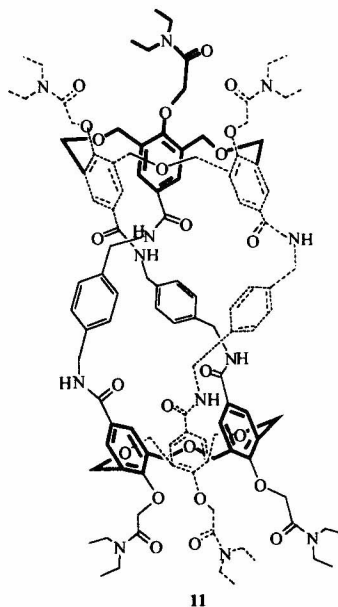
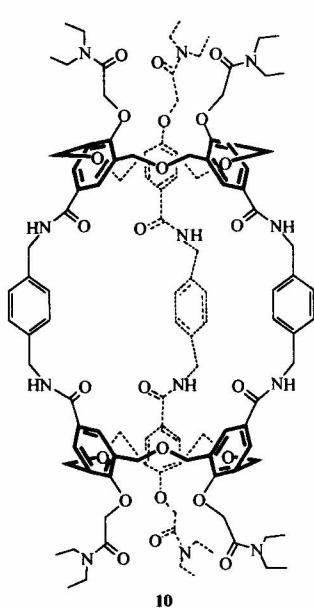
The X-ray analyses of **2e** and **2g** have been made. Both compounds exist in cone conformation, they form a network of bifurcated intra-molecular hydrogen bonds. The obtained hexahomotrioxacalix[3]arenes are promising as receptors for host-guest systems¹⁹.

In the study of hexahomotrioxacalix[3]arene **1b**²⁰ its complex with uranyl ion has been obtained. With the use of two basic agents, triethylamine and DABCO, two complexes $[(\text{UO}_2^{2+})(\text{L}^{3-})(\text{HNET}_3^+)] \cdot 3\text{H}_2\text{O}$ **8** and $[(\text{UO}_2^{2+})(\text{L}^{3-})(\text{HDABCO}^+)] \cdot 3\text{CH}_3\text{OH}$ **9**, respectively, have been synthesized (DABCO is 1,4-diazabicyclo[2,2,2]octane, H_3L is **1b**)¹⁸. In these complexes the trigonal coordination geometry for the UO_2^{2+} is observed, this fact being rather unusual in complexes of uranyl ion^{17,21-23}.



The capping of the homooxacalix[3]arene on the upper rim leads to cage molecules of high Cs^+ selectivity²⁴.

In the study of homooxacalix[3]arenes the capsular molecule **10** and self-threaded rotaxane **11**, its isomer, have been synthesized²⁵.

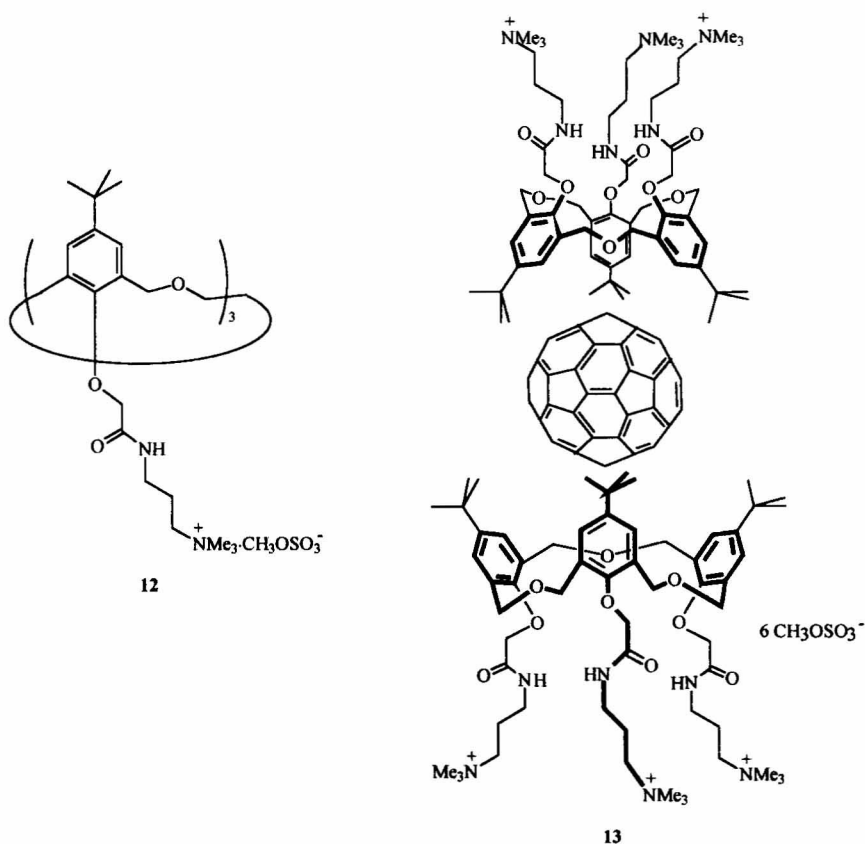


Capsule **10** has a large internal hole able to encapsulate bulky guest molecules; its three windows are large enough to allow the guests to get in and out. At the lower rims of **10** are two ionophoric sites which can bind alkali metal ions. In the case of **11** the hole exists no more.

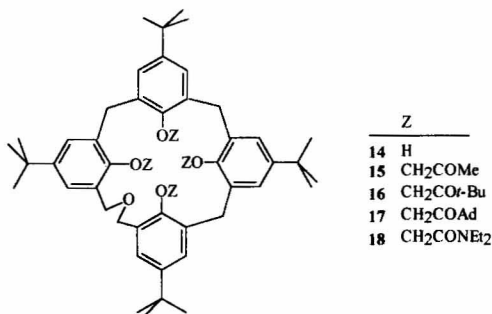
The interconversion between **10** and **11** is impossible due to the presence of the diethylacetamide groups at the phenolic oxygen atoms²⁵. However, when one molecule of homooxacalixarenes forming a capsule bears less sterically hindered groups than diethylacetamide moieties, the interconversion is possible and the capsule - rotaxane equilibrium takes

place. Capsule **10** can include methyl viologen, but in the case of propyl viologen it is impossible because of the steric hindrance²⁵.

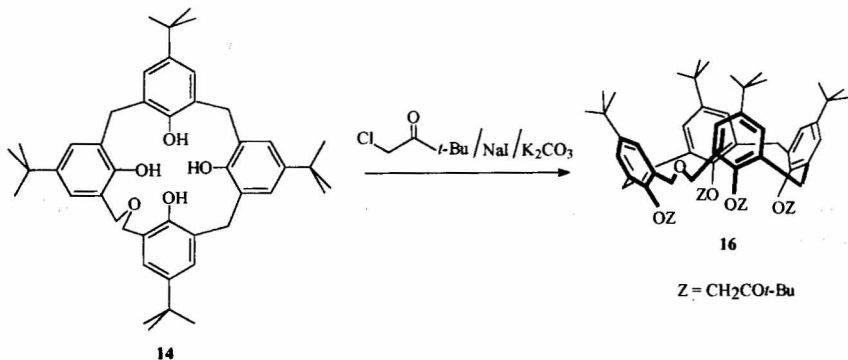
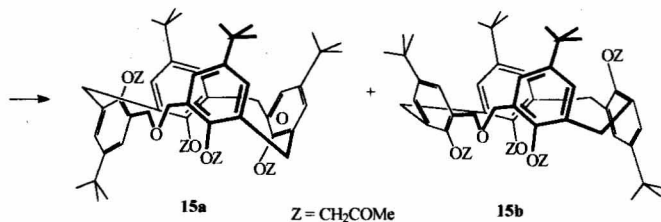
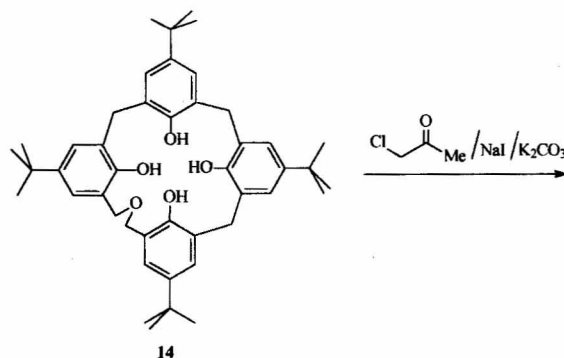
It was found that **1a-d** form with C_{60} in toluene complexes of the 1:1 stoichiometry¹⁷. In the preparation of fullerene thin films²⁶ it was observed that the water-soluble homooxacalixarene **12** forms with C_{60} a capsule-like 2:1 complex **13**, in this way enabling the solubilization of C_{60} ²⁷⁻²⁹. The complex **13** possesses six cationic charges and can be deposited on an anion-coated gold surface as a monolayer or as a monolayer-like ultrathin film^{27,30}. The obtained membrane shows a redox response in cyclic voltammetry and a photoelectrochemical response to visible light irradiation²⁷.

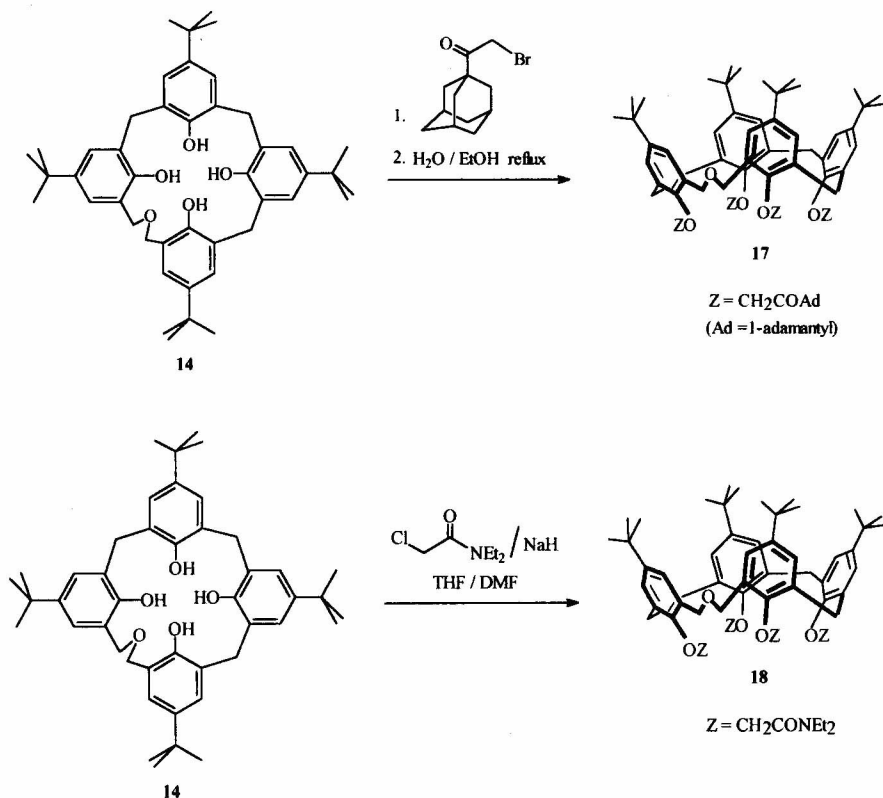


Investigating dihomooxacalix[4]arene **14**, compound containing four benzene rings, its derivatives **15** - **18** have been synthesized and their conformations determined by ¹H and ¹³C NMR analysis^{31,32}.



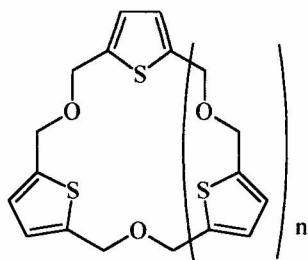
Compounds **15** - **18** have cavities of dimensions lying between those of the respective parent calix[4]arenes and calix[5]arenes, this fact allowing their use as hosts³¹. Synthetic approaches to **15** - **18** are given below.



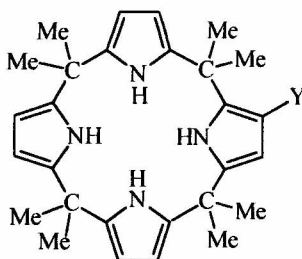


^1H and ^{13}C NMR analysis has shown that in the case of **15** two isolable partial cone conformers **15a** and **15b** are formed while **16** - **18** adopt the cone conformation. It was established that **16** - **18** are good extractants for alkali, alkaline-earth and transition metal ions³¹. Derivatives of tetra-homodioxacalix[4]arenes are also known³³.

One should mention here also homooxacalix[n]thiophenes **19** containing thiophene units instead of phenol rings, which are present in homooxacalixarenes¹⁴. These compounds are similar to homooxacalixarenes, and on the other hand they are to some extent related to heterocalixarenes. Heterocalixarenes are compounds in which benzene rings of calixarenes have been replaced by heterocyclic units; as an example may serve calix[4]pyrrole **20**^{34,35}.



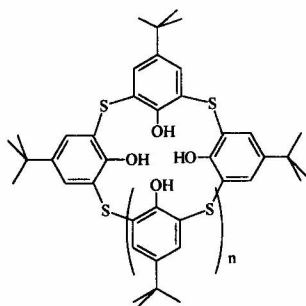
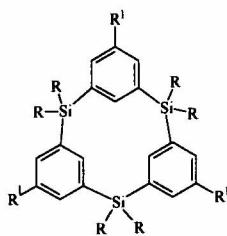
19

 $n = 1-5$ 

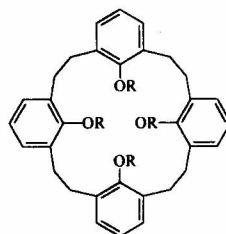
20

 $Y = \text{H, I, } \text{---H, } \text{---}\text{C}_6\text{H}_4\text{---Me}$

To heteracalixarenes belong intensively studied thiacalix[4]arenes **21**^{34,36} and far less investigated trisilacalix[3]arenes **22**³⁷ promising in the recovery of metal ions, e.g. Ag^+ by their complexation.

21 $n = 1,2,3$ 

22

 $R = \text{H, alkyl}$
 $R^1 = \text{H, alkoxyl}$


23

 $R = \text{H, Me, CH}_2\text{COOH, CH}_2\text{COOEt}$

An attention should be paid also to homocalixarenes, a subject of numerous publications^{34,38-40}. An example is all-homocalix[4]arene **23** in which four methylene groups have been replaced by ethylene bridges³⁴.

Homocalixarenes are promising as extracting agents, especially for platinum and palladium which are used in automobile catalytic converters, this application of homocalixarenes being of a great importance from the ecological viewpoint³⁴.

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Homooksakaliksareny i związki pokrewne

Streszczenie: Przedstawiono wyniki badań homooksakaliksarenów, nowej klasy analogów kaliksarenów, z podkreśleniem ich właściwości kompleksotwórczych; podano również przykłady związków pokrewnych.