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THE COMPLEX FORMATION OF α,ω-DICARBOXYLIC ACIDS AND α,ω-DIOLS WITH CUCURBITURIL AND α-CYCLODEXTRIN. THE FIRST STEP TO THE FORMATION OF ROTAXANES AND POLYROTAXENES OF THE POLYESTER TYPE

Hans-Jürgen Buschmann, Klaus Jansen and Eckhard Schollmeyer

Deutsches Textilforschungszentrum Nord-West e.V., Frankenring 2, D-47798 Krefeld, Germany

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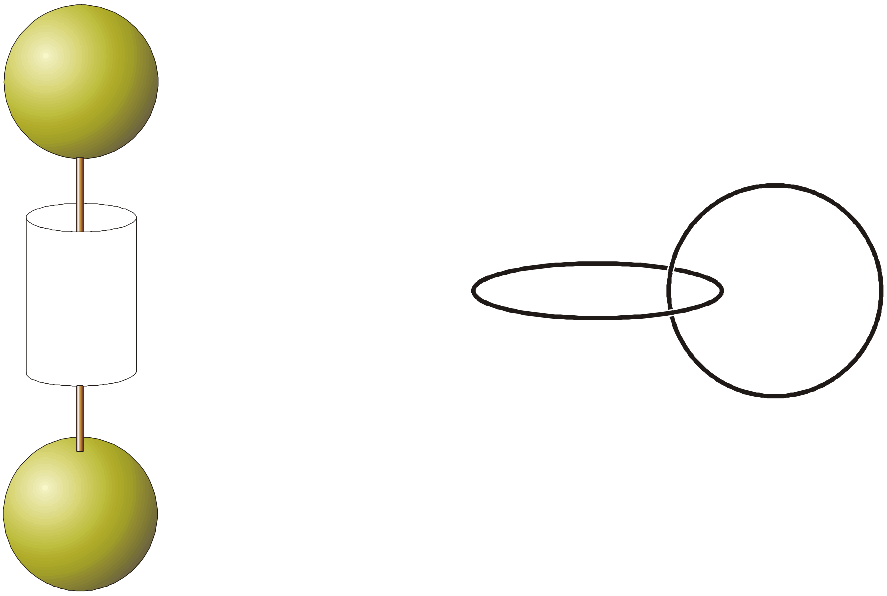
Abstract

The formation of mechanically bound molecules in relative high yields is only possible if preorganized molecules are used. Thus, the complex formation between α,ω-dicarboxylic acids and α,ω-diols and the macrocyclic ligands cucurbituril and α-cyclodextrin was examined using calorimetric titrations. Both ligands are able to form relative strong complexes with the molecules examined. However, for the formation of rotaxane-polyesters it is essential that the reactive groups of the complexed molecules are located outside of the cavities of the preorganized complexes.

INTRODUCTION

The formation of molecules by covalent bonds is familiar to each chemist. However, it is also possible to bind molecules permanently together only by mechanical bonds. These molecules are called rotaxanes and catenanes and they are schematically shown in Figure

1. A rotaxane looks like a dumbell with a threaded ring. A catenane consists of two or more interlocked rings.



Rotaxane Catenane

Figure 1. Rotaxanes and Catenanes

The first rotaxanes and catenanes were synthesized by classical synthetic strategies [1]. Also a statistical approach was used to obtain these molecules but the yields were very low [2]. With the development of the „Supramolecular Chemistry“ by C. Pedersen, J.-M. Lehn and D.J. Cram new strategies for the synthesis of rotaxanes and catenanes became available. Using the possibility of preorganization of molecules the synthesis of interlocked molecules became more efficient. In the meantime a large number of rotaxanes and catenanes has been synthesized from different preorganized molecules [3-7].

Crown ethers and cyclodextrins have most commonly been used as ring components for the formation of rotaxanes. Only few results have been reported with the macrocyclic ligand cucurbituril, see Figure 2. This molecule was first synthesized in 1905 [8]. However, the molecular structure was unknown until 1981 [9]. Cucurbituril forms stable complexes with diammonium ions [10,11]. The first rotaxane with cucurbituril reported contains cucurbituril, 1,6-diamino hexane and two tetraphenylborate ions as stopper groups [12]. In the meantime the formation of polyrotaxane nets due to metal coordination has been reported [13,14]. Also the formation of cucurbituril-rotaxanes and -polyrotaxanes by the reaction of cucurbituril complexes of 1,6-diamino hexane and different carboxylic acid chlorides is known [15,16].

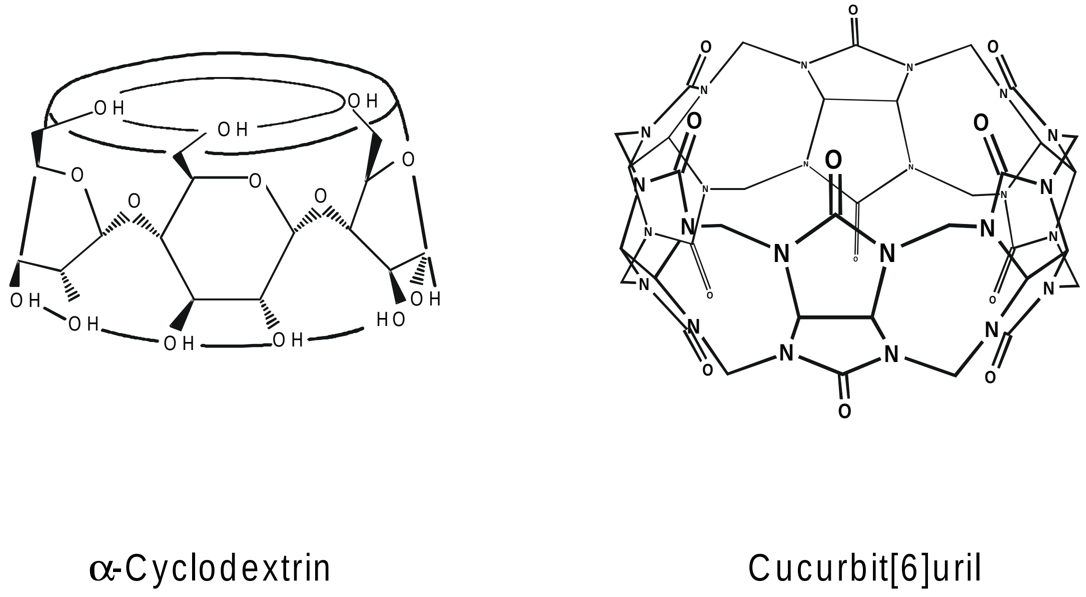


Figure 2. Structures of Cucurbituril and α-Cyclodextrin

Up to now only amine complexes of cucurbituril have been used as preorganized structures for the synthesis of rotaxanes. Nothing is known about the principal possibility to synthesize polyester rotaxanes with cucurbituril. For such a synthesis it is necessary that a diol or diacid forms stable complexes with cucurbituril. In this paper we will report the first results about the complex formation of α,ω-diols and α,ω-diacids with cucurbituril and for comparison with α-cyclodextrin in aqueous solution.

EXPERIMENTAL

The macrocyclic ligand cucurbituril is synthesized from urea, glyoxal and formaldehyde by known procedures [8]. The ligand is purified by several recrystallizations from aqueous hydrochloric acid. The elemental analysis of cucurbituril gives the following results: C 35.58 %; H 4.48 %; N 27.97 % (expected C 43.38 %; H 3.64 %; N 33.72 %). The estimated values are in agreement with those already reported [9,17,18]. The differences between the experimental and expected values of the elemental analysis are caused by strongly bonded water molecules [19]. The ^{1}H NMR spectrum in D_2O/DCl contains only three signals of equal intensity (δ 5.75, δ 5.70, δ 4.46).

α-Cyclodextrin is a commercial product from Wacker-Chemie GmbH (Munich, Germany). All diols and diacids used are purchased from Fluka. They are used without further purification.

Due to the low solubility of cucurbituril in aqueous solutions aqueous formic acid (50 vol %, Merck) is used. The complexation reactions with α-cyclodextrin are performed in bidistilled water. The pH value of the solutions is adjusted to 3 by the addition of hydrochloric acid if necessary.

Stability constants and the reaction enthalpies are calculated from calorimetric titrations using a Tronac Model 458 calorimeter. A solution of the ligand (0.03 - 0.08 mol/l) is titrated continuously into solutions of the diacids or diols ($2 - 5 \cdot 10^{-3}$ mol/l). After corrections of all non-chemical heat effects the heat Q produced during titration is related to the reaction enthalpy ΔH by the following equation:

$$Q = \Delta n \cdot \Delta H$$

with the number of moles Δn of the complex formed. Δn depends upon the stability of the complex formed. The mathematical treatment of the experimental data has already been described in detail [20-22]. The reliability of the results obtained from calorimetric titrations compared with those from potentiometric and conductometric titrations has been demonstrated [23].

RESULTS AND DISCUSSION

Stability constants and thermodynamic parameters for the complexation of α,ω-diols and α,ω-diacids with cucurbituril and α-cyclodextrin are summarized in Table 1.

Table 1

Stability constants log K (K in $\mathrm{l\cdot mol^{-1}}$) and thermodynamic values ΔH and TΔS ($\mathrm{kJ\cdot mol^{-1}}$) for the complexation of α,ω-diols and α,ω-diacids with cucurbituril (in aqueous formic acid 50 vol %) and α-cyclodextrin (in water, pH 3) at 25 °C

Guest molecule	Cucurbituril			α-Cyclodextrin		
	log K	-ΔH	TΔS	log K	-ΔH	TΔS
1,2-ethane diol	2.60±0.09	1.4±0.7	13.4±1.2	-[a]		
1,5-pentane diol	2.79±0.04	1.1±0.3	14.8±0.5	2.51±0.06	1.5±0.4	12.4±1.1
1,4-butane diacid	2.81±0.09	1.9±0.8	14.0±1.4	2.43±0.02	13.8±0.7	0.0±0.8
1,5-pentane diacid	2.79±0.04	1.1±0.3	14.8±0.5	2.53±0.02	25.9±1.2	-11.5±3.0
1,6-hexane diacid	2.23±0.05	2.7±0.5	10.0±0.8	2.56±0.01	25.4±0.2	-10.9±0.3
1,7-heptane diacid	2.71±0.10	1.5±0.6	13.9±1.2	2.51±0.03	37.5±1.2	-23.4±1.2
1,8-octane diacid	2.75±0.03	2.7±0.6	12.9±0.8	3.42±0.05	27.9±0.3	-8.5±1.4
1,9-nonane diacid	2.76±0.08	0.9±0.2	14.8±0.6	4.05±0.04	27.0±0.5	-4.0±0.7

[a] no 1:1 complex formation

The complex formation between cucurbituril and all guest molecules is only favoured by entropic contributions. The values of the reaction enthalpies are small. These findings are in accordance with the so-called hydrophobic effect. Only minor interactions take place between the ligand and host molecule. On the other side solvent molecules interacting with the ligand and the guest molecule are liberated during complex formation. As a result large positive values of the reaction entropies are observed. The chain length of the diols and diacids obviously has no influence upon the complex stabilities and the thermodynamic values.

The results for the complex formation of some diols and diacids with α-cyclodextrin are quite different. With 1,2-ethane diol the experimental results indicate the formation of 1:2 complexes (ratio of ligand to guest molecule). The results obtained for the complexation of 1,5-pentane diol with α-cyclodextrin are nearly identical with the results in the case of cucurbituril.

The number of methylene groups of the diacids plays an important role for the complex formation in case of α-cyclodextrin. The values of the reaction enthalpy reach a maximum for 1,7-heptane diacid. However, the stabilities of the complexes formed with aliphatic diacids are nearly constant up to 6 methylene groups. With longer alkyl chains the stabilities increase only due to entropic contributions.

The complex stabilities of aliphatic diacids with cucurbituril and α-cyclodextrin are high enough for the preorganization step necessary for the preparation of rotaxanes and polyrotaxanes. The thermal stability of cucurbituril is much higher as compared with α-cyclodextrin. A decomposition of cucurbituril is observed at temperatures higher than 270 °C whereas α-cyclodextrin decomposes noticeably at 220 °C even in the absence of oxygen. These results in principal show that the synthesis of polyester-rotaxanes with cucurbituril is possible. However, for the formation of polyesters it is essential that the reactive groups of the complexed molecules are located outside of the cavity of cucurbituril. Thus only alkyl chains with at least six or more methylene groups seem to be suitable for the synthesis of rotaxanes of the polyester-type.

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POVZETEK

Mehansko povezane molekule lahko pripravimo le, če izhajamo iz predhodno urejenih molekul. S kalorimetričnimi titracijami smo raziskali tvorbo kompleksov med α,ω-dikarboksilnimi kislinami in α,ω-dioli ter makrocikličnima ligandoma kukubrilom in α-ciklodekstrinom. Oba liganda s preiskovanimi molekulami tvorita relativno močne komplekse. Za tvorbo rotaksanov pa je potrebno, da so reaktivne skupine izven votline v predhodno tvorjenem kompleksu.