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Synthesis of Cucurbituril-spermine-[2]rotaxanes of the Amide-type

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[2]Rotaxanes with the macrocyclic ligand cucurbituril were prepared in yields between 10 and 90% from the reaction of the spermine complex with cucurbituril and different carboxylic acid chlorides in a two phase Schotten-Baumann reaction. This reaction type offers the possibility to synthesize a lot of different [2]rotaxanes. They are characterised by elemental analysis, ^{1}H-NMR spectroscopy and mass spectrometry.

Keywords: Cucurbituril, rotaxane, spermine

For chemists it is a fascinating idea to synthesize molecules held together not by covalent but only by mechanical bonds. Interlocked rings were first described by Wasserman in 1960 [1]. The principles of chemical topology were first discussed by Frisch in 1961 [2]. The name "rotaxane" was used by Schill in 1967 to describe a molecule which looks like a dumb-bell with a threaded ring [3]. A catenane consists of two or more interlocked rings. These molecules are schematically shown in Figure 1.

Using classical synthetic strategies it is possible but rather complicated to obtain rotaxanes and catenanes [4]. Using the principle of molecular recognition it becomes possible to preorganize the molecules just before the synthesis of rotaxanes and catenanes. This strategy increases the yields of molecules mechanically bound. Recently a large number of interlocked molecules has been described in the literature [5]. The formation of rotaxanes was mainly studied using cyclodextrins, crown ethers and cyclophanes as ring molecules. Another suitable candidate as ring component is the macrocyclic ligand cucurbituril, see Figure 2. This ligand possesses a rigid well-defined cavity similar to cyclodextrins. Cucurbituril was first synthesized in 1905 [6] but the chemical structure was reported by Mock in 1981 [7].

Obviously cucurbituril is an interesting ligand for the formation of rotaxanes because this ligand forms very stable complexes with different amines [8]. Thus, these complexes can be used as preorganized structures for the synthesis of rotaxanes. Quite recently, the formation of polyrotaxane nets of the spermine complex with cucurbituril due to metal coordination has

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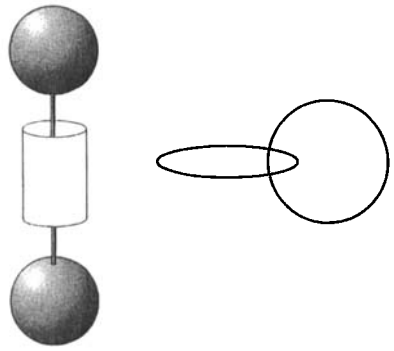


FIGURE 1 Schematic structures of a rotaxane and a catenane.

been reported [9]. The reaction of the 1,6-diaminohexane complex of cucurbituril with mono- and diacids leads to the formation of mono- and polyrotaxanes [10]. Also the formation of pseudorotaxanes of bipyridine derivatives with cucurbituril is known [11].

In this work we studied the formation of [2] rotaxanes from the spermine complex of cucurbituril with different carboxylic acid chlorides. The new rotaxanes are characterized by elemental analysis, NMR spectroscopy and mass spectrometry.

EXPERIMENTAL

The macrocyclic ligand cucurbituril is synthesized as described in the literature [6]. Spermine (Fluka) is of the highest purity available. The chlorides of carboxylic acids (Fluka or Merck) were used without further purification.

The complexes of cucurbituril with spermine are prepared by the addition of solid cucurbituril to an aqueous solution of spermine. The solid cucurbituril dissolves and as a result a clear solution is obtained. To this solution a solution of a carboxylic acid chloride (0.015 mol/l) in 50–150 ml diethylether is added. Upon stirring the reaction takes place at the phase boundary with the formation of a precipitate. This is filtered off, washed with hydrochloric acid (16% vol.), water and acetone or diethylether. During this treatment unthreaded cucurbituril or the pure diamides are dissolved and washed off.

The formation of the spermine complex and the reaction of the latter with benzoyl chloride is also performed under identical conditions in D_2O as solvent. The precipitate is washed with DCl, D_2O and acetone.

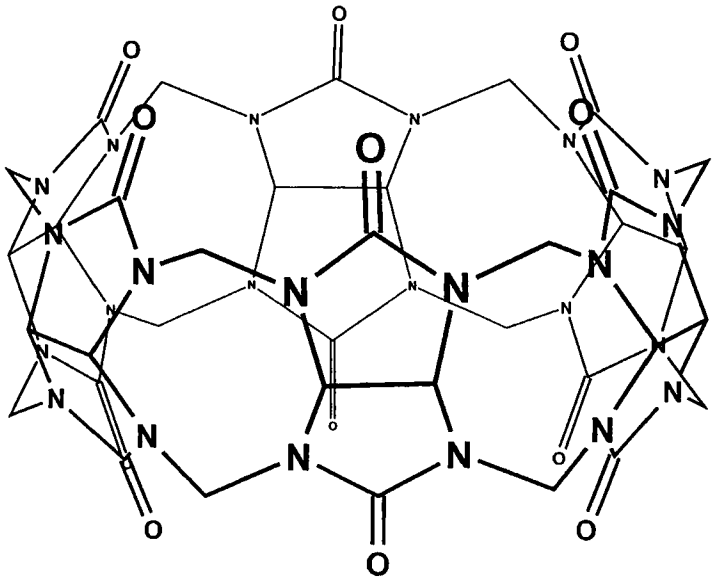


FIGURE 2 Chemical structure of cucurbituril.

All [2]rotaxanes reported in this paper are synthesized by the reaction of the spermine complex of cucurbituril with different carboxylic acids. Thus, these rotaxanes are named by the stopper groups used, like *e.g.*, benzoyl-rotaxane. The yields of the rotaxane syntheses are given in Table I.

Elemental Analysis

Due to the fact that cucurbituril strongly binds water molecules the interpretation of the results from the elemental analysis is only possible using the ratio of carbon to nitrogen [12]. These results together with those reported for cucurbituril are summarized in Table II. In most cases the experimental and the calculated C/N ratio are in excellent agreement. The reasons for some discrepancies cannot be given. However, it is known from the literature that of some cyclophanes *e.g.*, calixarenes no correct results for the elemental analysis are obtained [13].

Mass Spectrometry

Clear evidence for the formation of the rotaxanes was obtained from the mass spectra. They were measured from a glycerine matrix using the liquid-SIMS technique on an AMD 604 mass spectrometer. The experimental results are given in Table III.

IR Spectroscopy

Infrared spectra were measured using a FTS-45 spectrometer (Biorad) in solid using KBr. The spectra of the all compounds containing cucurbituril were dominated by the bands of cucurbituril. Only in the case of the rotaxanes an additional amide band (1546 cm^{-1}) and a

TABLE I Yields of [2]rotaxanes synthesized from the cucurbituril complexe with spermine

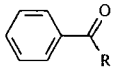
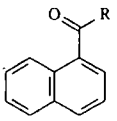
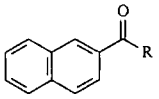
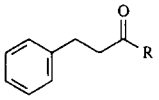
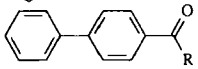
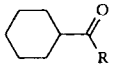
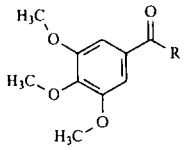
Stopper group	Rotaxane	Name	Total formula	Molecular weight [Da]	Yield [%]
	benzoyl-rotaxane	rotaxane 1	$C_{60}H_{70}N_{28}O_{14}$	1407.38	27
	1-naphthoyl- rotaxane	rotaxane 2	$C_{60}H_{74}N_{28}O_{14}$	1507.50	91
	2-naphthoyl- rotaxane	rotaxane 3	$C_{60}H_{74}N_{28}O_{14}$	1507.50	86
	3-phenyl propionyl-rotaxane	rotaxane 4	$C_{64}H_{78}N_{28}O_{14}$	1463.48	14
	biphenyl-4-carboxoyl-rotaxane	rotaxane 5	$C_{72}H_{78}N_{28}O_{14}$	1559.57	79
	cyclohexanoyl-rotaxane	rotaxane 6	$C_{60}H_{82}N_{28}O_{14}$	1419.47	68
	3,4,5-trimethoxy-benzoylrotaxane	rotaxane 7	$C_{66}H_{82}N_{28}O_{20}$	1587.53	21

TABLE II Results of the elemental analysis of cucurbituril, its complex with spermine and of the [2]rotaxanes formed

Substance	Calculated C%	Calculated H%	Calculated N%	Found C%	Found H%	Found N%	Calculated C/N	Found C/N	Ref.
cucurbituril	43.38	3.64	33.72	39.94	4.73	31.34	1.29	1.27	this work
				38.22	4.61	29.56		1.29	this work
				36.66	4.53	30.08		1.22	6
				40.92	4.17	30.17		1.36	7
				35.16	4.51	27.45		1.28	15
				36.30	4.45	28.10		1.30	16
				38.12	4.70	29.48		1.29	12c
				37.96	4.62	29.20		1.30	12c
				40.95	4.72	32.22		1.27	12c
spermine complex	46.07	5.21	32.70	41.48	5.45	28.88	1.41	1.44	this work
benzoyl-rotaxane	51.20	5.01	27.87	43.65	5.23	23.80	1.84	1.83	this work
1-naphthoyl-rotaxane	54.16	4.95	26.02	45.09	5.12	22.00	2.08	2.05	this work
2-naphthoyl-rotaxane	54.16	4.95	26.02	47.40	5.10	22.33	2.08	2.12	this work
3-phenyl propionyl-rotaxane	52.52	5.37	26.80	44.12	5.50	22.48	1.96	1.96	this work
biphenyl-4-carboxoyl-rotaxane	55.43	5.04	25.16	46.30	5.35	19.85	2.20	2.33	this work
cyclohexanoyl-rotaxane	50.75	5.83	27.64	43.53	6.26	22.88	1.84	1.90	this work
3,4,5-trimethoxybenzoyl-rotaxane	49.92	5.21	24.71	45.23	5.29	22.37	2.02	2.02	this work

TABLE III m/z peaks [Da] of the different [2]rotaxanes and of their most important fragments

Structure	Rotaxane 1	Rotaxane 2	Rotaxane 3	Rotaxane 4	Rotaxane 5	Rotaxane 6	Rotaxane 7
	1408.0	1507.7	1507.7	1463.6	1559.5	1419.4	1588.2
	1303.4	1353.3	1353.3	1331.7	1379.0	1309.6	1393.6
	704.5	754.3	754.3	732.5	780.3	–	–

carbonyl stretching band of the amide group (1639 cm^{-1}) were observed.

NMR Spectroscopy

The ^{1}H-NMR spectra were recorded with a Bruker WM300 using D_2O, a mixture of DCl/D_2O (37% vol.) or deuterated trifluoroacetic acid as solvents. As internal standard the sodium salt of trimethylsilyl propionic acid was used.

Spermine (DCl/D_2O) $\delta = 1.77-1.88$ (m, 4 H, CH_2), 2.09–2.22 (m, 4 H, CH_2), 3.12–3.25 (m, 12 H, CH_2).

Cucurbituril-spermine Complex (D_2O) $\delta = 0.51-0.59$ (m, 4 H, spermine-CH_2), $\delta = 2.00-2.10$ (m, 4 H, spermine-CH_2), $\delta = 2.30-2.40$ (m, 4 H, spermine-CH_2), $\delta = 2.90-2.99$ (m, 4 H, spermine-CH_2), $\delta = 3.30-3.39$ (m, 4 H, spermine-CH_2), $(AX)_6$ ($\delta_A = 4.43$ [12 H], $\delta_X = 5.75$ [12 H], $|^2J_{AX}| = 15$ Hz cucurbituril-CH_2, $\delta = 5.68$ (s, 12 H, cucurbituril-CH).

Benzoyl-rotaxane (DCl/D_2O) $\delta = 0.44-0.54$ (m, 4 H, spermine-CH_2), $\delta = 2.20-2.34$ (m, 4 H, spermine-CH_2), $\delta = 2.36-2.48$ (m, 4 H, spermine-CH_2), $\delta = 3.29-3.41$ (m, 4 H, spermine-CH_2), $\delta = 4.03-4.12$ (m, 4 H, spermine-CH_2), $(AX)_6$ ($\delta_A = 4.56$ [12 H], $\delta_X = 5.58$ [12 H], $|^2J_{AX}| = 15$ Hz, cucurbituril-CH_2), $\delta = 5.76$ (s, 12 H, cucurbituril-CH), $\delta = 6.53$ (m, 4 H, central spermine NH_2^+), $\delta = 7.62-7.71$ (m, 4 H, aryl-H), $\delta = 7.80-7.87$ (m, 2 H, aryl-H), $\delta = 7.88-7.95$ (m, 4 H, aryl-H).

RESULTS AND DISCUSSION

In Figure 3 the structure of the rotaxane formed from the spermine complex of cucurbituril and benzoylchloride is shown schematically.

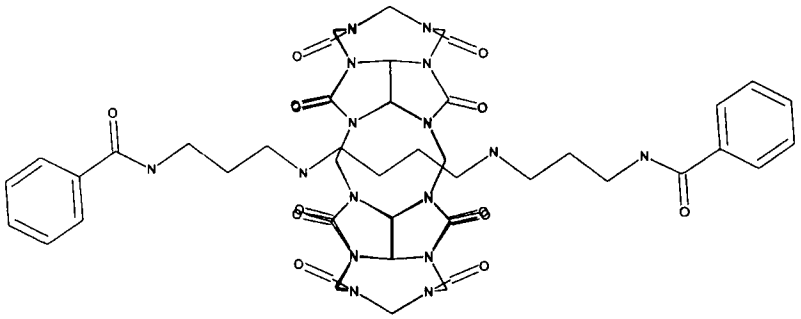


FIGURE 3 Schematic structure of the benzoyl-rotaxane.

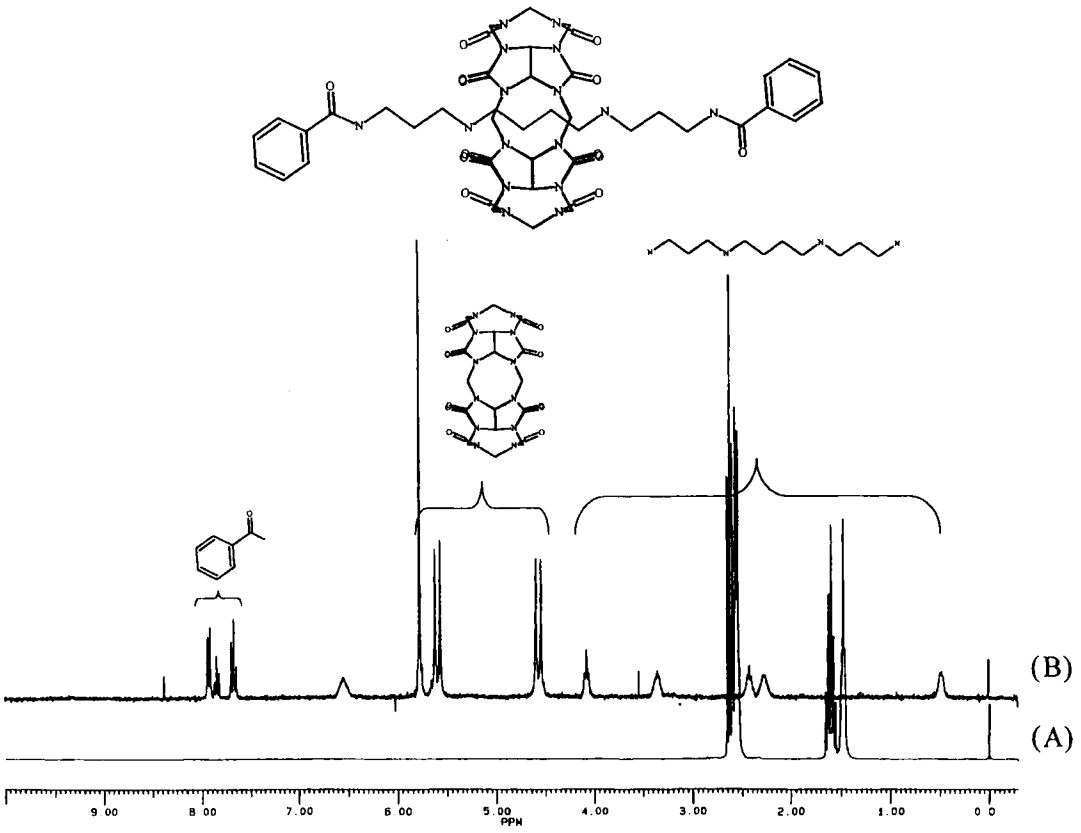


FIGURE 4 ^{1}H-NMR spectra of spermine (A), and of the benzoyl-rotaxane (B) recorded in DCl/D_2O.

Surprisingly the benzoyl group acts as a real stopper group [14]. No evidence is found for the dethreading of cucurbituril from this rotaxane. The reaction of the spermine complex with the stopper groups does not influence the NMR chemical shifts dramatically. The methylene groups located between both secondary amino groups are shielded by cucurbituril in the rotaxane. As a result the signals of the central methylene groups are shifted due to complex formation, see Figure 4.

The integration of the signals is in accordance with the expected signal intensities for the different protons. It should be noted that all spectra

have been obtained in acidified deuterated water, thus exchangeable protons would not give rise to integrateable signals. Thus, the spermine-cucurbituril complex does not show any signals attributable to NH protons at either the amide or central secondary ammonium groups. One additional resonance at 6.5 ppm for four protons is observed in the rotaxane ^{1}H-NMR spectrum. A similar resonance at 6.48 ppm has previously been observed for the rotaxane from cucurbituril and spermine with 2,4-dinitrophenyl stopper groups in deuterated dimethyl sulfoxide [9c]. The fact that in acidified D_2O a 4H signal at 6.5 ppm is observed thus means that this signal represents non-exchangeable protons. The best explanation is that the two central secondary amine functions are protonated [8a, b] and – being held inside the cucurbituril cavity – become unexchangeable with protons from "outside" water. After performing the complete synthesis of the rotaxane in D_2O as solvent this 6.5 ppm resonance can not longer be observed, since now the dideuterated ammonium groups are not exchanged against protons from the bulk.

The mass spectrum of the benzoyl-rotaxane is shown in Figure 5. Besides the m/z peak also the peaks for the molecule with only one stopper group, without any stopper group (spermine complex with cucurbituril), of cucurbituril and of the doubly charged rotaxane are observed. Comparable results are obtained for all other rotaxanes summarized in Table I. Thus, the spermine complex of cucurbituril can be used

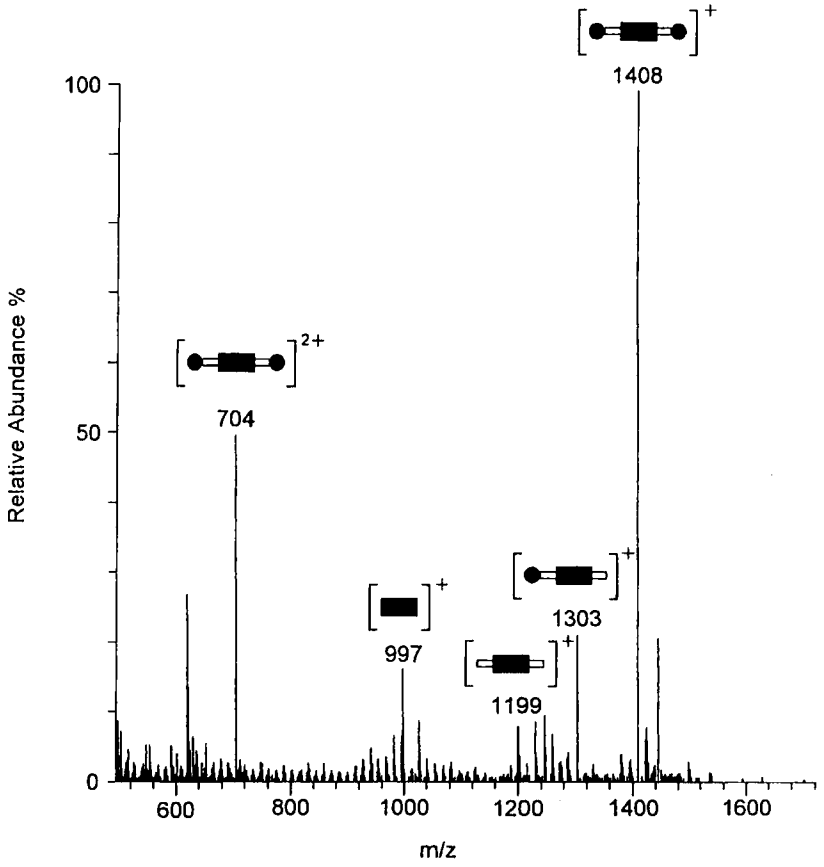


FIGURE 5 Mass spectrum of the benzoyl-rotaxane.

without any problems to synthesize [2]rotaxanes in high yields from starting materials commercially available. Instead of spermine other tetraamines or polyamines can be used for the synthesis of further cucurbituril-rotaxanes and polyrotaxanes. These results will be reported in the near future.

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