A [3]Rotaxane of the Amide Type

Fritz Vögtle,* Thomas Dünnwald, Mirko Händel, Ralf Jäger, Stephan Meier and Gabriele Harder

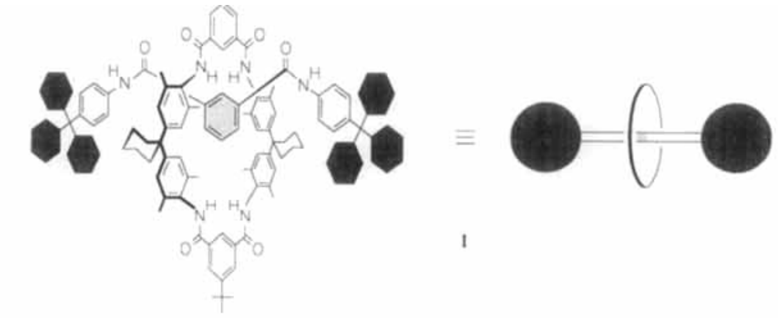
Dedicated to Professor H. A. Staab on the occasion of his 70th birthday

Abstract: Two new rotaxane types, the [2]rotaxanes **12a,b** and the [3]rotaxane **13**, have been synthesised by treating the "axle" **7** with the stopper component **9** in the presence of the "wheel" **8**. A nonionic template intermediate of type **10** is proposed. The [3]rotaxane **13** was only obtained when the chain of the "axle" had a certain length: with $n = 1$ only [2]rotaxane **12a** was isolated, whereas with $n = 2$ the [3]rotaxane **13** was formed besides the [2]rotaxane **12b**. This suggests that more extended rotaxanes and polyrotaxanes can be synthesised by the template strategy.

Keywords
lactam · macrocycles · rotaxanes · self-assembly · template syntheses

Introduction

Nonionic structure and formation via nonionic templates in organic solvents are the characteristics of amide-based rotaxane systems[1] (cf. **1**). Besides the few first examples, rotaxanes with a *para*-phenylene centre part, "axles" of five-membered heterocycles such as furan and thiophene, and sulfonamide bonds have so far been reported with yields as high as 41%.[2] It can be concluded that the template effect (molecular recognition among neutral molecules)[3] assumed for the synthesis tolerates structural changes, especially in the axle part of the rotaxane molecule, to a remarkably large degree.[2] It therefore appeared feasible to synthesise higher [*n*]rotaxanes[4] such as **13** (Scheme 2).



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Scheme 1. Amide-based [2]rotaxane **1** (dark grey = "stopper" area; light grey = isophthaloyl area).

[3]Rotaxanes are not just a game; they can serve as a testing array for template effects, in this case in a nonionic, mechanically intertwined system (compare **1**, **12**, **13**). In the future, higher catenanes and rotaxanes of this type will only be accessible when the molecular recognition processes involved in the template effect are better understood. Subsequently yields will also be improved with the increase in understanding of these template interactions. For the efficient synthesis of even more complicated topological systems (pretzel, knot, etc.) insight into the interactions of uncharged template partners will be essential. The synthesis of [3]rotaxanes was therefore an important challenge for our well-established template hypothesis.[3]

Results and Discussion

Scheme 2 shows the structural elements we used in the synthesis of the first [3]rotaxane **13** of the amide type. The synthetic strategy took into account the fact that, as in the synthesis of **1**, host/guest interactions are active in the course of the template effect (cf. $\mathbf{7} + \mathbf{8} \rightarrow \mathbf{10}, \mathbf{11}$). They are based on the steric complementarity between the electrically uncharged[3] host (wheel, **8**) and the nonionic guest (centre part of the axle, **7**), $\pi-\pi$ interactions, and probably hydrogen bonding between the amide groups of the guest and of the wheel.[5] In the synthesis of [3]rotaxane **13** we used the centre part **7** of the axle as the starting material and gave it the chance to thread through the wheel **8**[1] once or twice, with the wheel forming the electrically uncharged, concave template. It should then be feasible to react the host/guest complexes **10** (the arrangement shown in Scheme 2 is arbitrarily selected; the wheel can also be centred on the right-hand isophthaloyl unit) and **11** with the "stopper" **9** to give [2]- and [3]rotaxanes **12a,b** and **13**.

Initially, however, difficulties occurred: when we used the double isophthalic acid dichloride **7a** as the centre part of the

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[*] Prof. Dr. F. Vögtle, Dipl.-Chem. T. Dünnwald, Dipl.-Chem. M. Händel, Dipl.-Chem. R. Jäger, Dr. S. Meier, Dipl.-Chem. G. Harder
Institut für Organische Chemie und Biochemie der Universität Bonn
Gerhard-Domagk-Str. 1, 53121 Bonn (Germany)
Fax: Int. code +(228)73-5662
e-mail: voegtle@plumbum.chemie.uni-bonn.de

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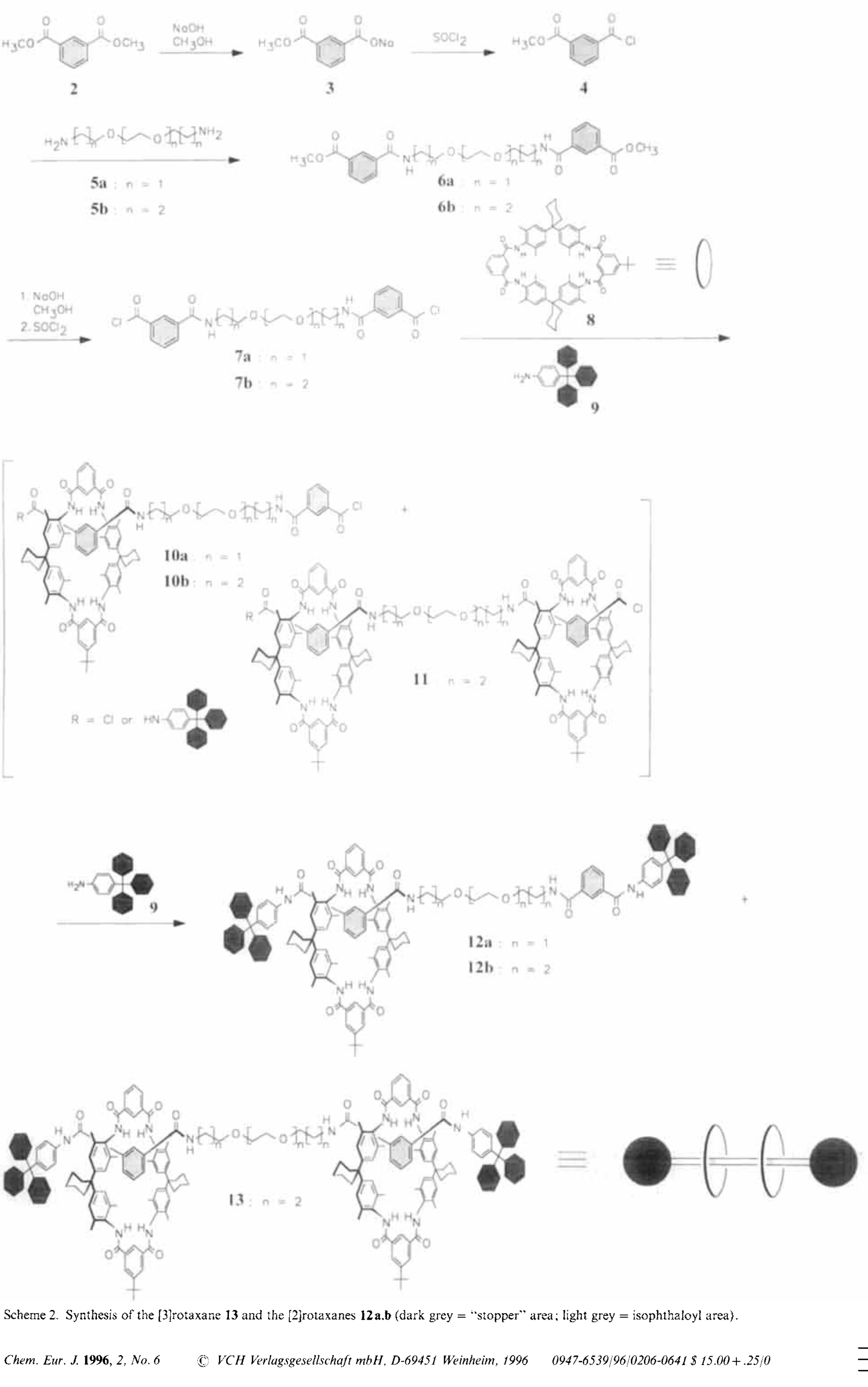

Scheme 2. Synthesis of the [3]rotaxane **13** and the [2]rotaxanes **12a**,**b** (dark grey = "stopper" area; light grey = isophthaloyl area).

axle, instead of the corresponding [3]rotaxane, only the [2]rotaxane **12a** was formed in 15% yield. When the thread was elongated ($n = 2$), [3]rotaxane **13** could be isolated in 2% yield besides [2]rotaxane **12b** in 6% yield. We assume that the axle is too short in the case of **7a**, possibly resulting in steric repulsion between the two wheels **8** in **12a**.

The [2]rotaxane **12b** could not be separated from the [3]rotaxane **13** by ordinary column chromatography; HPLC with Lichrosorb RP 18-5,[6] however, resulted in base-line separation.

The wheel (**8**) again proved to be remarkably tolerant towards variations in the axle unit, that is, the host/guest interactions in the formation of the template (**10**, **11**) in organic solvents (CH_2Cl_2) are not sensitive to structural variations, and the wheel acts as a general concave template.

The ^1H NMR spectra of the rotaxanes **12a,b** and **13** show the signals of both the axle and the wheel. Integration reveals a 1:1 axle:wheel relationship in the case of the [2]rotaxanes **12a** and **b**, whereas the spectrum of the [3]rotaxane has a 1:2 axle:wheel relationship. We also attempted to record the dynamic ^1H NMR spectra of both the [2]rotaxanes. The room-temperature spectra (293 K) proved the chemical identity of the two isophthalic units in the axle, so we presume that the wheel can shuttle from one isophthalic unit to the other. At low temperatures (in CD_2Cl_2 at 253 and 213 K) we observed only a spreading of the signals, but no coalescence point was found. These results show that the rotation and shuttling processes of the wheel on the axle are not particularly hindered at these temperatures.

Conclusion

The successful preparation of the nonionic rotaxane systems **12a,b** and **13** opens up further options for more complex uncharged catenanes, rotaxanes and possibly knots. In comparison with other rotaxanes[4, 7] this is the most simple system containing mechanical bonds that has been formed via a neutral template. We therefore do not consider the amide system a limitation to the preparation of higher catenanes and rotaxanes with a variety of building blocks, particularly once more knowledge has been gained about the nonionic template effect. Starting the synthesis with the wheel and then threading the axle unit through it has turned out to be a successful synthetic strategy which has once more supported our ideas of the template synthesis and the structure of the template.

It should also be possible to prepare rotaxanes by the "clipping" process,[8] as well as investigating the steric interactions of wheels and stoppers more closely by "slipping" processes.[8] This nonionic system exceeds the catenane and rotaxane systems hitherto known and opens up new perspectives, especially since the CONH units necessary for the template interactions can be replaced by sulfonamide units without significantly disturbing the catenane[9] or rotaxane[2] formation.

The above investigations may improve our understanding of molecular recognition processes with synthetic receptor molecules as well as of template synthesis based on electrically uncharged host/guest couples. Unlike their ionic counterparts, little is known about electrically neutral templates. In addition, knowledge about nanometer-sized and mechanically linked molecules can be gathered which may permit the construction of rotaxanes with, for example, built-in steric barriers that decrease the mobility of the wheel along the rotaxane axle. Such structural elements may prove useful as links in polymers with new, fine-tuned material properties. Rotaxanes could be prepared in a fashion comparable to the techniques of combinatorial chemistry by reacting a library of different wheels, axles and stoppers in a one-pot synthesis and determining the selectively formed reaction products. The mechanistic information collected would be of value when directed syntheses are planned.

Experimental Section

General methods: Chemicals were purchased from Aldrich and used as received, except thionyl chloride, purchased from Riedel de Haen. CH_2Cl_2 was dried with 4 Å molecular sieve. 3-Methoxycarbonylbenzoyl chloride **4** [10] and the macrocycle **8** [1] were prepared according to published literature. Thin-layer chromatography (TLC) was carried out on aluminium plates precoated with silica gel 60 F_{254} (Merck 1.05554). The plates were examined by UV light ($\lambda = 254$ nm). Column chromatography was carried out with silica gel 60 (Merck 15101). For HPLC we used a Hewlett Packard Series 1050 system fitted with a UV detector. The column we used was packed with Lichrosorb RP 18-5 [6]. Melting points were determined on a Kofler microscope heater (Reichert, Vienna) and not corrected. Microanalyses were performed by the Microanalytical Department at the Institut für Organische Chemie und Biochemie der Universität Bonn. Low-resolution electron-impact mass spectra (EIMS) were obtained on an A. E. I. MS 50 (Manchester, UK), whilst fast atom bombardment mass spectra (FABMS) were recorded on a Kratos Concept 1 H spectrometer. The matrix used was *m*-nitrobenzyl alcohol. MALDI spectra were recorded on a Kratos Kompakt MALDI 3, the matrices used were 9-nitroanthracene, 5-chlorosalicylic acid and 1,8-dihydroxyanthracene. The ^1H and ^{13}C NMR spectra were recorded on either a Bruker AM 250 (250 MHz (^1H) and 62.9 MHz (^{13}C)) or a Bruker AM 400 (400 MHz (^1H) and 100.6 MHz (^{13}C)) spectrometer.

3,3'[Bis(3,6-dioxaoctane)iminocarbonyl]bis(benzoic acid methyl ester) (6a): To a solution of 3-methoxycarbonylbenzoyl chloride **4** (4.29 g, 21.6 mmol) in dry CH_2Cl_2 (50 mL) a solution of 1,8-diamino-3,6-dioxaoctane **5a** (1.48 g, 10 mmol) in dry CH_2Cl_2 (30 mL) and triethylamine (2.82 mL, 20.4 mmol) was added at room temperature. This reaction mixture was stirred for 12 h, the solvent removed in vacuo, and the remaining residue purified by column chromatography (SiO_2, $CHCl_3$:CH_3OH 20:1; $R_f = 0.15$); 3.58 g (76% yield). FABMS: m/z 473.2 $[M+H]^+$; ^1H NMR (250 MHz, $CDCl_3$, 20 °C): $\delta = 3.65$ (m, 12H; CH_2), 3.90 (s, 6H; OCH_3), 6.95 (br, 2H; NH), 7.48 ("t", $^3J(H,H) = 7.8$ Hz, 2H; CH), 8.05 (d, $^3J(H,H) = 7.8$ Hz, 2H; CH), 8.10 (d, $^3J(H,H) = 7.8$ Hz, 2H; CH), 8.35 (s, 2H; CH); ^{13}C NMR (62.9 MHz, $CDCl_3$, 20 °C): $\delta = 39.80$ (CH_2N), 52.40 (OCH_3), 69.65, 70.20 (CH_2O), 127.70, 128.80, 130.30, 131.90, 132.30, 134.80 (arom.), 166.40, 166.50 (CO).

3,3'[Bis(3,6-dioxaoctane)iminocarbonyl]bis(benzoylchloride) (7a): **6a** (2.52 g, 5.3 mmol) was dissolved in methanol (70 mL) and water (0.7 mL) containing sodium hydroxide (0.42 g, 10.5 mmol) and refluxed for 20 h. The resulting disodium salt was precipitated by addition of diethyl ether (200 mL), filtered and dried in vacuo. To this compound (1.56 g, 3.2 mmol) thionyl chloride (40 mL) and DMF (5 drops) were added, and the reaction mixture was refluxed for 7.5 h. The surplus thionyl chloride was removed and the remaining residue dissolved in CH_2Cl_2 (30 mL) and filtered from the insoluble NaCl. Subsequently the solvent was removed and the product dried in vacuo; 1.34 g (88% yield). M.p. 76–77 °C; FABMS: m/z 481.0 $[M+H]^+$; ^1H NMR (250 MHz, $CDCl_3$, 20 °C): $\delta = 3.68$ (m, 4H; CH_2N), 3.72 (s, 4H; CH_2O), 3.90 (t, $^3J(H,H) = 4.2$ Hz, 4H; CH_2O), 6.90 (br, 2H; NH), 7.55 ("t", $^3J(H,H) = 8.0$ Hz, 2H; CH), 8.18 (d, $^3J(H,H) = 8.0$ Hz, 2H; CH), 8.30 (d, $^3J(H,H) = 8.0$ Hz, 2H; CH), 8.70 (s, 2H; CH); ^{13}C NMR (62.9 MHz, $CDCl_3$, 20 °C): $\delta = 54.29$ (CH_2N), 70.14, 70.72 (CH_2O), 129.15, 131.70, 133.63, 133.81, 135.32, 136.69 (arom.), 165.80, 167.91 (CO).

[2]Rotaxane 12a: *p*-Triphenylmethylaniline **9** (268 mg, 0.8 mmol) and triethylamine (0.11 mL, 0.8 mmol) were dissolved in dry CH_2Cl_2 (200 mL). To this mixture a solution of **8** (2.20 g, 2.3 mmol) and **7a** (200 mg, 0.4 mmol) in dry CH_2Cl_2 (150 mL) was added at room temperature over a period of 8 h. After removal of the solvent the remaining residue was purified by column chromatography (SiO_2, CH_2Cl_2:CH_3OH:$(C_2H_5)_2O$ 30:1:5, $R_f = 0.09$); 122 mg (15% yield). M.p. 169–171 °C; FABMS: m/z 2042.0 $[M+3H]^+$, 1080.5 $[M+2H-\text{macrocycle}]^+$, 961.5 $[\text{macrocycle}+H]^+$; MALDI: m/z 2041.6 $[M+2H]^+$; ^1H NMR (250 MHz, $CDCl_3$ + CD_3OD, 20 °C): $\delta = 1.25$ (s, 9H; *t*Bu), 1.40 (br, 4H; CH_2), 1.50 (br, 8H; CH_2), 1.75 (s, 12H; CH_3), 1.78 (s, 12H; CH_3), 2.18 (br, 8H; CH_2), 3.18 (m, 4H; CH_2N), 3.22 (m, 4H; CH_2O), 3.37 (s, 4H; CH_2O), 6.78 (s, 4H; wheel), 6.80 (s, 4H; wheel), 7.00 (d, $^3J(H,H) = 6.1$ Hz, 4H; stopper), 7.10 (m, 34H; stopper), 7.30 (d, $^3J(H,H) = 7.4$ Hz, 2H; isophth. axle), 7.45 ("t", $^3J(H,H) = 7.4$ Hz, 2H; isophth. axle), 7.55 (d, $^3J(H,H) = 7.4$ Hz, 2H; isophth. axle), 7.65 (br, 1H; isophth. wheel), 7.95 (s, 2H; isophth. wheel), 7.98 (d, $^3J(H,H) = 6.1$ Hz, 2H; isophth. wheel), 8.05 (s, 2H; isophth. axle), 8.15 (s, 1H; isophth. wheel), 8.25 (s, 1H; isophth. wheel), 8.57 (s, 2H; NH), 8.68 (s, 2H; NH), 9.10 (s, 2H; NH); ^{13}C NMR (62.9 MHz, $CDCl_3$ + CD_3OD, 20 °C): $\delta = 18.09$ (CH_3), 22.63, 26.04 (CH_2), 30.71 (CH_3 of *t*Bu), 34.72 (CH_2), 34.86 (C_{qu} of *t*Bu), 39.31 (CH_2N), 44.84 (C_{qu} of cycloh.), 64.33 (C_{qu} of trityl), 69.02, 69.65 (CH_2O), 120.24, 125.73, 127.22, 127.86, 128.00, 128.35, 128.46, 128.55, 129.09, 129.94, 130.47, 130.76, 131.05, 131.12, 131.18, 131.54,

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133.69, 134.03, 134.08, 134.50, 134.96, 135.12, 143.29, 146.35, 146.45, 147.90, 147.99, 152.90 (arom.), 166.29, 166.42, 167.63 (CO); $C_{136}H_{134}N_8O_{10}\cdot 4H_2O$: calcd. C 77.32%, H 6.77% N 5.30%; found C 77.38%, H 6.57%, N 5.11%.

3,3′[Bis(4,7,10-trioxatridecane)iminocarbonyl]bis(benzoic acid methyl ester) (6b): As for **6a** above, but with 4,7,10-trioxa-1,13-tridecanediamine **5b**. The crude material was purified by column chromatography (SiO_2, $CHCl_3$:CH_3OH 20:1, $R_f = 0.26$), 4.5 g (83% yield). MS (EI): *m/z* 543.2 (2%) $[M-H]^+$, 220.1 (95%) $[C_{12}H_{14}NO_3]^+$, 163.1 (100%) $[C_9H_7O_3]^+$; ^1H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 1.61$ ("quin", $^3J(H,H) = 6.3$ Hz, 4H; CH_2), 3.20 (t, $^3J(H,H) = 6.3$ Hz, 4H; CH_2N), 3.25–3.40 (m, 12H; CH_2O), 7.10 ("t", $^3J(H,H) = 7.7$ Hz, 2H; CH), 7.50 (d, $^3J(H,H) = 7.7$ Hz, 2H; CH), 7.78 (d, $^3J(H,H) = 7.7$ Hz, 2H; CH), 8.05 (s, 2H; CH); ^{13}C NMR (62.9 MHz, $CDCl_3$, 20 °C): $\delta = 28.88$ (CH_2), 39.04 (CH_2N), 52.35 (OCH_3), 70.20, 70.27, 70.57 (CH_2O), 127.87, 128.74, 130.40, 131.82, 135.16, 135.22 (arom.), 166.30, 166.46 (CO).

3,3′[Bis(4,7,10-trioxatridecane)iminocarbonyl]bis(benzoyl chloride) (7b): As for **7a** above, but with **6b**; 1.44 g (87% yield). FABMS: *m/z* 553.1 $[M+H]^+$; ^1H NMR (250 MHz, $CDCl_3$, 20 °C): $\delta = 1.88$ ("quin", $^3J(H,H) = 5.7$ Hz, 4H; CH_2), 3.50–3.65 (m, 16H; CH_2N, CH_2O), 7.58 ("t", $^3J(H,H) = 7.8$ Hz, 2H; CH), 8.18 ("t", $^3J(H,H) = 7.8$ Hz, 4H; CH), 8.47 (s, 2H; CH); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 28.47$ (CH_2), 39.48 (CH_2N), 68.60, 70.07, 70.60 (CH_2O), 129.42, 129.60, 131.76, 133.93, 134.20, 135.35 (arom.), 165.69, 168.01 (CO).

[2]- and [3]rotaxanes 12b, 13: To *p*-triphenylmethylaniline (**9**) (268 mg, 0.8 mmol) and triethylamine (0.11 mL, 0.8 mmol) in dry CH_2Cl_2 (200 mL) a solution of **8** (2.10 g, 2.1 mmol) and **7b** (221 mg, 0.4 mmol) in dry CH_2Cl_2 (150 mL) was added at room temperature over a period of 8 h. After removal of the solvent the remaining residue was purified by column chromatography (SiO_2, CH_2Cl_2:CH_3OH:$(C_2H_5)_2O$ 30:1:5, $R_f = 0.08$). The resulting product was a mixture of [2]- and [3]rotaxane, which was separated by HPLC on Lichrosorb RP 18-5 (liquid phase: CH_3OH).

[2]Rotaxane 12b: 52 mg (6% yield). M.p. 207–209 °C; FABMS: *m/z* 2112.8 $[M+H]^+$, 1151.4 $[M+H-\text{macrocycle}]^+$, 961.5 $[\text{macrocycle}+H]^+$; MALDI: *m/z* 2112.4 $[M+H]^+$; ^1H NMR (400 MHz, $CDCl_3$ + CD_3OD, 20 °C): $\delta = 1.30$ (s, 9H; *t*Bu), 1.40 (br, 4H; CH_2), 1.50 (br, 12H; CH_2), 1.80 (s, 12H; CH_3), 1.85 (s, 12H; CH_3), 2.20 (br, 8H; CH_2), 3.10 (t, $^3J(H,H) = 5.3$ Hz, 4H; CH_2N), 3.25 (m, 4H; CH_2O), 3.35 (m, 4H; CH_2O), 3.45 (m, 4H; CH_2O), 6.80 (s, 4H; wheel), 6.82 (s, 4H; wheel), 6.98 (br, 2H; NH), 7.05 (d, $^3J(H,H) = 8.4$ Hz, 4H; stopper), 7.15 (m, 34H; stopper), 7.45 ("t", $^3J(H,H) = 7.8$ Hz, 1H; isophth. wheel), 7.52 (d, $^3J(H,H) = 6.3$ Hz, 2H; isophth. axle), 7.60 (d, $^3J(H,H) = 7.0$ Hz, 2H; isophth. axle), 7.85 (br, 2H; isophth. axle), 7.95 (d, $^3J(H,H) = 7.8$ Hz, 2H; isophth. wheel), 8.00 (s, 2H; isophth. axle), 8.10 (s, 2H; isophth. wheel), 8.25 (s, 1H; isophth. wheel), 8.48 (s, 1H; isophth. wheel), 8.65 (s, 2H; NH), 8.82 (br, 2H; NH), 9.25 (s, 2H; NH); ^{13}C NMR (100.6 MHz, $CDCl_3$ + CD_3OD, 20 °C): $\delta = 18.51$ (CH_3), 22.91, 26.28, 28.86 (CH_2), 31.11 (CH_3 of *t*Bu), 35.17 (CH_2), 37.55 (CH_2N), 38.67 (C_{qu} of *t*Bu), 45.06 (C_{qu} of cycloh.), 64.57 (C_{qu} of trityl), 69.25, 69.72, 70.09 (CH_2O), 120.45, 124.19, 125.56, 126.01, 126.09, 127.49, 128.45, 128.67, 128.77, 129.39, 130.21, 130.44, 130.98, 131.04, 131.23, 131.31, 131.35, 131.42, 131.52, 134.07, 134.23, 134.40, 134.70, 135.06, 135.33, 143.52, 146.58, 147.99, 148.27, 153.16 (arom.), 166.32, 166.42, 166.52 (CO); $C_{140}H_{142}N_8O_{11}\cdot 5H_2O$: calcd C 76.34%, H 6.96%, N 5.09%; found C 76.31%, H 7.15%, N 4.72%.

[3]rotaxane 13: 26 mg (2% yield). M.p. 244–247 °C; FABMS: *m/z* 3074.1 $[M+2H]^+$, 2112.2 $[M+H-\text{macrocycle}]^+$, 961.6 $[\text{macrocycle}+H]^+$; MALDI: *m/z* 3075.1 $[M+3H]^+$; ^1H NMR (400 MHz, $CDCl_3$ + CD_3OD, 20 °C): $\delta = 1.09$ (s, 18H; *t*Bu), 1.20 (br, 12H; CH_2), 1.31 (br, 16H; CH_2), 1.60 (s, 24H; CH_3), 1.63 (s, 24H; CH_3), 2.00 (br, 16H; CH_2), 2.87 (t, $^3J(H,H) = 6.3$ Hz, 4H; CH_2N), 3.03 (m, 12H; CH_2O), 6.20 (br, 4H; NH), 6.60 (s, 8H; wheel), 6.65 (s, 8H; wheel), 6.71 (d, $^3J(H,H) = 6.3$ Hz, 4H; stopper), 6.91 (m, 34H; stopper), 7.00 (d, $^3J(H,H) = 7.0$ Hz, 2H; isophth. axle), 7.14 (d, $^3J(H,H) = 7.0$ Hz, 2H; isophth. axle), 7.27 (m, 4H; isophth. wheel, axle), 7.41 (s, 2H; isophth. axle), 7.75 (d, $^3J(H,H) = 7.8$ Hz, 4H; isophth. wheel), 7.87 (s, 4H; isophth. wheel), 8.07 (s, 2H; isophth. wheel), 8.20 (s, 2H; isophth. wheel), 8.80 (s, 4H; NH), 9.00 (br, 2H; NH), 9.35 (s, 2H; NH); ^{13}C NMR (100.6 MHz, $CDCl_3$ + CD_3OD, 20 °C): $\delta = 17.96$ (CH_3), 22.18, 25.92, 28.49 (CH_2), 30.53 (CH_3 of *t*Bu), 34.71 (CH_2), 34.84 (C_{qu} of *t*Bu), 38.37 (CH_2N), 44.64 (C_{qu} of cycloh.), 64.24 (C_{qu} of trityl), 67.84, 69.51, 69.95 (CH_2O), 117.57, 121.06, 121.58, 124.08, 125.68, 127.09, 127.46, 128.01, 128.08, 128.36, 128.98, 129.91, 130.53, 130.72, 130.97, 130.99, 131.05, 133.64, 134.01, 134.14, 134.61, 134.83, 134.85, 143.57, 146.21, 147.71, 147.85, 152.73 (arom.), 166.44, 166.57, 167.07, 167.73 (CO); $C_{204}H_{214}N_{12}O_{15}\cdot 10H_2O$: calcd C 75.30%, H 7.25%, N 5.17%; found C 75.06%, H 7.55%, N 4.84%.

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