Size Complementarity of Macrocyclic Cavities and Stoppers in Amide-Rotaxanes

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New [2]rotaxanes were prepared by the threading and the slipping procedure, the latter having the advantage of not needing templating interactions. As a consequence, the first [2]rotaxane consisting of a tetraamide macrocycle and a pure hydrocarbon thread was synthesized (see **12a** in *Scheme 2*). Sterically matching wheels and axles being the basic requirement of a successful slipping approach to rotaxanes, mono- and bishomologous wheels **5b**,**c** with larger diameters than the parent **5a** were synthesized and mechanically connected to amide axles **10a**–**c** which were stoppered with blocking groups of different spatial demand (*Scheme 1*). The deslipping kinetics of the resulting rotaxanes **8a**–**c** and **9a**,**b** were measured and compared; it emerges that even slight increases in the wheel size require larger stoppers to stabilize the mechanical bond. Moreover, when the deslipping rate of **8a** (amide wheel and amide axle) was determined in either DMF or THF, a strong dependence on the solvent polarity, which is caused by a differing extent of intramolecular H-bonds between the wheel and the axle, was observed. As expected, no such dependence was detected for rotaxane **12a** (amide wheel and hydrocarbon axle) whose components cannot interact *via* H-bonds. The comparison of the sterically matching pairs of macrocycles and blocking groups, found by a systematic fitting based on the results of slipping and deslipping experiments, with other rotaxane types bearing similar stoppers allows conclusions concerning the relative cavity size of wheels of various structure.

1. Introduction. – In principle, the mechanical bond of rotaxanes [2] can be built by three different approaches: In the clipping procedure [3], the macrocycle is formed from acyclic precursors around a preformed axle, whereas a threading process [4] takes place when the center part of the axle is embedded in the cavity of the wheel and blocked with sterically demanding stopper groups. The slipping method [5], finally, puts a macrocycle on a preformed axle at elevated temperatures.

Our threading syntheses were assisted by either a neutral [4k–m] [6] or an anionic [7] templated intermediate, yielding [2]rotaxanes with amide or ether axles, respectively. Amide-based rotaxanes have also been synthesized by slipping in the melt, which is not only simple and effective, but also has the advantage of not requiring any reactive groups as do the template-driven clipping and threading procedures [5i]. The only requirement that the reactants have to meet is the steric compatibility of the cavity of the wheel, the size of the stopper, and the axle.

First systematic studies on statistical syntheses of rotaxanes *via* threading and slipping were carried out by *Harrison* in 1972 [5a]. He examined the effect of size complementarity by reacting a mixture of cycloalkanes $(CH_2)_n$ with axles bearing stoppers of different steric demand. When a trityl blocking group was used, only the

[1]) Taken in part from the Ph. D. thesis of *C.H.* [1]

29-membered cycloalkane was able to pass over the stopper and form a rotaxane which is stable at room temperature. On the other hand, $(CH_2)_{28}$ was too small to slip on the axle, and rotaxanes with larger rings disassembled, even at room temperature. In 1986, *Schill et al*. took up *Harrison*'s strategy of rotaxane synthesis by thermal equilibration, but instead of using cycloalkane mixtures, pure macrocycles of defined ring size were employed [5e]. The effect of ring and stopper size on the synthesis of polyester rotaxanes was examined by *Gibson et al*. [4i].

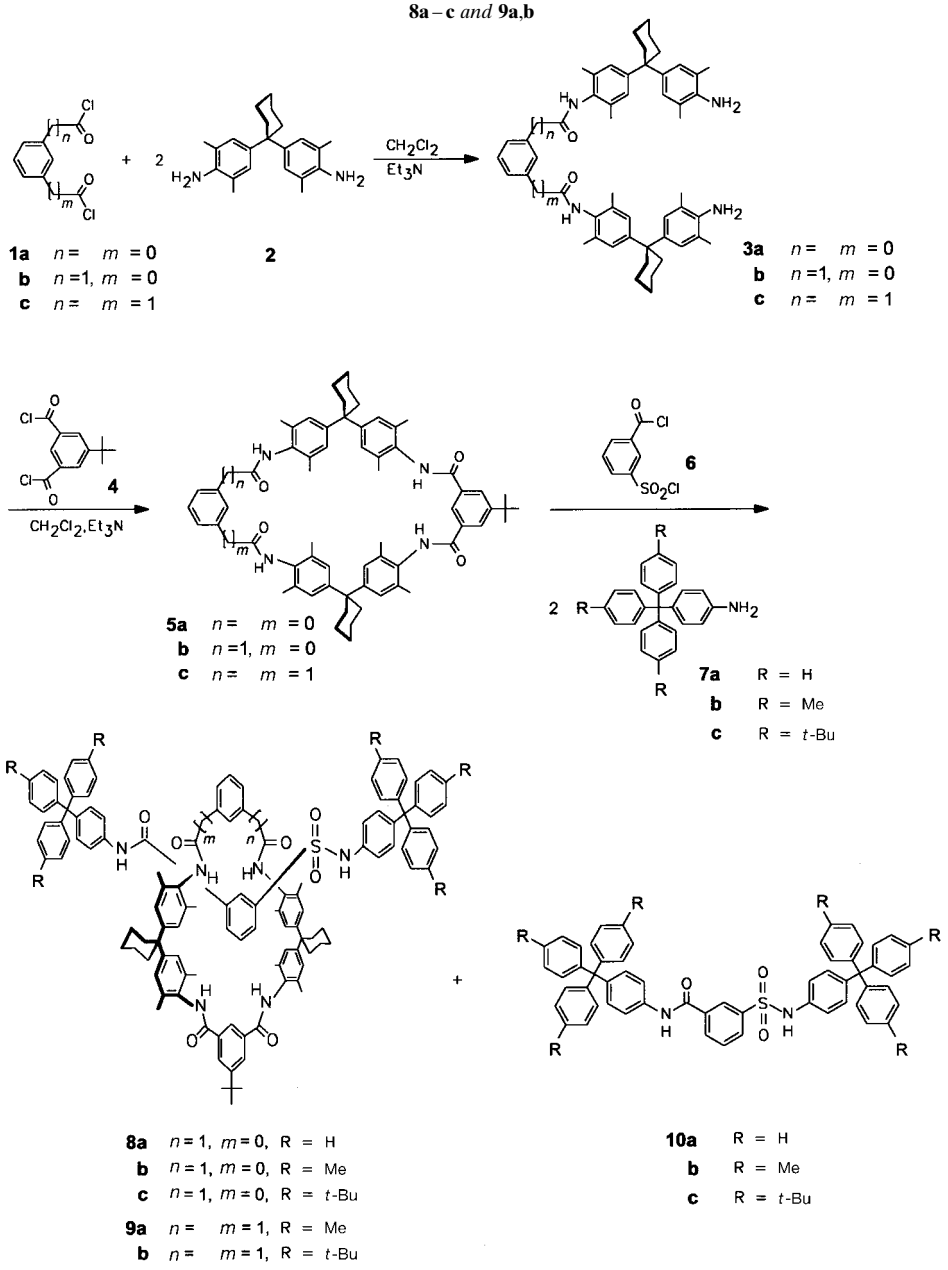
A new impetus to the slipping approach was given by *Stoddart* and co-workers in 1993 when they synthesized [2]- and [3]rotaxanes consisting of bipyridinium-based axles and arenediyldioxy-based macrocycles [5f,g]. In the meantime, a number of linear and branched rotaxanes has been prepared by this thermally promoted slipping method [8]. Recently, *Houk* and *Stoddart* examined the effect of the stopper size (different substituents on tetraarylmethane-based stoppers) with computational investigations and found two main energy barriers for the passage of the macrocycle over the blocking group [9].

We here present new pairs of sterically matching tetralactam macrocycles and stoppered axles as an approach to the final goal of establishing a more general reference system that allows an easy access to informations about size ratios for all types of wheels and stoppers.

2. Results and Discussion. – In the course of earlier studies on the mechanism of formation of amide-based rotaxanes, we incorporated additional methylene groups into the framework of the parent tetralactam macrocycle **5a** we had used so far as wheel. The new homologous macrocycle **5b** was synthesized from homoisophthaloyl dichloride (**1b**) and the diamine **2**, *via* **3b** and reaction with **4**, according to the established two-step procedure [10] (*Scheme 1*). Reaction of **5b** with 3-(chlorosulfonyl)benzoyl chloride (**6**) and two equiv. of the stopper compound **7a** led to the rotaxane **8a** (17% yield) *via* the H-bond template effect described earlier [2g]. This neutral template effect again was found to be tolerant to the increase of the ring size in going from **5a** to **5b** (*Scheme 1*).

Contrary to preliminary expectations based on CPK models, the new rotaxane **8a** was not stable, but disassembled already partially during the chromatographic workup. The corresponding deslipping process could be monitored by ^{1}H-NMR spectroscopy where especially the gradual change of the signal caused by the homoisophthaloyl methylene group from a geminal *AB* system (rotaxane **8a**) to a *s* (macrocycle **5b**) pictured the reaction. The quantitative evaluation of the relative intensity of signals of significant probe protons (aromatic region) allowed the calculation of the rate constant k and the half-life $t_{1/2}$ of this first-order reaction at room temperature. We expected the rate of the decomposition process to depend on medium effects: In a polar environment ((D_7)DMF), the intramolecular H-bonding motif between the axle and the wheel should be destroyed for the benefit of intermolecular interactions with the solvent, and consequently the deslipping of the wheel is hindered only by the (obviously insufficient) steric demand of the stopper groups. In a less polar solvent ((D_8)THF), however, the combination of mechanical bond and intercomponent interactions opposes the disassembling and, therefore, retards the reaction. Indeed, we found the half-life $t_{1/2}$ of **8a** in (D_7)DMF to be 13.6 ± 0.2 h and in (D_8)THF to be 115 ± 4 h (*Figs. 1* and *2*).

Scheme 1. *Two-Step Synthesis of the New Macrocyclic Hosts* **5b**,**c** *and Threading Approach to the Rotaxanes* **8a**–**c** *and* **9a**,**b**



Since the steric ratios of the cavity size and the stopper volume allow the disassembling of rotaxane **8a**, which is, as a consequence, strictly speaking a pseudorotaxane, the reverse reaction – the slipping synthesis of **8a** – should also be

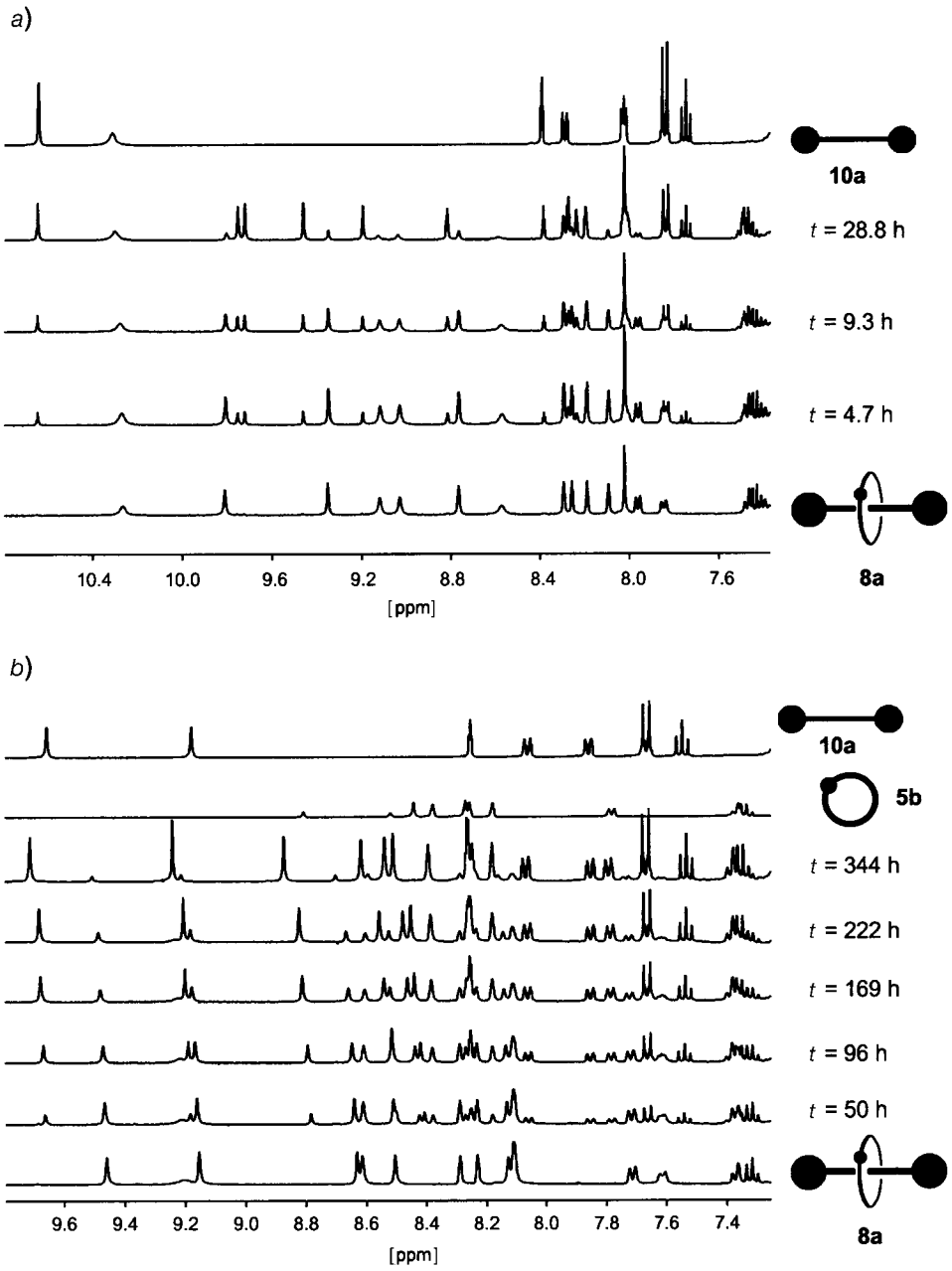


Fig. 1. *Disassembling of* **8a** *as observed by* ^{1}*H-NMR spectroscopy* a) *in* (D_7)*DMF and* b) *in* (D_8)*THF.* In polar (D_7)DMF, **8a** decomposed within 3 d, whereas in (D_8)THF, this reaction took significantly longer.

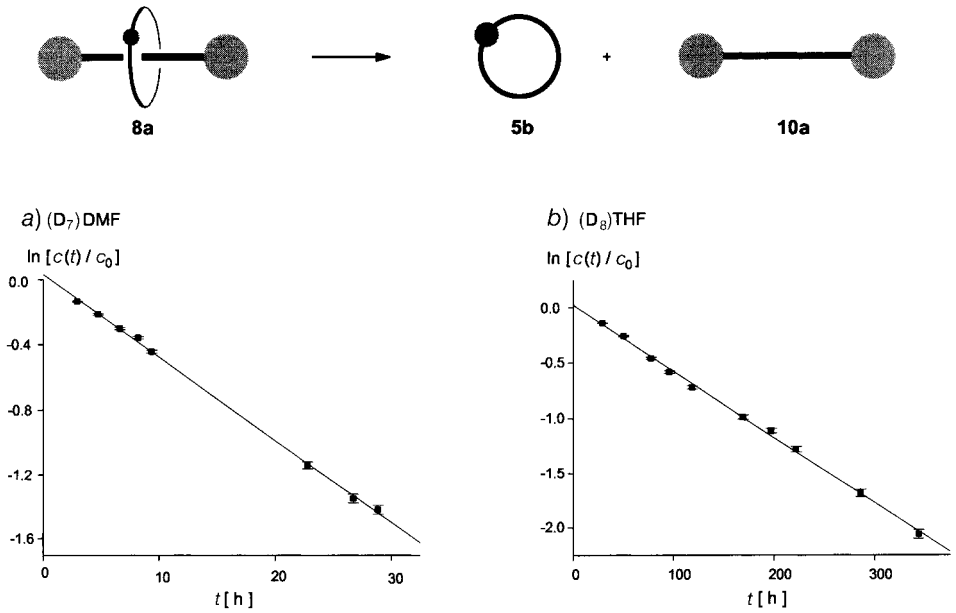


Fig. 2. *Decrease of the relative ratios of the concentration of* **8a** *as a function of time* a) *in (D7)DMF and* b) *in (D8)THF.* This was used to calculate the rate constants k of the disassembling and the half-lives $t_{1/2}$ *of* **8a**.

feasible. In fact when equimolar amounts of **5b** and **10a** were melted together, rotaxane **8a** could be unambiguously identified by TLC[2]). Therefore, it can be concluded that the cavity of the wheel **5b** is large enough to allow the passage over the *p*-tritylaniline stopper in both directions (slipping-on and slipping-off), or, in other words, the spatial demand of **7a** is not sufficient to close a stable mechanical bond between **5b** and **10a** at room temperature.

A stable rotaxane with wheel **5b** was obtained when the sterically more demanding *tert*-butyl derivative **7c** was used as stopper component. On the one hand, the resulting rotaxane **8c** was stable at room temperature and even at elevated temperatures (60°) as shown by ^{1}H-NMR spectroscopy and TLC; on the other hand, the stopper of **10c** is too bulky to allow the slipping synthesis in the melt of **8c**.

The steric demand of the methyl-substituted stopper compound **7b** lies between those of **7a** and **7c**. Rotaxane **8b** turned out to be stable at room temperature and in boiling THF. However, when the components **5b** and **10b** were melted together at 350°, rotaxane **8b** could be undoubtedly detected by TLC. This means that macrocycle **5b** and stopper compound **7b** are well matched in a way that, at high temperatures, the cavity of **5b** is wide enough to permit the passage over the stopper, but once cooled to room temperature, the resulting rotaxane is stable.

Encouraged by these results, we expanded the macrocyclic host by a second methylene group hoping *a*) that molecular recognition and amide receptor qualities [11] would allow the threading synthesis and *b*) that the cavity of the bis-homo wheel **5c**

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[2]) This slipping synthesis was carried out on only a qualitative level since the expected yield was significantly lower than for the threading method.

would then be large enough to allow even the passage of the *p*-(*tert*-butyl)-substituted trityl blocking group. While the mono-methylene derivative **5b** did not crystallize, single crystals of **5c** could be obtained from $CHCl_3$/MeOH (*Fig. 3*). Unlike other tetralactam macrocycles [12], the X-ray structure analysis of **5c** revealed two carbonyl groups (of the benzene-1,3-diacetamide unit) pointing to the inside of the cavity.

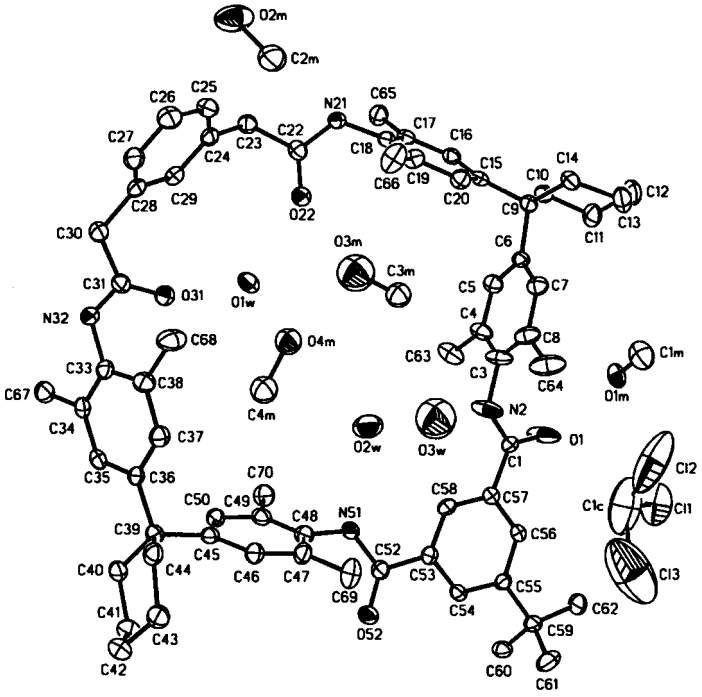


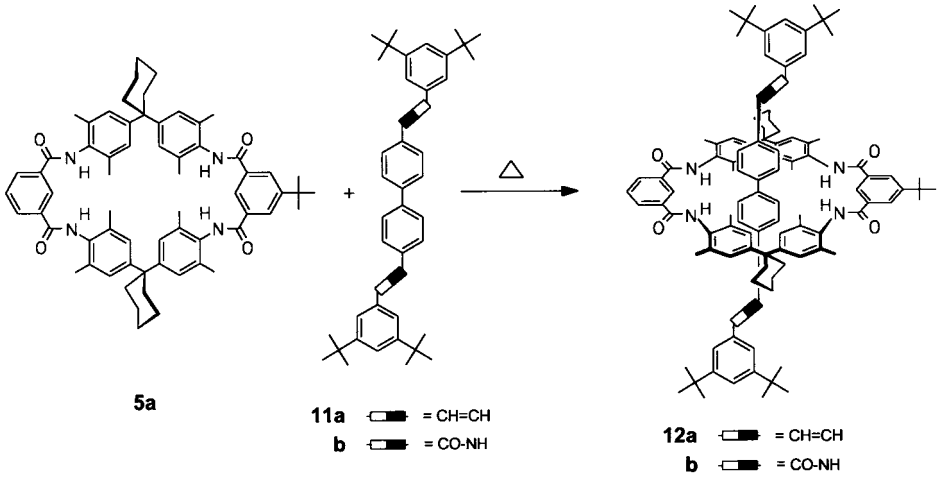
Fig. 3. *Crystal-structure analysis of* **5c**. Arbitrary numbering. H-Atoms are omitted for clarity. Only one split position of the disordered solvent is shown.

When macrocycle **5c** was reacted with the axle central piece **6** and the stoppers **7b**,**c**, the corresponding rotaxanes **9a**,**b** were isolated, characterized by NMR spectroscopy and mass spectrometry, and examined regarding their stability in solution. Yields were clearly lower compared to **8a**–**c**, since the precipitation of the macrocycle **5c** from the reaction mixture during the reaction could not be avoided. After four days at room temperature, a considerable portion (40%) of rotaxane **9a** was found to have disassembled in solution (THF). Also the slipping synthesis of **9a** in the melt was accomplished successfully. In contrast to this, the (*tert*-butyl)-substituted **9b** was stable in solution and could not be obtained by the melting procedure. Thus, a stopper molecule fitting to macrocycle **5c** in such a manner that not only the simple access to the rotaxane by the slipping method at high temperatures is possible, but also sufficient stability of the mechanical bond at room temperature is ensured, has still to be found.

The influence of intramolecular interactions on the stability of the mechanical bond can also be pictured by the comparison of the rotaxanes **12a** and **12b**. Both rotaxanes

were synthesized by brief melting of the corresponding axles **11a**,**b** and wheel **5a** (slipping method, *Scheme 2*). Interestingly, the deslipping rate of rotaxane **12a**, whose components – wheel **5a** and the pure hydrocarbon thread **11a** – are incapable of forming intramolecular H-bonds, did not depend on solvent effects. The half-lifes $t_{1/2}$ of **12a** in (D_7)DMF (26 ± 4.4 h) and in (D_8)THF (20 ± 2.9 h) were of the same order of magnitude. Due to solubility problems, the deslipping rates of **12a** and **12b** could not be compared quantitatively, but direct measurements clearly indicated that rotaxane **12a** disassembled faster than the amide derivative **12b**. We attribute this finding to the lack of intramolecular H-bonds in **12a**.

Scheme 2. *The Slipping Approach to the Rotaxanes* **12a** *and* **12b**



3. Conclusion. – Focusing on the size complementarity of macrocycles and stopper molecules, we have reported the synthesis of several new amide-based [2]rotaxanes. The deslipping reaction of **8a** and its dependence on medium effects has been studied in detail. *Fig. 4* summarizes the results of the slipping and deslipping reactions.

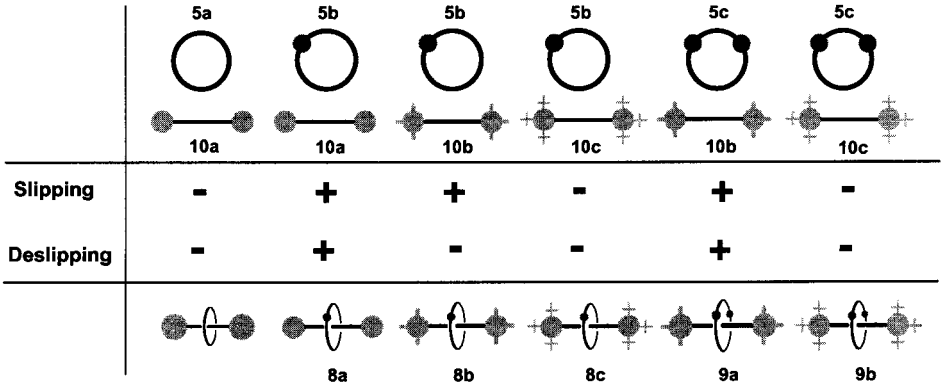


Fig. 4. *Summary of the results obtained from slipping and deslipping experiments of the rotaxanes* **8a**–**c** *and* **9a**,**b**

When these results are compared to the early slipping experiments of *Harrison* [5a,b] and of *Schill et al.* [5e], it can be concluded that the cavities offered by macrocycle **5b** and the cycloalkane $(CH_2)_{29}$ are of about the same size. Similar to *Harrison*'s results, no rotaxane formation was detected when axles with *tert*-butyl-substituted stoppers were reacted with the macrocycles **5b** and **5c**. However, *Harrison* could isolate a rotaxane with the 34-membered cycloalkane $(CH_2)_{34}$ and a (*tert*-butyl)-substituted trityl blocking group when the reaction was carried out under acid catalysis, but the resulting rotaxane was stable only below 0°. In contrast to this, rotaxane **9b**, which also bears a 34-membered ring, was stable. Obviously, the enhanced flexibility of $(CH_2)_{34}$ compared to **5c** allows the macrocycle to pass over the bulky *tert*-butyl groups, whereas the tetraamide **5c** is too rigid to slip off.

A successful slipping synthesis with the sterical demanding blocking group **7c** was reported by *Stoddart* and co-workers [8d]. Two 2,7-naphthylene units in a crown ether afford a wide open cavity that permits the slipping-on process.

These examples outline the difficulties which arise when macrocycles of different structure are compared. We, therefore, suggest determining the cavity size by rotaxanation and relating the matching stopper molecule to the corresponding cycloalkane, which then could serve as basic unit for ring-size comparisons.

Experimental Part

General. Solvents were purified by standard methods and dried if necessary. Reagents used were in commercial quality. TLC: *Merck* silica gel *60* F_{254} plates; visualization by UV light. Column chromatography (CC): silica gel *60* (40–63 μm, 63–100 μm, *Merck*). M.p.: *Kofler* hot stage (*Reichert*); uncorrected. ^{1}H- and ^{13}C-NMR: *AM-400* (^{1}H: 400 MHz; ^{13}C: 100.6 MHz) of *Bruker Physik AG*, Karlsruhe, with solvent peak as reference; abbrevations: Ar = aryl, *t*Bi = 5-(*tert*-butyl)isophthaloyl, Cy = cyclohexyl, Hiso = homoisophthaloyl, 3Sb = 3-sulfonylbenzoyl, *m*Xyl = *m*-xylylene. EI-MS: *A. E. I. MS 50*, Manchester; *m*/*z* (%). FAB-MS: *Concept 1 H*, *Kratos Analytical*, Manchester; with 3-nitrobenzyl alcohol (3-NBA) as matrix. MALDI-TOF-MS: *TOF Spec E*, *Micromass*, Manchester; with 9-nitroanthracene (9-NA) or 2,5-dihydroxybenzoic acid (2,5-DHB) as matrix. Elemental analyses were preformed by the Microanalytical Department of the 'Kekulé-Institut für Organische Chemie und Biochemie', University of Bonn. The following compounds were prepared according to literature methods: **2** [10a][13], **3a** [10a] (CC eluant: CH_2Cl_2/AcOEt 4:1), **6** [14], **7c** [15], **11a** [16], **11b** [5i].

Homoisophthaloyl Dichloride (= *3-(Chlorocarbonyl)benzeneacetyl Chloride*; **1b**). A mixture of homoisophthalic acid [17] (1.0 g, 5.6 mmol), thionyl chloride (30 ml), and 3 drops of DMF was heated under reflux and N_2 for 2 h. Excess of thionyl chloride was removed *in vacuo* yielding 0.9 g (75%) of **1b** as orange oil which was used without further purification. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.24 (*s*, CH_2); 7.53 ('*t*', ^3J = 7.9, 1 arom. H); 7.59 (*d*, ^3J = 7.9, 1 arom. H); 8.00 (*s*, 1 arom. H); 8.09 (*d*, ^3J = 7.9, 1 arom. H). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 53.01 (CH_2); 130.35, 131.89, 132.89, 137.01 (CH); 133.16, 134.63 (quat. C); 168.64, 172.02 (C=O). EI-MS: 216 (3, M^+), 181 (71), 153 (36), 145 (100), 117 (34).

Benzene-1,3-diacetyl Dichloride (**1c**). A mixture of benzene-1,3-diacetic acid (2.0 g, 10 mmol), thionyl chloride (50 ml), and 7 drops of DMF was heated under reflux and N_2 for 5 h. Removal of excess of thionyl chloride *in vacuo* yielded an orange oil which was purified by cooling (−18°) petroleum ether solns. made at room temperature: 1.1 g (46%) of **1c**. M.p. 27–29°. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.15 (*s*, 2 CH_2); 7.18 (*s*, H–C(2)); 7.25 (*dd*, ^3J = 7.6, ^4J = 1.6, H–C(4), H–C(6)); 7.38 (*t*, ^3J = 7.6, H–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 53.50 (CH_2); 130.05, 130.26, 131.34, 132.71 (arom. C), 171.78 (C=O). EI-MS: 230 (21, M^+), 194 (24), 167 (100), 131 (34), 103 (29).

N,N'-*Bis{4-[1-(4-amino-3,5-dimethylphenyl)cyclohexyl]-2,6-dimethylphenyl}homoisophthalamide* (= N-*{4-[1-(4-Amino-3,5-dimethylphenyl)cyclohexyl]-2,6-dimethylphenyl}-3-{[{4-[1-(4-amino-3,5-dimethylphenyl)cyclohexyl]-2,6-dimethylphenyl}amino}carbonyl]benzeneacetamide*; **3b**) was prepared from **1b** (2.17 g, 10.0 mmol) and diamine **2** (20.0 g, 62.0 mmol) according to the procedure reported for **3a** [10a]. Purification by CC (silica

gel (40–63 μm), CH_2Cl_2/AcOEt 4:1; R_f 0.09) yielded 2.3 g (29%) of **3b**. Colorless solid. M.p. 226–229°. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.4–1.6 (br., 12 H, CH_2); 2.04 (*s*, 2 Me); 2.10 (*s*, 2 Me); 2.14 (*s*, 2 Me); 2.19 (*s*, 2 Me); 2.1–2.3 (br., 8 H, CH_2); 3.44 (br., 2 NH_2); 3.76 (*s*, CH_2CO); 6.62 (*s*, 1 NH); 6.79 (*s*, 2 H, Ar); 6.85 (*s*, 2 H, Ar); 6.91 (*s*, 2 H, Ar); 7.00 (*s*, 2 H, Ar); 7.40 (*s*, 1 NH); 7.44 ('*t*', ^3J = 7.7, 1 H, Hiso); 7.52 (*d*, ^3J = 7.7, 1 H, Hiso); 7.78 (*d*, ^3J = 7.7, 1 H, Hiso); 7.93 (*s*, 1 H, Hiso). ^{13}C-NMR (100.6 MHz, (D_7)DMF): 18.18, 18.22, 18.68, 18.70 (Me); 23.41, 23.45, 26.83, 37.19, 37.22 (CH_2); 43.21 (CH_2CO); 44.84, 44.90 (quat. C, Cy), 121.15, 121.18 (quat. C); 126.15, 126.63, 126.66, 127.05, 127.11, 128.83, 129.15, 132.63 (CH); 132.96, 133.22, 135.10, 135.49, 135.83, 135.98, 137.75, 142.25, 142.29, 148.78, 149.05 (quat. C); 166.02, 169.25 (C=O). FAB-MS: 788.5 (M^+). Anal. calc. for $C_{53}H_{64}N_4O_2$ (789.11): C 80.67, H 8.17, N 7.10; found: C 80.40, H 8.02, N 6.90.

N,N′-*Bis{4-[1-(4-amino-3,5-dimethylphenyl)cyclohexyl]-2,6-dimethylphenyl}benzene-1,3-diacetamide* (**3c**) was prepared from **1c** (0.56 g, 2.4 mmol) and diamine **2** (5.0 g, 15.5 mmol) according to the procedure reported for **3a** [10a]. Purification by CC (silica gel (40–63 μm), CH_2Cl_2/AcOEt 4:1; R_f 0.05) yielded 1.0 g (52%) of **3c**. Colorless solid. M.p. 245–247°. ^{1}H-NMR (400 MHz, (D_7)DMF): 1.45–1.51 (br., 12 H, CH_2); 2.10 (*s*, 4 Me); 2.12 (*s*, 4 Me); 2.16–2.30 (br., 8 H, CH_2); 3.72 (*s*, 2 CH_2CO); 4.40 (*s*, 2 NH_2); 6.88 (*s*, 4 H, Ar); 7.03 (*s*, 4 H, Ar); 7.28–7.35 (*m*, 3 H, *m*Xyl), 7.50 (*s*, 1 H, *m*Xyl); 9.34 (*s*, 2 NH). ^{13}C-NMR (100.6 MHz, (D_7)DMF): 18.19, 18.71 (Me); 23.41, 26.80, 37.20 (CH_2); 43.39 (CH_2CO); 44.93 (quat. C, Cy); 121.13 (quat. C); 126.58, 127.04, 127.84, 128.70, 130.49 (CH); 133.03, 135.11, 136.01, 137.34, 142.26, 148.68 (quat. C); 169.44 (C=O). FAB-MS: 802.6 (M^+). Anal. calc. for $C_{54}H_{66}N_4O_2$ (803.14): C 80.76, H 8.28, N 6.98; found: C 80.63, H 8.23, N 6.80.

*5-(*tert*-Butyl)isophthaloyl Dichloride* (**4**). A mixture of 5-(*tert*-butyl)isophthalic acid (11.1 g, 50.0 mmol), thionyl chloride (150 ml), and 10 drops of DMF was heated under reflux for 5 h. Excess thionyl chloride was removed, and the residue was recrystallized from petroleum ether: 11.5 g (87%) of **4**. Colorless crystals. M.p. 44–45°. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.40 (*s*, 3 Me); 8.40 (*s*, H–C(2)); 8.70 (*s*, H–C(4), H–C(6)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 31.02 (Me_3C); 35.34 (Me_3C); 131.68, 134.09 (CH); 134.26, 153.97 (C); 167.67 (C=O). EI-MS: 258 (4, M^+), 243 (65), 223 (100), 215 (21).

*11′-(*tert*-Butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyldispiro[cyclohexane-1,2′-[7,15,25,33]tetraazaheptacyclo[32.2.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{3,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20′,1″-cyclohexane]-8′,14′,26′,32′-tetrone* (**5a**). A soln. of **3a** (1.2 g, 1.55 mmol) and Et_3N (0.4 ml) in dry CH_2Cl_2 (250 ml) and a soln. of **4** (0.40 g, 1.55 mmol) in dry CH_2Cl_2 (250 ml) were added dropwise to dry CH_2Cl_2 (1000 ml) within 8 h. The mixture was then stirred for further 2 d, the solvent evaporated, and the residue purified by CC (silica gel (40–63 μm), CH_2Cl_2/AcOEt 4:1; R_f 0.43). M.p. >300°. For further anal. data, see [4k].

*11′-(*tert*-Butyl)-5′,17′,23′,36′,39′,41′,44′,46′-octamethyldispiro[cyclohexane-1,2′-[7,15,25,34]tetraazaheptacyclo[33.2.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]heptatetraconta[3,5,9,11,13(45),16,18,21,23,27,29,31(40),35,37,38,41,43,46]octadecaene-20′,1″-cyclohexane]-8′,14′,26′,33′-tetrone* (**5b**) was prepared from **3b** (1.0 g, 1.27 mmol) and **4** (0.33 g, 1.27 mmol) as described for **5a**: 0.68 g (54%) of **5b**. Colorless solid. R_f 0.57 (CH_2Cl_2/AcOEt 4:1). Tetrone **5b** could be recrystallized from $CHCl_3$/MeOH 1:1. M.p. 263–265°. ^{1}H-NMR (400 MHz, (D_8)THF): 1.41 (*s*, Me_3C); 1.55–1.66 (br., 12 H, CH_2); 2.01 (*s*, 2 Me); 2.10 (*s*, 2 Me); 2.19 (*s*, 2 Me); 2.20 (*s*, 2 Me); 2.05–2.21 (br., 4 H, CH_2); 2.36–2.40 (br., 2 H, CH_2); 2.48–2.52 (br., 2 H, CH_2); 3.64 (*s*, CH_2CO); 6.70 (*s*, 2 H, Ar); 6.93 (*s*, 2 H, Ar); 7.05 (*s*, 2 H, Ar); 7.10 (*s*, 2 H, Ar); 7.32–7.38 (*m*, 2 H, Hiso); 7.78 (*d*, ^3J = 7.8, 1 H, Hiso); 8.18 (*s*, 1 H, Hiso); 8.25 (*s*, 1 H, *t*Bi); 8.26 (*s*, 1 H, *t*Bi); 8.38 (*s*, 1 H, *t*Bi); 8.44 (*s*, 2 NH); 8.52 (*s*, 1 NH); 8.81 (*s*, 1 NH). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 19.37, 19.42, 19.60, 19.72 (Me); 23.49, 23.50, 23.56, 36.39, 37.34 (CH_2); 31.83 (Me_3C); 35.95 (Me_3C); 43.41 (CH_2CO); 45.78, 46.12 (quat. C, Cy); 122.54, 125.84, 126.89, 127.19, 127.43, 128.10, 128.46, 129.60, 129.78, 129.86, 131.41, 131.54, 131.87, 131.93, 133.42, 135.06, 135.19, 135.28, 135.48, 135.52, 135.72, 136.52, 146.56, 149.11, 154.46 (C, Ar); 166.10, 166.37, 166.43, 169.61 (C=O). FAB-MS: 975.5 ([M + H]$^+$). Anal. calc. for $C_{65}H_{74}N_4O_4 \cdot C_4H_8O_2 \cdot H_2O$ (1081.44): C 76.63, H 7.83, N 5.18; found: C 76.61, H 7.81, N 5.04.

*11′-(*tert*-Butyl)-5′,17′,23′,37′,40′,42′,45′,47′-octamethyldispiro[cyclohexane-1,2′-[7,15,25,35]tetraazaheptacyclo[34.2.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{28,32}]octatetraconta[3,5,9,11,13(46),16,18,21,23,28,30,32(41),36,38,39,42,44,47]octadecaene-20′,1″-cyclohexane]-8′,14′,26′,34′-tetrone* (**5c**) was prepared from **3c** (1.0 g, 1.25 mmol) and **4** (0.32 g, 1.25 mmol) as described for **5a**: 0.70 g (57%) of **5c**. Colorless solid. R_f 0.18 (CH_2Cl_2/AcOEt 4:1). M.p. 258–260°. ^{1}H-NMR (400 MHz, $CDCl_3$/CD_3OD 1:1): 1.14 (*s*, Me_3C); 1.17–1.23 (br., 4 H, CH_2); 1.28–1.34 (br., 8 H, CH_2); 1.82 (*s*, 4 Me); 1.92 (*s*, 4 Me); 1.95–2.08 (br., 8 H, CH_2); 3.46 (*s*, 2 CH_2CO); 6.66 (*s*, 4 H, Ar); 6.74 (*s*, 4 H, Ar); 6.96–7.00 (*m*, 3 H, *m*Xyl); 7.09 (*t*, ^3J = 7.5, 1 H, *m*Xyl); 7.94 (*s*, 2 H, *t*Bi); 8.07 (*s*, 1 H, *t*Bi). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD 1:1): 18.39, 18.53 (Me); 22.98, 26.48, 36.18 (CH_2); 31.13 (Me_3C); 35.36 (Me_3C); 42.91 (CH_2CO); 45.03 (quat. C, Cy); 123.36, 126.33, 126.72, 128.19, 129.04, 129.37, 132.34 (CH); 131.33, 131.41, 134.05, 135.21, 135.41, 135.63, 147.49, 148.29, 153.60 (quat. C); 167.09, 171.93 (C=O). FAB-MS: 989.5 ([M + H]$^+$). MALDI-TOF-MS: 989.6 ([M + H]$^+$), 1011.6 ([M + Na]$^+$), 1027.6 ([M + K]$^+$).

X-Ray Crystal Structure of **5c**: Crystals were obtained by slow evaporation of a $CHCl_3$/MeOH 1:1 soln. $C_{66}H_{76}N_4O_4 \cdot CHCl_3 \cdot 4\,CH_3OH \cdot 3H_2O$, M 1290.89; colorless crystals, dimensions $0.25 \times 0.20 \times 0.15$ mm; monoclinic, space group $P2_1/n$ (No. 14); $a = 17.3595(4)$, $b = 21.9631(8)$, $c = 18.2976(6)$ Å, $\beta = 92.694(2)^\circ$, $V = 6968.6(4)$ Å^3, $Z = 4$, $D_c = 1.230$ Mg m^{-3}; linear absorption coefficient 0.192 mm^{-1}. Intensities were measured with a *Nonius-KappaCCD* diffractometer (MoK_α, $\lambda = 0.71073$ Å), rotation in φ and ω, 1°, 532 frames, $\theta = 2.0$–25°, $T = 123(2)$ K. The structure was solved by direct methods; refinement (full-matrix least-squares on F^2, 818 parameters, 83 restraints): non-H-atoms were refined anisotropically, H-atoms localized by difference electron density and refined using a 'riding' model. Number of measured reflections 74945, number of unique reflections 12259 ($R_{int} = 0.0459$), number of observed reflections ($I > 2\sigma(I)$) 7424, $R(I > 2\sigma(I)) = 0.078$, $wR_2 = 0.249$, $S = 1.03$, max./min. difference peak 1.22–1.06 eÅ^{-3}. The solvent (H_2O, CH_3OH) is disordered. Computer programs used, see [18]. The crystallographic data of **5c** has been deposited at the *Cambridge Crystallographic Data Centre* as deposition No. CCDC 114802. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-1223 336033; e-mail: deposit@ccc.cam.ac.uk).

4-[Tris(4-methylphenyl)methyl]benzenamine (**7b**). A mixture of tris(4-methylphenyl)methyl chloride [19] (3.0 g, 9.3 mmol) and freshly distilled aniline (45 ml) was heated under reflux and N_2 for 5 h. The purple-colored mixture was precipitated in 200 ml of 10% HCl soln., and the crude product was washed with H_2O, K_2CO_3 soln., and again with H_2O. The solid was dissolved in CH_2Cl_2 and filtered through a short column filled with silica gel. After the evaporation of the yellowish filtrate, the residue was washed with hexane and dried *in vacuo:* 2.91 g (82%) of **7b**. Colorless solid. M.p. 235–238°. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.30 (*s*, *t*-Bu); 3.65 (br., NH_2); 6.55 (*d*, $^3J = 8.6$, 2 H, Ar); 6.96 (*d*, $^3J = 8.6$, 2 H, Ar); 7.02 (*d*, $^3J = 8.4$, 6 H, Ar); 7.08 (*d*, $^3J = 8.4$, 6 H, Ar). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 21.58 (Me); 63.86 (Ar_3C); 114.80, 128.68, 131.59, 132.61, 135.69, 138.20, 144.55, 145.28 (C, Ar). EI-MS: 377 (39, M^+), 286 (100). HR-EI-MS: 377.2141 ($C_{28}H_{27}N$, M^+; calc. 377.2143).

The rotaxanes **8a**–**c** and **9a**,**b** were all prepared as described for rotaxane **8a**; the corresponding axles were isolated as by-products. In the case of **10b** and **10c**, additional CC (silica gel (63–100 μm), CH_2Cl_2) was required to separate the axle from the corresponding stopper components **7b** and **7c**, resp.

Rotaxane **8a** *and Axle* **10a**. Macrocycle **5b** (488 mg, 0.50 mmol) and 3-(chlorosulfonyl)benzoyl chloride (**6**; 120 mg, 0.50 mmol) were dissolved in CH_2Cl_2 (100 ml). A soln. of stopper component **7a** (336 mg, 1.00 mmol) and Et_3 (0.4 ml) in CH_2Cl_2 (150 ml) was added dropwise, and the mixture was then stirred for further 8 h. After evaporation, the residue was purified by CC (silica gel (63–100 μm), CH_2Cl_2/AcOEt 20:1): 150 mg (17%) of rotaxane **8a** (R_f 0.37) and 64 mg (30%) of axle **10a** (R_f 0.66).

*[2]{*N*-[4-(Triphenylmethyl)phenyl]-3-{{[4-(triphenylmethyl)phenyl]amino}sulfonyl}benzamide}-{11′-(tert-butyl)-5′,17′,23′,36′,39′,41′,44′,46′-octamethyldispiro[cyclohexane-1,2′-[7,15,25,34]tetraazaheptacyclo[33.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]heptatetraconta[3,5,9,11,13(45),16,18,21,23,27,29,31(40),35,37,38,41,43,46]octadecaene-20′,1″-cyclohexane]-8′,14′,26′,33′-tetrone}rotaxane* (**8a**): Colorless solid. M.p. 238–241°. ^{1}H-NMR (400 MHz, (D_7)DMF: 1.36 (*s*, *t*-Bu); 1.43 (br., 4 H, CH_2); 1.51 (br., 8 H, CH_2); 1.61 (*s*, 2 Me); 1.73 (*s*, 2 Me); 2.02 (*s*, 2 Me); 2.10 (*s*, 2 Me); 2.38 (br., 8 H, CH_2); 3.76 (*d*, *AB*, $^2J = 14.9$, 1 H, CH_2CO); 3.80 (*d*, *AB*, $^2J = 14.9$, 1 H, CH_2CO); 6.67 (*m*, 3 H, Ar); 6.74 (*s*, 2 H, Ar); 6.98 (*s*, 6 H, Ar); 7.06–7.11 (*m*, 4 H, Ar); 7.16–7.33 (*m*, 32 H, Ar); 7.38–7.49 (*m*, 3 H, Ar); 7.85 (*d*, $^3J = 7.8$, 1 H, 3 Sb); 7.97 (*d*, $^3J = 7.0$, 1 H, Hiso); 8.10 (*s*, 1 H, Hiso); 8.20 (*s*, 1 H, *t*Bi); 8.26 (*s*, 1 H, *t*Bi); 8.30 (*s*, 1 H, 3 Sb); 8.58 (*s*, 1 NH); 8.77 (*s*, 1 H, *t*Bi); 9.04 (*s*, 1 NH); 9.12 (*s*, 1 NH); 9.35 (*s*, 1 NH); 9.81 (*s*, 1 NH); 10.27 (*s*, 1 NH). ^{13}C-NMR (100.6 MHz, (D_8)THF): 18.42, 18.64, 18.85, 18.89 (Me); 23.85, 23.92, 27.33, 27.38, 35.69, 37.60 (CH_2); 31.50 (Me_3C); 35.60, 35.94 (Me_3C); 43.45 (CH_2CO); 45.67, 46.45 (quat. C, Cy); 65.22, 65.46 (Ph_3C); 119.10, 122.53, 122.92, 125.28, 126.36, 126.56, 126.61, 126.70, 127.25, 127.86, 128.09, 128.12, 128.49, 128.84, 128.93, 129.30, 129.50, 130.78, 131.76, 131.79, 131.89, 131.94, 132.37, 132.60, 132.63, 132.87, 132.97, 133.36, 135.26, 135.39, 135.53, 135.65, 135.94, 136.19, 136.44, 136.56, 136.89, 137.63, 141.60, 142.85, 144.11, 147.35, 147.59, 147.71, 149.24, 150.02, 153.39 (C, Ar); 164.32, 164.52, 167.21, 167.37, 170.05 (C=O). MALDI-TOF-MS: 1811.2 ($[M + H]^+$), 1833.2 ($[M + Na]^+$), 1849.2 ($[M + K]^+$). Anal. calc. for $C_{122}H_{118}N_6O_7S \cdot C_4H_8O_2 \cdot 2H_2O$ (1936.51): C 78.15, H 6.77, N 4.34; found: C 78.43, H 6.47, N 4.15.

N*-[4-(Triphenylmethyl)phenyl]-3-{{[(4-(triphenylmethyl)phenyl]amino}sulfonyl}benzamide* (**10a**): ^{1}H-NMR (400 MHz, (D_8)THF): 6.96–7.24 (*m*, 36 H, Ar); 7.55 ('*t*', $^3J = 7.9$, 1 H, 3 Sb); 7.66 (*d*, $^3J = 8.9$, 2 H, Ar); 7.86 (*d*'*t*', $^3J = 7.9$, $^4J = 1.5$, 1 H, 3Sb); 8.06 (*d*'*t*', $^3J = 7.9$, $^4J = 1.5$, 1 H, 3Sb); 8.25 ('*t*', $^4J = 1.5$, 1 H, 3Sb); 9.18 (*s*, 1 NH); 9.66 (*s*, 1 NH). ^{13}C-NMR (100.6 MHz, (D_7)DMF): 65.02, 65.22 (Ph_3C); 120.15, 120.61, 126.67, 126.94, 128.32, 128.37, 130.13, 130.25, 131.37, 131.44, 131.72, 132.26, 132.50, 136.54, 136.77, 137.93, 141.11, 142.97, 143.63, 147.30, 147.57 (C, Ar); 164.87 (C=O). FAB-MS: 837.3 ($[M + H]^+$).

Rotaxane **8b** *and Axle* **10b** were prepared from **5b** (351 mg, 0.36 mmol), **6** (86 mg, 0.36 mmol), and **7b** (272 mg, 0.72 mmol).

*[2]{*N*-{4-[Tris(4-methylphenyl)methyl]phenyl}-3-{{{4-[tris(4-methylphenyl)methyl]phenyl}amino}sulfonyl}-benzamide}-{11′-(*tert*-butyl)-5′,17′,23′,36′,39′,41′,44′,46′-octamethyldispiro[cyclohexane-1,2′-[7,15,25,34]tetraazaheptacyclo[33.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]heptatetraconta[3,5,9,11,13(45),16,18,21,23,27,29,31(40),35,37,38,41,43,46]octadecaene-20′,1″-cyclohexane]-8′,14′,26′,33′-tetrone}rotaxane* (**8b**): Yield 89 mg (13%). Colorless solid. R_f 0.49 (CH_2Cl_2/AcOEt 20:1). M.p. 250–252°. ^{1}H-NMR (400 MHz, (D_8)THF): 1.39 (*s*, *t*-Bu); 1.42–1.55 (br., 12 H, CH_2); 1.64 (*s*, 2 Me); 1.75 (*s*, 4 Me); 1.98 (*s*, 2 Me); 2.22 (*s*, 3 Me); 2.27 (*s*, 3 Me); 2.30–2.43 (br., 8 H, CH_2); 3.65 (*d*, *AB*, ^2J = 14.0, 1 H, CH_2CO); 3.74 (*d*, *AB*, ^2J = 14.0, 1 H, CH_2CO); 6.46 (*d*, ^3J = 8.4, 2 H, Ar); 6.54 (*s*, 2 H, Ar); 6.70–6.75 (*m*, 4 H, Ar); 6.87 (*s*, 2 H, Ar); 6.91–6.96 (*m*, 16 H, Ar); 6.98–7.03 (*m*, 14 H, Ar); 7.06–7.13 (*m*, 2 H, Ar); 7.32 (‘*t*’, ^3J = 7.7, 1 H, Ar); 7.37 (*d*, ^3J = 7.7, 1 H, Ar); 7.64 (*d*, ^3J = 7.4, 1 H, Ar); 7.73 (*d*, ^3J = 7.7, 1 H, Ar); 8.10 (*s*, 1 H, Ar); 8.12 (*s*, 1 H, Ar); 8.17 (*s*, 1 NH); 8.24 (*s*, 1 H, *t*Bi); 8.30 (*s*, 1 H, *t*Bi); 8.53 (*s*, 1 NH); 8.61 (*s*, 1 H, *t*Bi); 8.68 (*s*, 1 NH); 9.20 (*s*, 1 NH); 9.35 (*s*, 1 NH); 9.49 (*s*, 1 NH). ^{13}C-NMR (100.6 MHz, (D_8)THF): 18.29, 18.54, 18.77, 20.73, 20.76 (Me); 23.77, 23.86, 27.29, 35.52, 35.84, 37.51 (CH_2); 30.18 (Me_3C); 31.41 (Me_3C); 43.33 (CH_2CO); 45.58, 46.32 (quat. C, Cy); 64.08, 64.34 (Ar_3C); 118.80, 122.46, 122.82, 125.23, 126.27, 126.45, 127.15, 128.39, 128.59, 128.77, 128.87, 129.19, 129.41, 130.67, 131.49, 131.66, 131.70, 132.19, 132.87 (CH); 132.52, 132.54, 132.75, 132.88, 133.25, 135.10, 135.45, 135.51, 135.59, 135.68, 135.87, 136.10, 136.33, 136.82, 137.49, 141.59, 143.18, 144.61, 144.89, 144.98, 147.37, 149.85, 153.27 (quat. C); 164.22, 164.40, 167.26, 167.35, 170.02 (C=O). MALDI-TOF-MS: 1896.1 ([*M* + H]$^+$), 1918.4 ([*M* + Na]$^+$), 1934.3 ([*M* + K]$^+$). Anal. calc. for $C_{128}H_{130}N_6O_7S \cdot C_4H_8O_2 \cdot H_2O$ (2002.65): C 79.17, H 7.05, N 4.19; found: C 79.22, H 7.10, N 4.11.

N*-{4-[Tris(4-methylphenyl)methyl]phenyl}-3-{{{4-[tris(4-methylphenyl)methyl]phenyl}amino}sulfonyl}-benzamide* (**10b**): Colorless solid. R_f 0.12 (CH_2Cl_2). M.p. 178–180°. ^{1}H-NMR (400 MHz, (D_8)THF): 2.22 (*s*, 3 Me); 2.27 (*s*, 3 Me); 6.92–7.06 (*m*, 28 H, Ar); 7.12 (*d*, ^3J = 8.9, 2 H, Ar); 7.54 (‘*t*’, ^3J = 7.9, 1 H, 3Sb); 7.66 (*d*, ^3J = 8.9, 2 H, Ar); 7.85 (*d*‘*t*’, ^3J = 7.9, ^4J = 1.5, 1 H, 3Sb); 8.07 (*d*‘*t*’, ^3J = 7.9, ^4J = 1.5, 1 H, 3Sb); 8.27 (‘*t*’, ^4J = 1.5, 1 H, 3Sb); 9.16 (*s*, 1 NH); 9.65 (*s*, 1 NH). ^{13}C-NMR (100.6 MHz, (D_8)THF): 20.96, 20.97 (Me); 64.37, 64.54 (Ar_3C); 119.54, 120.51, 126.97, 128.80, 129.05, 129.67, 130.24, 131.80, 131.87, 132.16, 132.21, 132.67, 135.97, 136.01, 136.63, 137.68, 138.20, 142.01, 143.68, 147.54, 145.03, 145.30 (C, Ar); 164.78 (C=O). FAB-MS: 920.5 (M^+), 943.3 ([*M* + Na]$^+$).

Rotaxane **8c** *and Axle* **10c** were prepared from **5b** (476 mg, 0.49 mmol), **6** (117 mg, 0.49 mmol), and **7c** (492 mg, 0.98 mmol).

*[2]{*N*-{4-{Tris[4-(*tert*-butyl)phenyl]methyl}phenyl}-3-{{{4-{tris[4-(*tert*-butyl)phenyl]methyl}phenyl}amino}-sulfonyl}benzamide}-{11′-(*tert*-butyl)-5′,17′,23′,36′,39′,41′,44′,46′-octamethyldispiro[cyclohexane-1,2′-[7,15,25,-34]tetraazaheptacyclo[33.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]heptatetraconta[3,5,9,11,13(45),16,18,21,23,27,29,31(40),35,37,38,41,43,46]octadecaene-20′,1″-cyclohexane]-8′,14′,26′,32′-tetrone}rotaxane* (**8c**). Yield 235 mg (22%). Colorless solid. R_f 0.57 (CH_2Cl_2/AcOEt 20:1). M.p. 285–287°. ^{1}H-NMR (400 MHz, (D_7)DMF): 1.24 (*s*, 6 *t*-Bu); 1.38 (*s*, 1 *t*-Bu); 1.50 (br., 12 H, CH_2); 1.62 (*s*, 2 Me); 1.64 (*s*, 2 Me); 2.01 (*s*, 2 Me); 2.04 (*s*, 2 Me); 2.38 (br., 8 H, CH_2); 3.79 (*d*, *AB*, ^2J = 14.9, 1 H, CH_2CO); 3.88 (*d*, *AB*, ^2J = 14.9, 1 H, CH_2CO); 6.46 (*d*, ^2J = 8.4, 2 H, Ar); 6.69 (*s*, 2 H, Ar); 6.95–7.02 (*m*, 6 H, Ar); 7.07–7.13 (*m*, 13 H, Ar); 7.17–7.21 (*m*, 8 H, Ar); 7.28–7.35 (*m*, 10 H, Ar); 7.43–7.50 (*m*, 3 H, Ar); 7.92 (*d*, ^3J = 7.9, 1 H, 3Sb); 7.98 (*d*, ^3J = 7.4, 1 H, Hiso); 8.22 (*s*, 1 H, Hiso); 8.23 (*s*, 1 H, *t*Bi); 8.30 (*s*, 1 H, *t*Bi); 8.32 (*s*, 1 H, 3Sb); 8.54 (*s*, 1 NH); 8.82 (*s*, 1 H, *t*Bi); 9.08 (*s*, 1 NH); 9.31 (*s*, 1 NH); 9.42 (*s*, 1 NH); 9.66 (*s*, 1 NH); 10.38 (*s*, 1 NH). ^{13}C-NMR (100.6 MHz, (D_7)DMF): 18.49, 18.70, 18.89 (Me_3); 23.41, 26.68, 35.05, 35.87, 36.38, 37.38 (CH_2); 31.27, 31.32, 31.34 (Me_3C); Me_3C hidden by solvent; 42.08 (CH_2CO); 45.41, 45.85 (quat. C, Cy); 63.86, 64.10 (Ar_3C); 119.32, 122.15, 123.90, 125.01, 125.73, 126.22, 126.47, 126.64, 127.44, 128.43, 128.55, 128.78, 129.79, 130.06, 130.84, 130.91, 131.08, 131.64, 131.99, 133.25 (CH); 132.71, 132.89, 133.12, 133.35, 134.99, 135.14, 135.28, 135.34, 135.74, 135.85, 136.00, 136.17, 136.59, 137.60, 141.50, 143.39, 144.03, 144.54, 144.91, 148.81, 148.90, 153.16 (quat. C); 165.02, 165.19, 165.94, 166.77, 169.61 (C=O). MALDI-TOF-MS: 2148.5 ([*M* + H]$^+$), 2170.5 ([*M* + Na]$^+$), 2186.6 ([*M* + K]$^+$). Anal. calc. for $C_{146}H_{166}N_6O_7S \cdot 2H_2O$ (2185.05): C 80.25, H 7.84, N 3.85; found: C 80.24, H 7.73, N 3.75.

N*-{4-{Tris[4-(*tert*-butyl)phenyl]methyl}phenyl}-3-{{{4-{tris[4-(*tert*-butyl)phenyl]methyl}phenyl}amino}sulfonyl}benzamide* (**10c**): Colorless solid. R_f 0.17 (CH_2Cl_2). M.p. > 300°. ^{1}H-NMR (400 MHz, (D_7)DMF): 1.23 (*s*, 3 *t*-Bu); 1.28 (*s*, 3 *t*-Bu); 7.06 (*d*, ^3J = 8.6, 6 H, Ar); 7.11–7.20 (*m*, 12 H, Ar); 7.29 (*d*, ^3J = 8.6, 6 H, Ar); 7.34 (*d*, ^3J = 8.6, 6 H, Ar); 7.75 (‘*t*’, ^3J = 7.8, 1 H, 3Sb); 7.84 (*d*, ^3J = 8.9, 2 H, Ar); 8.05 (*d*, ^3J = 7.8, 1 H, 3Sb); 8.30 (*d*, ^3J = 7.8, 1 H, 3Sb); 8.31 (*s*, 1 H, 3Sb); 10.30 (br., 1 NH); 10.62 (*s*, 1 NH). ^{13}C-NMR (100.6 MHz, (D_7)DMF): 31.34 (Me_3C); 34.71, 34.75 (Me_3C); 63.82, 63.98 (Ar_3C); 119.94, 120.89, 125.06, 125.09, 126.91, 130.21, 131.06, 131.12, 131.63, 132.12, 132.42, 134.06, 136.63, 137.89, 143.30, 144.06, 144.13, 144.57, 144.76, 149.08 (Ar); 163.74 (C=0). MALDI-TOF-MS: 1173.8 ([*M* + H]$^+$), 1195.9 ([*M* + Na]$^+$), 1211.8 ([*M* + K]$^+$).

Rotaxane **9a** was prepared from **5c** (350 mg, 0.35 mmol), **6** (85 mg, 0.35 mmol), and **7b** (267 mg, 0.71 mmol).

*[2]{*N*-{4-[Tris(4-methylphenyl)methyl]phenyl}-3-{{{4-[tris(4-methylphenyl)methyl]phenyl}amino}sulfonyl}-benzamide}-{11′-(*tert*-butyl)-5′,17′,23′,37′,40′,42′,45′,47′-octamethyldispiro[cyclohexane-1,2′-[7,15,25,35]tetraaza-heptacyclo[34.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{28,32}]octatetraconta[3,5,9,11,13(46),16,18,21,23,28,30,32(41),36,38,39,42,44,47]octadecaene-20′,1″-cyclohexane]-8′,14′,26′,34′-tetrone}rotaxane* (**9a**): Yield 25 mg (4%). Colorless solid. R_f 0.19 (CH_2Cl_2/AcOEt 20:1). ^{1}H-NMR (400 MHz, (D_8)THF): 1.39 (*s*, *t*-Bu); 1.50–1.60 (br., 12 H, CH_2); 1.72 (*s*, 4 Me); 1.93 (*s*, 4 Me); 2.00–2.10 (br., 8 H, CH_2); 2.22 (*s*, 3 Me); 2.29 (*s*, 3 Me); 3.62 (*s*, 2 CH_2CO); 6.49 (*d*, ^3J = 8.6, 2 H, Ar); 6.56 (‘*t*’, ^3J = 7.9, 1 H, 3Sb); 6.67 (*s*, 4 H, Ar); 6.85 (*d*, ^3J = 8.6, 2 H, Ar); 6.89–7.14 (*m*, 34 H, Ar); 7.23 (*d*, ^3J = 7.4, 2 H, *m*Xyl); 7.32 (*s*, 1 H, *m*Xyl); 7.45 (*d*, ^3J = 7.9, 1 H, 3Sb); 7.95 (*s*, 1 H, 3Sb); 8.23 (*s*, 2 H, *t*Bi); 8.40 (*s*, 1 H, *t*Bi); 8.42 (*s*, 2 NH); 8.70 (*s*, 2 NH); 9.09 (*s*, 1 NH); 9.59 (*s*, 1 NH). MALDI-TOF-MS: 1910.4 ([*M* + H]$^+$), 1932.4 ([*M* + Na]$^+$), 1948.4 ([*M* + K]$^+$).

Rotaxane **9b** was prepared from **5c** (240 mg, 0.24 mmol), **6** (58 mg, 0.24 mmol), and **7c** (244 mg, 0.48 mmol).

*[2]{*N*-{4-{Tris[4-(*tert*-butyl)phenyl]methyl}phenyl}-3-{{{4-{tris[4-(*tert*-butyl)phenyl]methyl}phenyl}amino}-sulfonyl}benzamide}-{11′-(*tert*-butyl)-5′,17′,23′,37′,40′,42′,45′,47′-octamethyldispiro[cyclohexane-1,2′-[7,15,25,35]tetraazaheptacyclo[34.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{28,32}]octatetraconta[3,5,9,11,13(46),16,18,21,23,28,30,32(41),36,38,39,42,44,47]octadecaene-20′,1″-cyclohexane]-8′,14′,26′,34′-tetrone}rotaxane* (**9b**): Yield 35 mg (7%). Colorless solid. R_f 0.17 (CH_2Cl_2/AcOEt 40:1). M.p. 257–260°. ^{1}H-NMR (400 MHz, (D_7)DMF/$CDCl_3$ 1:1): 1.19 (*s*, 6 *t*-Bu); 1.26 (*s*, 1 *t*-Bu); 1.35–1.45 (br., 12 H, CH_2); 1.53 (*s*, 4 Me); 1.97 (*s*, 4 Me); 2.13–2.35 (br., 8 H, CH_2); 3.66 (*d*, *AB*, ^2J = 14.4, 1 CH_2CO); 3.74 (*d*, *AB*, ^2J = 14.4, 1 CH_2CO); 6.06 (*d*, ^3J = 8.2, 2 H, Ar); 6.58 (*d*, ^3J = 8.2, 2 H, Ar); 6.64 (*s*, 4 H, Ar); 6.99–7.26 (*m*, 36 H, Ar); 7.43 (*d*, ^3J = 7.8, 1 H, 3Sb); 7.58 (*s*, 1 H, *m*Xyl); 7.79 (*d*, ^3J = 7.8, 1 H, 3Sb); 8.10 (*s*, 2 NH); 8.20 (*s*, 1 H, 3Sb); 8.27 (*s*, 2 H, *t*Bi); 8.82 (*s*, 1 H, *t*Bi); 8.98 (*s*, 2 NH); 9.41 (*s*, 1 NH); 10.39 (*s*, 1 NH). ^{13}C-NMR (100.6 MHz, $CDCl_3$/CD_3OD 1:1): 18.21, 18.84 (Me); 23.07, 26.60, 36.69 (CH_2); 31.30, 31.47, 31.51 (*Me*$_3$C); 34.49, 34.54, 35.51 (Me$_3$*C*); 42.88 (*C*H_2CO); 45.52 (quat. C, Cy); 63.52, 63.72 (Ar$_3$*C*); 119.71, 121.95, 124.40, 124.50, 126.41, 127.22, 128.04, 129.45, 129.92, 130.92, 130.96, 131.42, 131.81, 132.27 (CH); 134.22, 135.28, 135.68, 136.02, 140.18, 144.00, 144.23, 144.73, 148.83, 148.87, 153.79 (quat. C); 166.27, 166.65, 171.61 (C=O). MALDI-TOF-MS: 2163.5 ([*M* + H]$^+$), 2185.4 ([*M* + Na]$^+$), 2201.4 ([*M* + K]$^+$). Anal. calc. for $C_{147}H_{168}N_6O_7S \cdot C_4H_8O_2 \cdot 2H_2O$ (2287.18): C 79.30, H 7.93, N 3.67; found: C 79.37, H 7.95, N 3.66.

*[2]{(*E,E*)-4,4′-Bis{2-[3,5-di(*tert*-butyl)phenyl]ethenyl}-1,1′-biphenyl}-{11′-(*tert*-butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyldispiro[cyclohexane-1,2′-[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetra-conta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20′,1″-cyclohexane]-8′,14′,26′,32′-tetrone}rotaxane* (**12a**). Equimolar amounts of macrocycle **5a** (356 mg, 0.37 mmol) and axle **11a** (216 mg, 0.37 mmol) were mixed thoroughly. Portions of 20–30 mg of this mixture were then melted with the help of a heat gun at *ca*. 350° and subsequently chilled in cold water. The residue was dissolved in CH_2Cl_2/MeOH 5:1 and subjected to CC (silica gel (63–100 μm), CH_2Cl_2/AcOEt 30:1): 17 mg (3%) of **12a**. Yellow solid. R_f 0.40 (CH_2Cl_2/AcOEt 30:1). M.p. 208°. ^{1}H-NMR (400 MHz, (D_8)THF): 1.33 (*s*, 4 *t*-Bu); 1.37 (*s*, 1 *t*-Bu); 1.48 (br., 4 H, CH_2); 1.71 (br., 8 H, CH_2); 1.97 (*s*, 8 Me); 2.47 (br., 8 H, CH_2); 6.90 (*d*, ^3J = 16.4, 2 olef. H); 6.97 (*d*, ^3J = 8.5, 4 H, Ar); 7.04 (*d*, ^3J = 8.7, 4 H, Ar); 7.05 (*d*, ^3J = 15.7, 2 olef. H); 7.15 (*s*, 8 H, Ar); 7.35 (*t*, ^4J = 1.7, 2 H, Ar); 7.37 (*d*, ^4J = 1.7, 4 H, Ar); 7.51 (*t*, ^3J = 7.6, 1 H, Ar); 7.75 (*t*, ^4J = 1.4, 1 H, Ar); 7.85 (*s*, 2 NH); 7.93 (*d*, ^4J = 1.6, 1 H, Ar); 7.95 (*d*, ^3J = 7.6, 2 H, Ar); 8.04 (*d*, ^4J = 1.4, 2 H, Ar); 2 NH underneath the signal at 7.95. ^{13}C-NMR (125 MHz, (D_8)THF): 16.62, 16.81, 16.85, 29.13, 29.42, 34.30 (Me); 21.66 (2 signals), 22.89 (under the THF signal), 25.09 (2 signals) (CH_2); 119.36, 120.17, 122.66, 124.76, 124.82, 125.25, 125.53 (2 signals), 125.75, 127.16, 127.78, 128.36 (CH); 33.07, 43.93, 131.34, 131.41, 133.43, 134.12, 134.38, 134.97, 135.36, 136.96, 145.99, 149.22, 150.75, 163.38, 163.53 (quat. C). FAB-MS 1543.9 (*M*$^+$). Anal. calc. for $C_{108}H_{126}N_4O_4 \cdot 2H_2O$ (1580.24): C 82.09, H 8.29, N 3.55; found: C 82.19, H 8.49, N 2.99.

*[2]{*N,N′*-Bis[3,5-di(*tert*-butyl)phenyl][1,1′-biphenyl]-4,4′-dicarboxamide}-{11′-(*tert*-butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyldispiro[cyclohexane-1,2′-[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexa-tetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20′,1″-cyclohexane]-8,14,26,32-tetrone}rotaxane* (**12b**). As described for **12a**, from **5a** (346 mg, 0.36 mmol) and **11b** (222 mg, 0.36 mmol): 40 mg (7%) of **12b**. Colorless solid. R_f 0.45 (CH_2Cl_2/AcOEt 10:1). M.p. > 300°. ^{1}H-NMR (500 MHz, (D_7)DMF): 1.29 (*s*, 4 *t*-Bu); 1.39 (*s*, 1 *t*-Bu); 1.50 (br., 4 H, CH_2); 1.60 (br., 8 H, CH_2), 2.01 (*s*, 8 Me); 2.45 (br., 8 H, CH_2); 7.09 (*d*, ^3J = 7.1, 4 H, Ar); 7.25 (*s*, 8 H, Ar); 7.27 (*s*, 2 H, Ar); 7.55 (*d*, ^3J = 7.9, 4 H, Ar); 7.67 (*s*, 4 H, Ar); 7.69 (*t*, ^3J = 7.4, 1 H, Ar); 8.08 (*d*, ^3J = 7.7, 2 H, Ar); 8.14 (*s*, 2 H, Ar); 8.30 (*s*, 1 H, Ar); 8.45 (*s*, 1 H, Ar); 9.00 (*s*, 2 NH); 9.02 (*s*, 2 NH); 9.72 (*s*, 2 NH). ^{13}C-NMR (125 MHz, (D_7)DMF): 19.02, 31.38, 31.61 (Me); 23.62, 26.89, 35.39 (CH_2); 115.44, 118.70, 126.35, 126.85, 127.20, 128.06, 128.63, 128.82, 129.81, 131.18 (CH); 35.50, 35.72, 45.73, 133.50, 133.56, 134.87, 135.53, 135.56, 135.76, 135.91, 139.46, 142.72, 147.94, 151.67, 153.01, 166.01, 166.25, 166.67 (quat.

C). FAB-MS: 1578.1 (M^+). Anal. calc. for $C_{106}H_{124}N_6O_6 \cdot 2H_2O$ (1614.21): C 78.87, H 7.99, N 5.21; found: C 78.96, H 8.59, N 5.18.

REFERENCES

[1] C. Heim, 'Neue [2]Rotaxane des Amid-Typs: Sterische Komplementarität von Stopperkomponenten und Makrocyclen', Doctoral Thesis, University of Bonn, 1998.

[2] Reviews: a) G. Schill, 'Catenanes, Rotaxanes, and Knots', Academic Press, New York, 1971; b) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725; c) D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242; *ibid., Int. Ed. Engl.* **1996**, *35*, 1154; d) H. W. Gibson, M. C. Bheda, P. T. Engen, *Prog. Polym. Sci.* **1994**, *19*, 843; e) H. W. Gibson, in 'Large Ring Molecules', Ed. J. A. Semlyen, Wiley, Chichester, 1996, p. 191; f) G. Wenz, *Angew. Chem.* **1994**, *106*, 951; *ibid., Int. Ed. Engl.* **1994**, *33*, 803; g) R. Jäger, F. Vögtle, *ibid.* **1997**, *109*, 966; *ibid., Int. Ed. Engl.* **1997**, *36*, 930; h) J.-P. Sauvage, *Acc. Chem. Res.* **1998**, *31*, 611; i) Ed. J.-P. Sauvage, 'Molecular Topology: Catenanes, Rotaxanes and Knots', VCH-Wiley, 1999, in press.

[3] P. R. Ashton, M. R. Johnston, J. F. Stoddart, M. S. Tolley, J. W. Wheeler, *J. Chem. Soc., Chem. Commun.* **1992**, 1128; A. G. Johnston, D. A. Leigh, A. Murphy, J. P. Smart, M. D. Deegan, *J. Am. Chem. Soc.* **1996**, *118*, 10662; D. A. Leigh, A. Murphy, J. P. Smart, A. M. Z. Slawin, *Angew. Chem.* **1997**, *109*, 752; *ibid., Int. Ed. Engl.* **1997**, *36*, 728.

[4] a) I. T. Harrison, S. Harrison, *J. Am. Chem. Soc.* **1967**, *89*, 5723; b) D. J. Cárdenas, P. Gavina, J.-P. Sauvage, *J. Chem. Soc., Chem. Commun.* **1996**, 1915; c) M. Linke, J.-C. Chambron, V. Heitz, J.-P. Sauvage, *J. Am. Chem. Soc.* **1997**, *119*, 11329; d) N. Armaroli, F. Diederich, C. O. Dietrich-Buchecker, L. Flamigni, G. Marconi, J.-F. Nierengarten, J.-P. Sauvage, *Chem.–Eur. J.* **1998**, *4*, 406; e) P. L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delago, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent, D. J. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 193; f) P. R. Ashton, P. T. Glink, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem.-Eur. J.* **1996**, *2*, 729; g) G. Wenz, F. Wolf, M. Wagner, S. Kubik, *New J. Chem.* **1993**, *17*, 729; h) W. Herrmann, M. Schneider, G. Wenz, *Angew. Chem.* **1997**, *109*, 2618; *ibid., Int. Ed. Engl.* **1997**, *36*, 2511; i) H. W. Gibson, S. Liu, P. Lecavalier, C. Wu, Y. X. Shen, *J. Am. Chem. Soc.* **1995**, *117*, 852; k) F. Vögtle, M. Händel, S. Meier, S. Ottens-Hildebrandt, F. Ott, T. Schmidt, *Liebigs Ann. Chem.* **1995**, 739; *cf.* L. F. Lindoy, *Nature (London)* **1995**, *376*, 293; l) F. Vögtle, R. Jäger, M. Händel, S. Ottens-Hildebrandt, W. Schmidt, *Synthesis* **1996**, 353; m) F. Vögtle, T. Dünnwald, M. Händel, R. Jäger, S. Meier, G. Harder, *Chem.-Eur. J.* **1996**, *2*, 640.

[5] a) I. T. Harrison, *J. Chem. Soc., Chem. Commun.* **1972**, 231; b) I. T. Harrison, *J. Chem. Soc., Perkin Trans. 1* **1974**, 301; c) G. Agam, D. Graiver, A. Zilkha, *J. Am. Chem. Soc.* **1976**, *98*, 5206; d) G. Agam, A. Zilkha, *ibid.* **1976**, *98*, 5214; e) G. Schill, W. Beckmann, N. Schweikert, H. Fritz, *Chem. Ber.* **1986**, *119*, 2647; f) P. R. Ashton, M. Belohradský, D. Philp, J. f. Stoddart, *J. Chem. Soc., Chem. Commun.* **1993**, 1269; g) P. R. Ashton, M. Belohradský, D. Philp, N. Spencer, F. Stoddart, *ibid.* **1993**, 1274; h) D. H. Macartney, *J. Chem. Soc., Perkin Trans. 2* **1996**, 2775; i) M. Händel, M. Plevoets, S. Gestermann, F. Vögtle, *Angew. Chem.* **1997**, *109*, 1248; *ibid., Int. Ed. Engl.* **1997**, *36*, 1199.

[6] O. Braun, F. Vögtle, *Synlett* **1997**, 1184; T. Schmidt, R. Schmieder, W. M. Müller, B. Kiupel, F. Vögtle, *Eur. J. Org. Chem.* **1998**, 2003.

[7] G. M. Hübner, J. Gläser, C. Seel, F. Vögtle, *Angew. Chem.* **1999**, *111*, 395; *ibid., Int. Ed. Engl.* **1999**, *38*, 383.

[8] a) D. B. Amabilino, P. R. Ashton, M. Belohradsky, F. M. Raymo, J. F. Stoddart, *J. Chem. Soc., Chem. Commun.* **1995**, 747; b) D. B. Amabilino, P. R. Ashton, M. Belohradsky, F. M. Raymo, J. F. Stoddart, *ibid.* **1995**, 751; c) P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi, D. J. Williams, *J. Am. Chem. Soc.* **1996**, *118*, 4931; d) M. Asakawa, P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradský, M. T. Gandolfi, O. Kocian, L. Prodi, F. M. Raymo, J. F. Stoddart, M. Venturi, *ibid.* **1997**, *119*, 302; D. B. Amabilino, M. Asakawa, P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, A. Credi, M. Higuchi, F. M. Raymo, T. Shimizu, J. F. Stoddart, M. Venturi, K. Yase, *New J. Chem.* **1998**, 959.

[9] F. M. Raymo, K. N. Houk, J. F. Stoddart, *J. Am. Chem. Soc.* **1998**, *120*, 9318.

[10] a) C. A. Hunter, *J. Am. Chem. Soc.* **1992**, *114*, 5303; b) C. A. Hunter, D. H. Purvis, *Angew. Chem.* **1992**, *104*, 779; *ibid., Int. Ed. Engl.* **1992**, *31*, 792; c) S. Ottens-Hildebrandt, S. Meier, W. Schmidt, F. Vögtle, *ibid.* **1994**, *106*, 1818; *ibid., Int. Ed. Engl.* **1994**, *33*, 1767; d) S. Ottens-Hildebrandt, M. Nieger, K. Rissanen,

J. Rouvinen, S. Meier, G. Harder, F. Vögtle, *J. Chem. Soc., Chem. Commun*. **1995**, 777; e) S. Ottens-Hildebrandt, T. Schmidt, J. Harren, F. Vögtle, *Liebigs Ann. Chem.* **1995**, 1855.
[11] C. Seel, A. Parham, O. Safarowsky, G. M. Hübner, F. Vögtle, *J. Org. Chem.* **1999**, in press.
[12] C. Fischer, M. Nieger, O. Mogck, V. Böhmer, R. Ungaro, F. Vögtle, *Eur. J. Org. Chem.* **1998**, 155; S. Braschohs, 'I. Lactam/Thiolactam-Rotaxane II. Palladium- und Silber-Extraktion mit Thioamiden', Doctoral Thesis, University of Bonn, 1998.
[13] C. A. Hunter, *J. Chem. Soc., Chem. Commun*. **1991**, 749.
[14] H. Limpricht, L. v. Uslar, *Liebigs Ann. Chem.* **1857**, *102*, 239.
[15] H. W. Gibson, S.-H. Lee, P. T. Engen, P. Lecavalier, J. Sze, Y. X. Shen, M. Bheda, *J. Org. Chem.* **1993**, *58*, 3748.
[16] R. Schenk, H. Gregorius, K. Meerholz, J. Heinze, K. Müllen, *J. Am. Chem. Soc*. **1991**, *113*, 2634.
[17] V. N. Ipatieff, J. E. Germain, W. W. Thompson, H. Pines, *J. Org. Chem.* **1952**, *17*, 272.
[18] a) G. M. Sheldrick, 'SHELXS-97', *Acta Crystallogr., Sect. A* **1990**, *46*, 467; b) G. M. Sheldrick, 'SHELXL-97', University of Göttingen, **1997**.
[19] G. L. Davies, D. H. Hey, G. H. Williams, *J. Chem. Soc*. **1956**, 4397.

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