Chemical Reactions in the Axle of Rotaxanes – Steric Hindrance by the Wheel

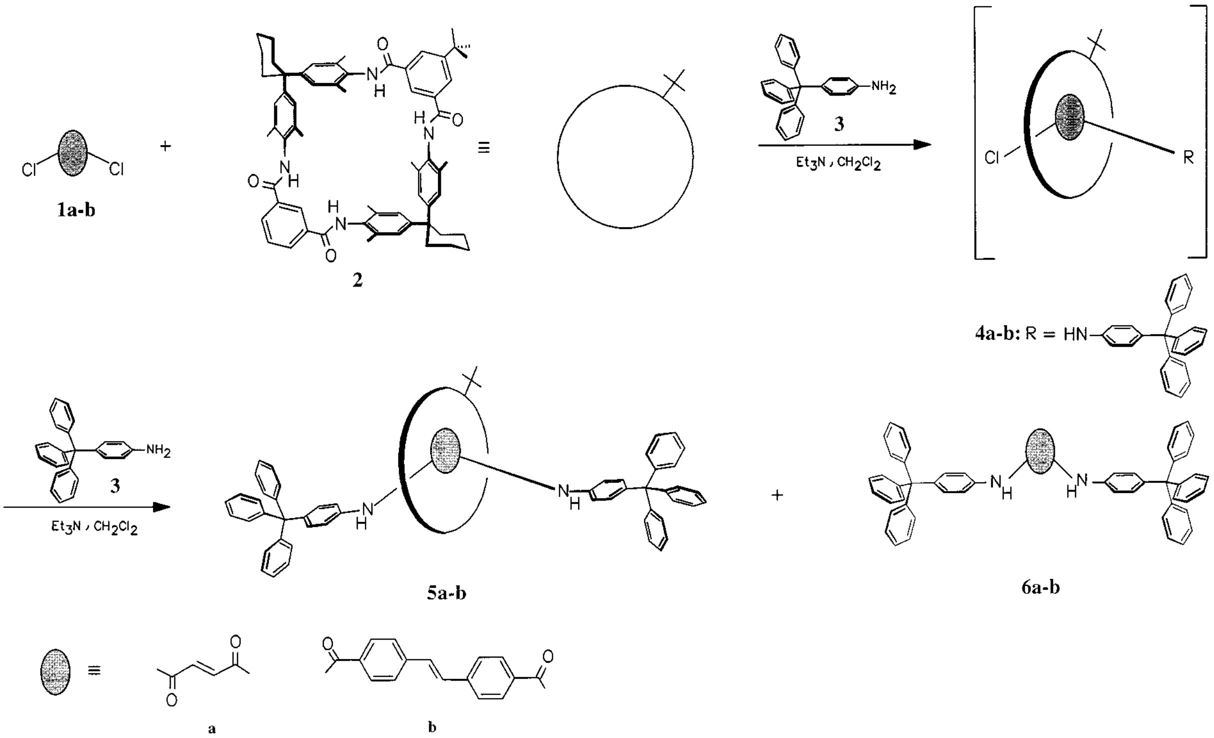
Amir Hossain Parham,[a] Björna Windisch,[a] and Fritz Vögtle*[a]

Keywords: Electrophilic additions / Bromine addition to double bonds / Hydrogenation of double bonds / Rotaxanes / Supramolecular chemistry

Here we report on the possibility of using rotaxane wheels as noncovalent protecting groups which significantly decrease the activity of functional groups in the central part of the axle. The amide-linked rotaxanes **5a** and **5b**, each containing a C=C double bond in their axle, have been synthesised. The catalytic hydrogenation of these two rotaxanes proceeds slower than those of the corresponding free axle compounds **6a** and **6b**, indicating steric hindrance of the C=C double bond by the wheel of the rotaxane in each case. Nontheless, the rotaxane **9** with an aliphatic (succinic acid) middle region in its axle can be prepared in this manner. Dehydrobromination of the axle in the rotaxane **15** yields the rotaxane **16** with a C≡C triple bond located in the centre of the axle.

Introduction

In recent years, considerable progress has been made in the synthesis of rotaxanes.[1−10] Chemical reactions on rotaxanes have not, however, been examined extensively hitherto. Though some conversions on rotaxanes, such as nucleophilic substitution[11], condensation[12], and protonation[13] on rotaxane axles, have been carried out earlier, the influence of the ring on the reaction rate has hardly been investigated. This situation can find an explanation in the difficulties of adding or interconverting functional groups in the first preparatively accessible rotaxanes[1,5−7] on account of synthetic reasons. While C≡C triple bonds have already been introduced into water-soluble rotaxanes,[14] the incorporation of double bonds into the axle of neutral amide-linked rotaxanes described in this paper for the first time, demonstrates the suitability of mechanically



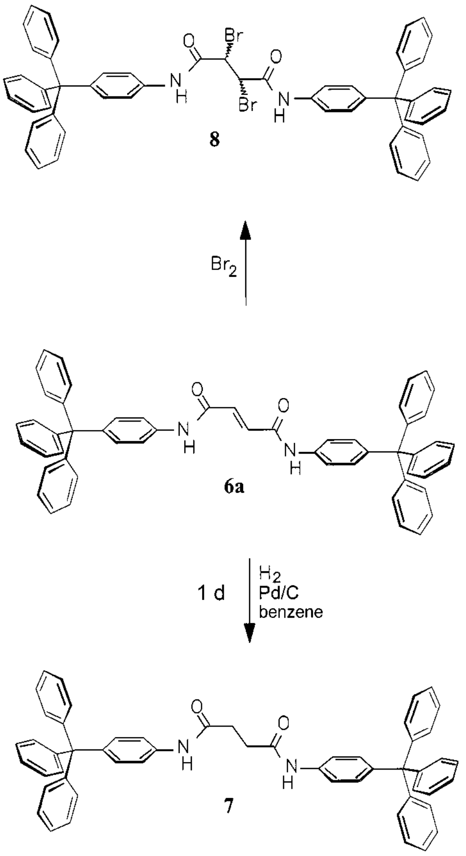
Scheme 1

---

[a] Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn,
Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany
Fax: (internat.) + 49(0)228/735662
E-mail: voegtle@uni-bonn.de

1434−193X/99/0505−1233 $ 17.50+.50/0

interlocked molecules as substrates for chemical reactions. In addition, it allows to compare the reactivity of the C=C double bond in the free axle with that in the rotaxane. Consequently, it is possible to gain an impression of the extent of steric hindrance provided by the wheel in chemical reactions performed on the axle component of rotaxanes.



Scheme 2a

Results and Discussion

a) Synthesis of Rotaxanes

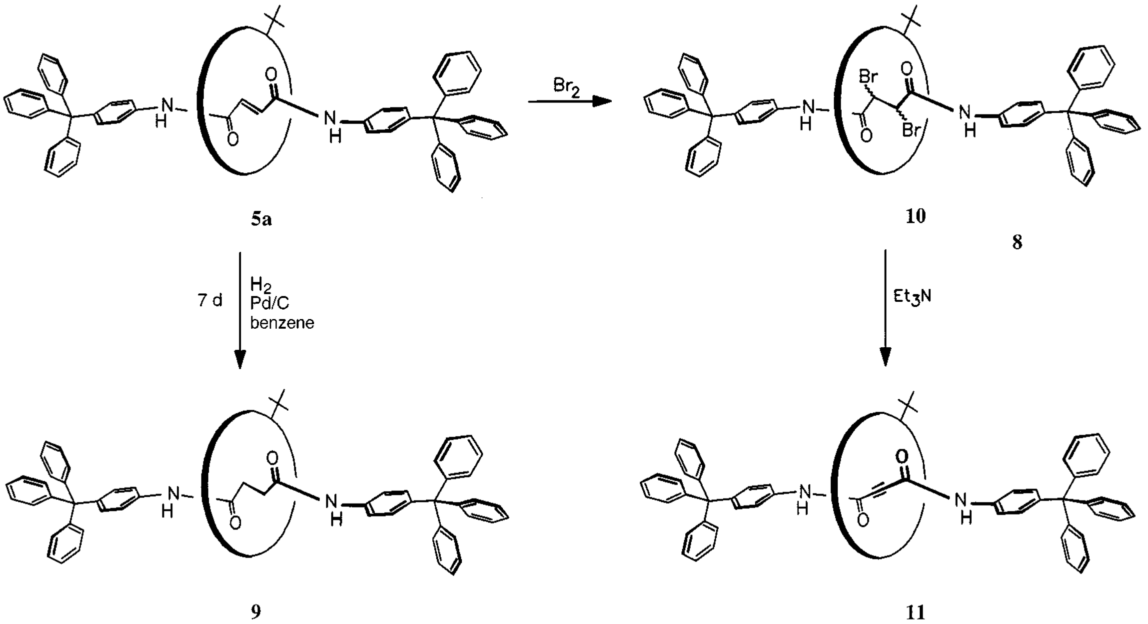
Starting from the dicarboxylic acid chlorides **1a** and **b** the rotaxanes **5a** and **b** were prepared by our threading procedure[11] in 18−23% yield.[15] In this reaction the corresponding semi-rotaxanes **4a** and **b** are assumed to act as intermediates (Scheme 1).

b) Chemical Reactions on Rotaxanes

Hydrogenation

To investigate an effect caused by the macrocyclic wheel **2** the free axle molecules **6a** and **6b** (Schemes 2a and 3a) and the corresponding rotaxanes **5a** and **5b** (Schemes 2b and 3b) were catalytically hydrogenated with Pd/C under the same conditions. Hydrogenation was continued until no further conversion was found. As can be seen from Table 1, the yields of the hydrogenated rotaxanes **5a** and **5b** are substantially lower than those of the hydrogenated free axles **6a** and **6b** after the same reaction time. The hydrogenated free axles **7** and **12** (Schemes 2a and 3a) and the corresponding rotaxanes **9** and **14** (Schemes 2b and 3b) were isolated and characterized.

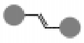
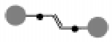
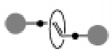
As assumed in previous studies,[12] the axle in the rotaxanes appears not to be completely shielded by the wheel. Differences in behaviour between the rotaxane and the free axle are obviously due to the steric hindrance of the reaction by the wheel. Thus, double bonds in rotaxane axles are shielded by the wheel and consequently react more slowly. Formerly, in the direct threading synthesis of the succinic acid rotaxane **9** from succinic acid dichloride and the corresponding stopper amine the expected product was detected, but it was difficult to separate the rotaxane from the



Scheme 2b

free axle which is simultaneously formed.[16] By the new indirect way of hydrogenating rotaxane **5a** as described here, however, this amide-linked rotaxane with an aliphatic central part is easily obtained in a pure form and in preparative scale. Hence, the integration of a double bond in the centre of the axle represents an alternative way to rotaxanes with aliphatic axles which are not or hardly accessible by direct threading.

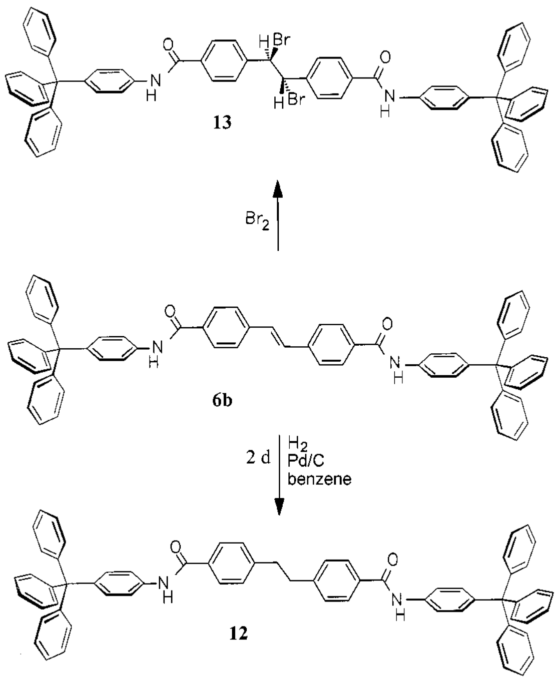
Table 1. Yield of hydrogenation (Pd/H_2) of rotaxanes and their corresponding free axles

parent compound		hydrogenation yield (%)		
No.	symbol	after 18 h	after 63 h	after 120 h
6a		91	–[a]	–[a]
5a		6	89	–[a]
6b		48	85	–[a]
5b		2	33	87

[a] No further conversion could be observed.

Addition of Bromine

As shown in Schemes 2b and 3b, the rotaxanes **5a** and **5b** can also be derivatised by bromine addition to give the corresponding dibromo rotaxanes **10** and **15**, which were not separated into its isomers. For comparison the axles **6a** and **6b** (Schemes 2a and 3a) were also treated with elementary bromine in trichloromethane under analogous conditions following standard synthetic procedures to yield the dibrominated axles **8** and **13**.

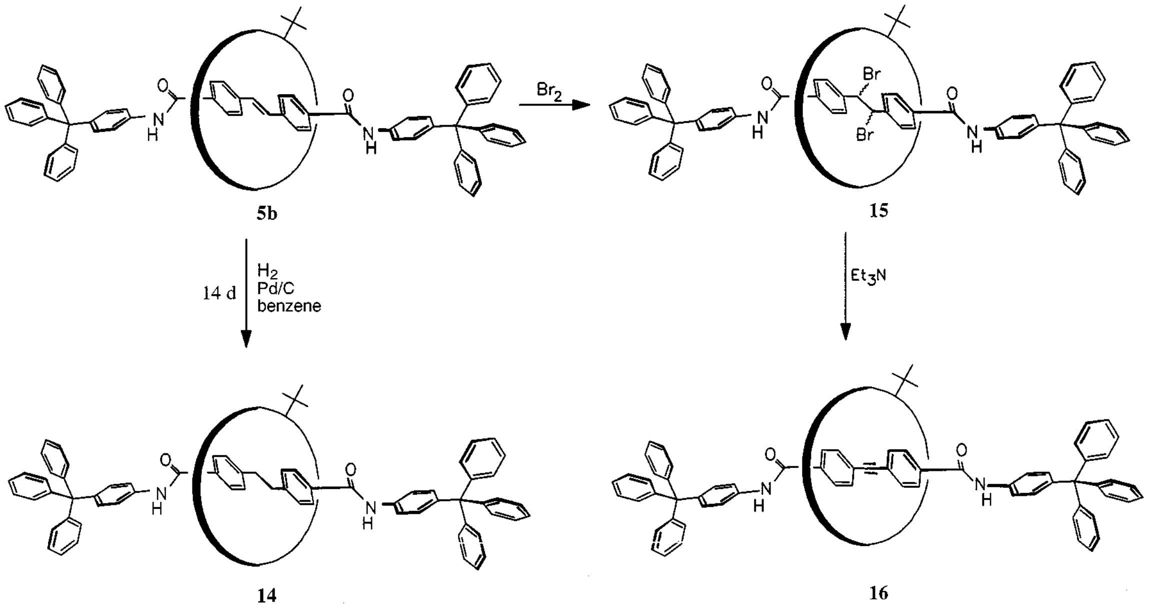


Scheme 3a

Elimination

Twofold dehydrohalogenation of the brominated rotaxane **15** yielded the new amide-linked rotaxane **16** with a C≡C triple bond in the centre of the axle (Scheme 3b). Long reaction times, however, increase the risk of the amide bonds being cleaved in the basic reaction medium. That is probably why rotaxane **16** with tolane in the centre of the axle was obtained in only 20% yield and rotaxane **11** could merely be detected by mass spectrometry.

The free axles can only be dissolved with difficulty. Since dehydrobromination does not proceed within the necessarily diluted solution, the elimination did not succeed with these axles.



Scheme 3b

Conclusion

In future investigations the steric shielding of the wheel, in the sense of a macrocyclic, noncovalent protecting group noticed here as a reduced addition rate, could be used to protect functional groups in rotaxane axles. Since the "slipping" method[17] allows wheels to be mechanically slipped onto axles without the formation of a covalent bond, the "rotaxanation" − to introduce the wheel as protecting group − and deprotection by "deslipping" is no longer an insurmountable barrier in strategies, that involve e.g. the reaction of a functional group in the stopper unit in the presence of a likewise reactive but sterically protected group in the centre of the axle. Furthermore, the derivatisation of brominated rotaxanes might be used for building up larger rotaxane units up to rotaxane networks.

Experimental Section

General Remarks: Solvents were purified by standard methods and dried if necessary. Commercial quality reagents were used. − TLC was carried out on silica gel 60 F254 and CC on silica gel 60, mesh size 63−100µm (Merck, Darmstadt, Germany). − Melting points were determined on a microscope heating unit by Reichert, Vienna, Austria, and are not corrected. − The NMR spectra were recorded on AM-250 (^{1}H: 250 MHz, ^{13}C: 62.9 MHz), AM-400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz) and DRX-500 (^{1}H: 500 MHz) of Bruker Physik AG, Karlsruhe, Germany. The assignment of the NMR signals was supported by HH-COSY and DEPT 135 experiments (abbreviations: ol: olefinic, ar: aromatic, iso: isophthaloyl, cy: cyclohexyl). − Microanalyses: Microanalytical Department of "Kekulé-Institut für Organische Chemie und Biochemie", University of Bonn. − FAB-MS, with *m*-nitrobenzyl alcohol as matrix: Concept 1H and MALDI TOF-MS, with 2,5-dihydroxy benzoic acid as matrix: Kompakt MALDI 3 of Kratos Analytical Ltd., Manchester, UK.

General Procedure for the Rotaxane Synthesis via Threading: 0.4 mmol of macrocycle **2** and 0.4 mmol of acid chloride were dissolved in 200 mL of dichloromethane. At room temperature a solution of 0.79 mmol of 4-aminophenyl-triphenylmethane **3** and 25 drops of triethylamine in 200 mL of dichloromethane were added dropwise over a period of 4 h. After another 2 h of stirring the solvent was removed in vacuo, and the crude product was purified by column chromatography (SiO_2; 63−100 µm).

Rotaxane 5a and Axle 6a

[2]{*N*,*N*′-Bis[4-(triphenylmethyl)phenyl]fumardiamide}{10-*tert*-butyl-4,16,22,34,48,49,52,53-octamethyl-6,14,24,32-tetraazanonacyclo-[36^{1,1}.5^{1,1}.5^{19,19}.2^{2,5}.2^{15,18}.2^{20,23}.2^{33,36}.1^{8,12}.1^{26,30}]hexapentaconta-2,4,8,10,12(55),15,17,20,22,26,28,30(56),33,35,47,49,51,53-octadecaene-7,13,25,31-tetraone}rotaxane (5a): Colourless solid, yield 170 mg (26%), mp. 289°C, R_f = 0.46 (dichloromethane/ethyl acetate, 25:1). − ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$, 20°C): δ = 1.38 (s, 9 H, $C(CH_3)_3$), 1.48 (br, 4 H, CH_2), 1.57 (br, 8 H, CH_2), 1.98 (s, 12 H, CH_3), 2.01 (s, 12 H, CH_3), 2.23 (br, 8 H, CH_2), 6.60 (d, ^3J = 8.6 Hz, 4 H, ArH), 6.65 (s, 2 H, fumaric-H), 6.81 (s, 4 H, ArH), 6.83 (s, 4 H, ArH), 7.02 (d, ^3J = 8.6 Hz, 4 H, ArH), 7.09−7.23 (signal group , 30 H, ArH), 7.60 (t, ^3J = 7.7 Hz, 1 H, Iso-H), 8.07 (d, ^3J = 7.7 Hz, 2 H, Iso-H), 8.13 (s, 2 H, *t*-Bi-iso-H), 8.32 (s, 1 H, *t*-Bi-iso-H), 8.54 (s, 1 H, Iso-H). − ^{13}C NMR (100.6 MHz, $CDCl_3/CD_3OD$): δ = 17.58 ($ArCH_3$), 21.83, 25.29, 34.01 (cy-CH_2), 28.56 ($C(CH_3)_3$), 30.10 ($C(CH_3)_3$), 43.77 (cy-C), 63.45 ($C(Ph)_4$), 119.46, 124.79, 124.83, 124.92, 126.01, 126.44, 126.65, 126.91, 128.01, 129.67, 129.85, 130.18, 132.61 (CH), 131.14, 131.25, 133.51, 133.74, 133.99, 134.08, 134.52, 142.05, 145.57, 146.32, 151.30 (Cq), 162.06, 164.13, 164.53 (C=O). − MALDI TOF: *m*/*z* = 1712.1 [M + H]$^+$, 1735.1 [M + Na]$^+$, 1751 [M + K]$^+$. − $C_{118}H_{114}N_6O_6 \cdot H_2O$ (1712.19): calcd. C 81.16, H 6.70, N 4.81; found C 81.10; H 6.52, N 4.34.

***N*,*N*′-Bis[4-(triphenylmethyl)phenyl]fumardiamide (6a):** Colourless solid, yield 77 mg (26%), mp. 310°C, R_f = 0.47 (dichloromethane/ethyl acetate, 25:1). − MALDI TOF: *m*/*z* = 751.2 [M + H]$^+$, 773.7 [M + Na]$^+$, 791.7 [M + K]$^+$. − $C_{54}H_{42}N_2O_2 \cdot 2\ H_2O$ (750.91): calcd. C 86.37, H 5.64, N 3.73; found C 86.29, H 5.64, N 3.06.

Rotaxane 5b and Axle 6b

[2]{[*N*,*N*′-Bis[4-(triphenylmethyl)phenyl]-4,4′-stilbenedicarboxamide}{10-*tert*-butyl-4,16,22,34,48,49,52,53-octamethyl-6,14,24,32-tetraazanonacyclo[36^{1,1}.5^{1,1}.5^{19,19}.2^{2,5}.2^{15,18}.2^{20,23}.2^{33,36}.1^{8,12}.1^{26,30}]hexapentaconta-2,4,8,10,12(55),15,17,20,22,26,28,30(56),33,35,47,49,51,53-octadecaene-7,13,25,31-tetraone}rotaxane (5b): Colourless solid, yield 130 mg (18%), mp. 240°C, R_f = 0.41 (dichloromethane/ethyl acetate, 25:1). − ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$, 20°C): δ = 1.27 [s, 9 H, $C(CH_3)_3$], 1.45 (br, 4 H, CH_2), 1.56 (br, 8 H, CH_2), 1.97 (d, 24 H, CH_3), 2.22 (br, 8 H, CH_2), 6.55 (s, 2 H, CH=CH), 6.51 (d, ^3J = 9.1 Hz, 4 H, ArH), 6.9 (s, 4 H, ArH), 7.1 (s, 4 H, ArH), 7.20 (d, ^3J = 9.1 Hz, 4 H, ArH), 7.22−7.35 (signal group , 38 H, ArH), 7.52 (t, ^3J = 7.4 Hz, 1 H, Iso-H), 8.05 (d, ^3J = 7.7 Hz, 2 H, Iso-H), 8.2 (s, 2 H, *t*-Bi-iso-H), 8.3 (s, 1 H, *t*-Bi-iso-H), 8.64 (s, 1 H, Iso-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.78 ($ArCH_3$), 21.11, 26.41, 34.77 (cy-CH_2), 29.74 [$C(CH_3)_3$], 31.20 [$C(CH_3)_3$], 45.12 (cy-C), 64.63 [$C(Ph)_4$], 119.72, 124.79, 124.83, 125.92, 126.09, 126.44, 126.65, 126.91, 127.08, 127.60, 128.10, 128.82, 129.52, 129.55, 130.84, 131.46 (CH), 131.08, 131.13, 133.51, 133.74, 133.97, 134.08, 134.98, 140.00, 143.39, 145.57, 146.65, 153.37 (Cq), 162.06, 164.13, 164.53 (C=O). − MALDI TOF: *m*/*z* = 1864.4 [M + H]$^+$, 1886.5 [M + Na]$^+$, 1902.4 [M + K]$^+$. − $C_{130}H_{122}N_6O_6 \cdot 2\ H_2O$ (1864.35): calcd. C 83.73, H 6.60, N 4.51; found C 83.35, H 6.80, N 4.24.

***N*,*N*′-Bis[4-(triphenylmethyl)phenyl]-4,4′-stilbenedicarboxamide (6b):** Colourless solid, yield 71 mg (20%), mp. 165°C, R_f = 0.72 (dichloromethane/ethyl acetate, 25:1). − ^{1}H NMR (250 MHz, $CDCl_3$, 20°C): δ = 6.68 (s, 2 H; CH=CH), 7.10−7.41 (signal group, 30 H, ArH), 7.50 (d, ^3J = 8.6 Hz, 4 H, ArH), 7.61 (d, ^3J = 8.6 Hz, 4 H, ArH), 7.85 (d, ^3J = 8.5 Hz, 4 H, ArH), 8.15 (s, 1 H, amide-H), 8.37 (s, 4 H, ArH). − MALDI TOF: *m*/*z* = 903.1 [M + H]$^+$, 925.2 [M + Na]$^+$, 942.1 [M + K]$^+$. − $C_{66}H_{50}N_2O_2 \cdot 0.5\ H_2O$ (903.11): calcd. C 87.17, H 5.58, N 3.10; found C 87.16, H 5.38, N 2.87.

General Hydrogenation Procedure: 0.16 mmol each of the rotaxane and the axle were suspended in 200 mL of benzene. At room temperature the substrates were hydrogenated in presence of 20 mg of palladium on activated carbon (10%) under a hydrogen pressure of 3 bar using a shaker. After 15 h the reaction was stopped, and the catalyst was filtered off. The solvent was removed in vacuo and the crude product purified by column chromatography (SiO_2; 63−100 µm).

Rotaxane 9 and Axle 7

[2]{*N*,*N*′-Bis[4-(triphenylmethyl)phenyl]succindiamide}{[10-*tert*-butyl-4,16,22,34,48,49,52,53-octamethyl-6,14,24,32-tetraazanonacyclo-[36^{1,1}.5^{1,1}.5^{19,19}.2^{2,5}.2^{15,18}.2^{20,23}.2^{33,36}.1^{8,12}.1^{26,30}hexapentaconta-2,4,8,10,12(55),15,17,20,22,26,28,30(56),33,35,47,49,51,53-octa-

decaene-7,13,25,31-tetraone}rotaxane (9): Colourless solid, yield 16 mg (6%), mp. >350°C, R_f = 0.60 (petroleum ether/ethyl acetate/methanol, 8:2:1). − ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$, 20°C): δ = 1.27 [s, 9 H, $C(CH_3)_3$], 1.45 (br, 4 H, CH_2), 1.50 (br, 8 H, CH_2), 1.72 (s 4 H, CH_2) 1.79 (s, 12 H, CH_3), 1.80 (s, 12 H, CH_3), 2.18 (br, 8 H, CH_2), 6.51 (d, ^3J = 8.4 Hz, 4 H, ArH), 6.78 (s, 8 H, ArH), 6.85 (d, ^3J = 8.4 Hz, 4 H, ArH), 7.00−7.22 (signal group, 30 H, ArH), 7.45 (t, ^3J = 7.7 Hz, 1 H, Iso-H), 7.98 (d, ^3J = 7.7 Hz, 2 H, Iso-H), 8.09 (s, 2 H, *t*-Bi-iso-H), 8.27 (s, 1 H, *t*-Bi-iso-H), 8.47 (s, 1 H, iso-H). − ^{13}C NMR (100.6 MHz, $CDCl_3/CD_3OD$): δ = 18.68 ($ArCH_3$), 21.46, 26.48, 35.35 (cy-CH_2), 32.84 (CH_2), 32.31 [$C(CH_3)_3$], 32.31 [$C(CH_3)_3$], 45.17 (cy-C), 64.68 [$C(Ph)_4$], 120.20, 124.10, 126.17, 127.09, 127.24, 127.59, 127.65, 127.89, 128.73, 129.68, 131.00, 131.18, 131.35, 131.39, 131.61, 134.09, 134.45, 135.27, 135.43, 143.31, 146.78, 148.32, 153.38, 166.65, 166.82, 171.82. − MALDI TOF: *m*/*z* = 1714.0 ($[M+H]^+$, 1736.80 $[M+Na]^+$, 1753.81 $[M+K]^+$. − $C_{118}H_{116}N_6O_6 \cdot 2\ H_2O$ (1714.21): calcd. C 82.68, H 6.82, N 4.90; found C 82.29, H 6.07, N 4.42.

***N*,*N*′-Bis[4-(triphenylmethyl)phenyl]succindiamide (7):** Colourless solid, yield 110 mg (91%), mp. 270°C, R_f = 0.45 (dichloromethane/ethyl acetate, 20:1). − ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$, 20°C): δ = 2.57 (s, 4 H, CH_2), 7.02−7.31 (signal group, 38 H, ArH), − ^{13}C NMR (100.6 MHz, $CDCl_3/CD_3OD$): δ = 32 (CH_2), 64.46 ($C(Ph)_4$), 118.81, 125.79, 127.35, 130.96, 131.46 (CH), 135.58, 142.58, 146.66 (Cq), 171.41 (C=O). − MALDI TOF: *m*/*z* = 753.3 $[M + H]^+$, 775.3 $[M + Na]^+$, 792.3 $[M + K]^+$.− $C_{54}H_{44}N_2O_2 \cdot 2\ H_2O$ (752.94): calcd. C 86.14, H 5.89, N 3.72; found C 86.49, H 6.51, N 3.01.

Rotaxane 14 and Axle 12

[2]{*N*,*N*′-Bis[4-(triphenylmethyl)phenyl]bibenzyl-4,4′-dicarboxamide}-{10-*tert*-butyl-4,16,22,34,48,49,52,53-octamethyl-6,14,24,32-tetraazanonacyclo[$36^{1,1}.5^{1,1}.5^{19,19}.2^{2,5}.2^{15,18}.2^{20,23}.2^{33,36}.1^{8,12}.1^{26,30}$]hexapentaconta−2,4,8,10,12(55),15,17,20,22,26,28,30(56),33,35,47,49,51,53-octadecaene-7,13,25,31-tetraone}rotaxane (14): Colourless solid, yield 6 mg (2%), mp. 250°C, R_f = 0.68 (petroleum ether/ethyl acetate/methanol, 8:2:1). − ^{1}H NMR (250 MHz, $CDCl_3$, 20°C): δ = 1.38 [s, 9 H, $C(CH_3)_3$], 1.50 (br, 4 H, CH_2), 1.63 (br, 8 H, CH_2), 1.88 (s, 24 H, CH_3), 2.31 (br, 8 H, CH_2), 2.97 (s, 4 H, CH_2), 6.85−7.31 (signal group, 46 H, ArH), 7.47 (t, ^3J = 7.7 Hz, 1 H, Iso-H), 8.09 (d, ^3J = 7.7 Hz, 2 H, Iso-H), 8.19 (s, 2 H, *t*-Bi-iso-H), 8.32 (s, 1 H, *t*-Bi-iso-H), 8.44 (s, 1 H, Iso-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.86 ($ArCH_3$), 23.08, 26.52, 34.98 (cy-CH_2), 35.38 (CH_2), 29.46 [$C(CH_3)_3$], 31.35 [$C(CH_3)_3$], 45.27 (cy-C), 64.72 [$C(Ph)_4$], 119.97, 124.79, 124.83, 124.92, 126.01, 126.44, 126.65, 127.21, 127.68, 129.67, 129.85, 130.18, 131.14, 131.18, 131.54, 132.88, 133.74, 133.99, 135.14, 135.62, 143.40, 144.91, 146.76, 147.24, 148.44, 153.40, 165.34, 167.15, 171.33 . − MALDI TOF: *m*/*z* = 1867.4 ($[M + H]^+$) 1890.4 $[M + Na]^+$, 19064 $[M + K]^+$. − $C_{130}H_{124}N_6O_6 \cdot H_2O$ (1866.40): calcd. C 83.66, H 6.70, N 4.50; found C 82.95, H 6.84, N 4.23.

***N*,*N*′-Bis[4-(triphenylmethyl)phenyl]bibenzyl-4,4′-dicarboxamide (12):** Colourless solid, yield 70 mg (48%), mp. 230°C, R_f = 0.71 (petroleum ether/ethyl acetate/methanol, 8:2:1). − ^{1}H NMR (250 MHz, $CDCl_3$, 20°C): δ = 2.87 (s, 4 H, CH_2), 7.02−7.31 (signal group, 38 H), 7.67 (d, ^3J = 8.75 Hz, 4 H, ArH), 7.85 (d, ^3J = 8.75 Hz, 4 H, ArH). − ^{13}C NMR (100.6 MHz, $CDCl_3/CD_3OD$): δ = 37 (CH_2), 65.34 [$C(Ph)_4$], 119.24, 126.47, 127.97, 128.16, 129.00, 131.83, 131.99, 134.39, 138.57, 142.37, 145.68 (Cq), 147.79,165.41. − MALDI TOF: *m*/*z* = 905.3 $[M + H]^+$, 927.3 $[M + Na]^+$, 944.2 $[M + K]^+$. − $C_{66}H_{52}N_2O_2$ (905.13): calcd. C 87.58, H 5.79, N 3.09; found C 87.56, H 5.71, N 2.93.

General Bromination Reaction: 0.16 mmol each of the rotaxane and the axle were dissolved in 20 mL of trichloromethane. Under exclusion of light a solution of 0.16 mmol of bromine in 40 mL of trichloromethane was added dropwise. After 50 h under exclusion of light the excessive bromine and the solvent were removed in vacuo. The crude product was purified by column chromatography (SiO_2; 63−100 μm).

Rotaxane 10 and Axle 8

[2]{*N*,*N*′-Bis[4-(triphenylmethyl)phenyl]-2,3-dibromosuccindiamide}-{10-*tert*-butyl-4,16,22,34,48,49,52,53-octamethyl-6,14,24,32-tetraazanonacyclo[$36^{1,1}.5^{1,1}.5^{19,19}.2^{2,5}.2^{15,18}.2^{20,23}.2^{33,36}.1^{8,12}.1^{26,30}$]-hexapentaconta-2,4,8,10,12(55),15,17,20,22,26,28,30(56),33,35,47,49,51,53-octadecaene-7,13,25,31-tetraone}rotaxane (10): Colourless solid, yield 27 mg (9%), mp. 268°C, R_f = 0.34 (trichloromethane/ethyl acetate/*n*-hexane, 5:3:1). − ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$, 20°C): δ = 1.37 [s, 9 H, $C(CH_3)_3$], 1.46 (br, 4 H, CH_2), 1.57 (br, 8 H, CH_2), 1.95 (s, 12 H, CH_3), 1.98 (s, 12 H, CH_3), 2.20 (br, 8 H, CH_2), 3.31 (s, 2 H, CHBr) 6.70 (d, ^3J = 8.6 Hz, 4 H, ArH), 7.21 (s, 8 H, ArH), 7.02 (d, ^3J = 8.6 Hz, 4 H, ArH), 7.07−7.21 (signal group, 30 H, ArH), 7.45 (t, ^3J = 7.7 Hz, 1 H, Iso-H), 7.81 (d, ^3J = 7.7 Hz, 2 H, Iso-H), 7.93 (s, 2 H, *t*-Bi-iso-H), 7.98 (s, 1 H, *t*-Bi-iso-H), 8.03 (s, 1 H, Iso-H). − ^{13}C NMR (100.6 MHz, $CDCl_3/CD_3OD$): δ = 17.62 ($ArCH_3$), 23.15, 26.68, 35.39 (cy-CH_2), 29.87 [$C(CH_3)_3$], 31.30 [$C(CH_3)_3$], 45.28 (cy-C), 64.99 [$C(Ph)_4$], 121.96, 126.14, 126.44, 127.77, 127.91, 129.02, 129.19, 130.57, 131.13, 131.20, 131.35, 131.77, 131.91, 131.98, 132.02, 133.23, 134.55, 134.87, 135.56, 144.31, 146.26, 146.99, 152.92 , 165.74, 166.20, 171.28. − MALDI TOF: *m*/*z* = 1871.99 $[M + H]^+$ 1895.0 $[M + Na]^+$, 1911.0 $[M + K]^+$. − $C_{118}H_{114}Br_2N_6O_6 \cdot H_2O$ (1871.99): calcd. C 75.71, H 6.14, N 4.49; found C 75.38, H 6.27, N 4.19.

***N*,*N*′-Bis[4-(triphenylmethyl)phenyl]-2,3-dibromosuccindiamide (8):** Colourless solid, yield 33 mg (23%), mp. 125°C, R_f = 0.65 (dichloromethane/ethyl acetate, 10:1). − ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$, 20°C): δ = 3.18 (s, 2 H, CHBr), 6.75 (s, 8 H, ArH), 6.95 −7.01. − MALDI TOF: *m*/*z* = 910.2 $[M + H]^+$ 931.2 $[M + Na]^+$, 947.1 $[M + K]^+$. − $C_{54}H_{42}Br_2N_2O_2 \cdot 2\ H_2O$ (910.71): calcd. C 71.22, H 4.65, N 3.08; found C 71.09, H 4.93, N 2.74.

Rotaxane 15 and Axle 13

[2]{[*N*,*N*′-Bis{4-(triphenylmethyl)phenyl}-α,α′-dibromobibenzyl-4,4′-dicarboxamide}{10-*tert*-butyl-4,16,22,34,48,49,52,53-octamethyl-6,14,24,32-tetraazanonacyclo[$36^{1,1}.5^{1,1}.5^{19,19}.2^{2,5}.2^{15,18}.2^{20,23}.2^{33,36}.1^{8,12}.1^{26,30}$]hexapentaconta-2,4,8,10,12(55),15,17,20,22,26,28,30(56),33,35,47,49,51,53-octadecaene-7,13,25,31-tetraone}rotaxane (15): Colourless solid, yield 22 mg (7%), mp. 260°C, R_f = 0.47 (trichloromethane/ethanol, 9.2:0.8). − ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$, 20°C): δ = 1.35 [s, 9 H, $C(CH_3)_3$], 1.50 (br, 4 H, CH_2), 1.67 (br, 8 H, CH_2), 1.98 (s, 24 H, CH_3), 2.26 (br, 8 H, CH_2), 5.47 (s, 2 H, CHBr), 6.85 (d, ^3J = 7.4 Hz, 4 H, ArH), 7.11−7.39 (signal group , 42 H, ArH), 7.45 (t, ^3J = 7.7 Hz, 1 H, Iso-H), 8.08 (d, ^3J = 7.7 Hz, 2 H, Iso-H), 8.21 (s, 2 H, *t*-Bi-iso-H), 8.32 (s, 1 H, *t*-Bi-iso-H), 8.42 (s, 1 H, Iso-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.13 ($ArCH_3$), 21.00, 25.29, 34.01 (cy-CH_2), 29.61 [$C(CH_3)_3$], 30.10 [$C(CH_3)_3$], 43.77 (cy-C), 53.40, 56.72 (CHBr), 64.01 [$C(Ph)_4$], 113.14, 120.32, 120.57, 120.69, 126.14, 126.36, 126.59, 127.79, 127.95, 128.52, 129.34, 130.74, 130.86, 130.91, 131.26, 131.44, 132.39, 132.57, 133.46, 133.68, 133.71, 133.85, 134.65, 141.15, 145.18, 145.49, 145.97, 162.12, 164.22, 171.09. − MALDI TOF: *m*/*z* = 2025.86 $[M + H]^+$ 2047.52 $[M + Na]^+$, 2064.22 $[M + K]^+$. − $C_{130}H_{122}Br_2N_6O_6 \cdot 2\ H_2O$ (2024.14): calcd. C 77.14, H 6.07, N 4.15; found C 76.51, H 5.88, N 3.95.

***N,N′*-Bis[4-(triphenylmethyl)phenyl]-α,α′-dibromobibenzyl-4,4′-dicarboxamide (13):** Colourless solid, yield 28 mg (17%), mp. 155°C, R_f = 0.55 (petroleum ether/ethyl acetate/methanol, 8:2:1). − ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$, 20°C): δ = 4.59 (s, 2 H, CHBr), 7.10−7.21 (signal group, 38 H), 7.41 (d, ^3J = 8.68 Hz, 4 H, ArH), 7.56 (d, ^3J = 8.68 Hz, 4 H, ArH). − FAB-MS: *m*/*z* = 1063.2 [M + H]$^+$. − $C_{66}H_{50}Br_2N_2O_2 \cdot 3\ H_2O$ (1062.91): calcd. C 74.58, H 4.74, N 2.64; found C 74.12, H 4.92, N 2.39.

Rotaxanes 16 and 11: At room temperature 1.6 mmol triethylamine were added dropwise to a solution of 0.08 mmol of rotaxane in 30 mL of dichloromethane. The mixture was then refluxed for 32 h. After evaporating the solvent the crude product was purified by column chromatography (SiO_2; 63−100 µm).

Rotaxane 16 and Axle 11

[2]{*N,N′*-Bis[4-(triphenylmethyl)phenyl]diphenylacetylene-4,4′-dicarboxamide}{10-*tert*-butyl-4,16,22,34,48,49,52,53-octamethyl-6,14,24,32-tetraazanonacyclo[$36^{1,1}.5^{1,1}.5^{19,19}.2^{2,5}.2^{15,18}.2^{20,23}.2^{33,36}.1^{8,12}.1^{26,30}$]hexapentaconta-2,4,8,10,12(55),15,17,20,22,26,28,30(56),33,35,47,49,51,53-octadecaene-7,13,25,31-tetraone}rotaxane (16): Colourless solid, yield 30 mg (20%), mp. 197°C, R_f = 0.72 (trichloromethane/ethanol, 9.2:0.8). − ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$, 20°C): δ = 1.28 [s, 9 H, $C(CH_3)_3$], 1.32 (br, 4 H, CH_2), 1.63 (br, 8 H, CH_2), 1.98 (s, 24 H, CH_3), 2.31 (br, 8 H, CH_2), 6.80 (d, ^3J = 7.4 Hz, 4 H, ArH), 7.11−7.39 (signal group, 38 H, ArH), 7.56 (d, ^3J = 8.1 Hz, 4 H, ArH), 7.68 (d, ^3J = 8.1 Hz, 4 H, ArH), 7.79 (t, ^3J = 7.7 Hz, 1 H, Iso-H), 8.07 (d, ^3J = 7.7 Hz, 2 H, Iso-H), 8.21 (s, 2 , *t*-Bi-iso-H), 8.32 (s, 1 H, *t*-Bi-iso-H), 8.42 (s, 1 H, Iso-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.23 ($ArCH_3$), 18.80, 23.91, 31.43 (cy-CH_2), 29.86 [$C(CH_3)_3$], 30.52 [$C(CH_3)_3$], 45.34 (cy-C), 53.30, 56.12 (CHBr), 64.79 [$C(Ph)_4$], 91.20 (C≡C), 113.14, 120.01, 123.69, 125.89, 126.24, 126.41, 127.18, 127.73, 127.91, 128.97, 131.05, 131.22, 131.38, 131.75, 131.81, 132.39, 132.57, 133.46, 133.68, 134.23, 134.79, 135.33, 146.73, 147.21, 147.51, 153.20, 165.12, 166.230, 168.09. − MALDI TOF: *m*/*z* = 1862.49 [M + H]$^+$, 1884.3 [M + Na]$^+$, 1902.4 [M + K]$^+$. − $C_{130}H_{120}N_6O_6 \cdot 3\ H_2O$ (1862.37): calcd. C 83.88, H 5.95, N 3.00; found C 82.4, H 6.08, N 3.23.

***N,N′*-Bis[4-(triphenylmethyl)phenyl]acetylenedicarboxamide (11):** MALDI TOF: *m*/*z* = 1710 [M+H]$^+$.

[1] G. Schill, *Nachr. Chem. Tech. Lab.* **1967**, *15*, 149; G. Schill, H. Zollenkopf, *Justus Liebigs Ann. Chem.* **1969**, *721*, 53.

[2] C. Wu, P. R. Lecavalier, Y. X. Shen, H. W. Gibson, *Chem. Mater.* **1991**, *3*, 569.

[3] D. B. Amabilino, J. F. Stoddart, *Pure Appl. Chem.* **1993**, *65*, 2351; S. L. Langford, L. Pérez-García, J. F. Stoddart, *Supramol. Chem.* **1995**, *6*, 11; D. Pasini, F. M. Raymo, J. F. Stoddart, *Gazz. Chim. Ital.* **1995**, *125*, 431; P. R. Ashton, A. N. Collins, M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, D. J. Williams, *Angew. Chem* **1997**, *109*, 59; *Angew. Chem Int. Ed. Engl.* **1997**, *36*, 59; P. R. Ashton, R. Ballardini, V. Balzani, I. Baxter, A. Credi, M. C. T. Fyfe, M. T. Gandolfi, M. Gómez-López, M.-V. Martínez-Díaz, A. Piersanti, N. Spencer, J. F. Stoddart, M. Venturi, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.***1998**, *120*, 11932.

[4] D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725; D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154; D. B. Amabilino, F. M. Raymo, J. F. Stoddart, *Compreh. Supramol. Chem.* **1996**, *9*, 85.

[5] J.-C. Chambron, V. Heitz, J.-P. Sauvage, *J. Chem. Soc., Chem. Commun*. **1992**, 1131.

[6] J.-C. Chambron, V. Heitz, J.-P. Sauvage, *J. Am. Chem. Soc.* **1993**, *115*, 12378.

[7] P. R. Ashton, M. Grognuz, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, *Tetrahedron Lett.* **1991**, *32*, 6235; P. L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado. 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. Vincent, D. J. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 193.

[8] Z.-T. Li, J. Becher, *J. Chem. Soc., Chem. Commun.* **1996**, 639; Z.-T. Li, P. C. Stein, J. Becher, D. Jensen, P. Mørk, N. Svenstrup, *Chem. Eur. J.* **1996**, *2*, 624.

[9] F. Vögtle, M. Händel, S. Meier, S. Ottens-Hildebrandt, F. Ott, T. Schmidt, *Liebigs Ann.* **1995**, 739; vgl. L. F. Lindoy, *Nature* **1995**, *376*, 293.

[10] A. G. Johnston, D. A. Leigh. A. Murphy, J. P. Smart, M. D. Deegan, *J. Am. Chem. Soc.* **1996**, *118*, 10662.

[11] R. Jäger, F. Vögtle, *Angew. Chem.* **1997**, *109*, 966.

[12] T. Dünnwald, A. H. Parham, F. Vögtle, *Synthesis* **1998**, *3,* 339.

[13] M.-V. Martínez-Díaz, N. Spencer, J. F. Stoddart, *Angew. Chem.* **1997**, *109*, 1991; *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 1904; crown ethers as noncovalent protecting groups for NH_3^+ sites in substrates also containing NH_2^+ centres: A. G. M. Barrett, J. C. A. Lana, *J. Chem. Soc., Chem. Commun.* **1978**, 471.

[14] S. Anderson, H. L. Anderson, *Angew. Chem.* **1996**, *108*, 2075; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1956.

[15] F. Vögtle, R. Jäger, M. Händel, S. Ottens-Hildebrandt, W. Schmidt, *Synthesis* **1994**, 353.

[16] R. Jäger, doctoral thesis, Bonn, **1997**.

[17] C. Heim, F. Vögtle, in preparation.

Received December 22, 1998
[O98576]