# A Self-Threaded "Molecular 8"

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**Abstract:** A new type of [1]rotaxanes containing two aliphatic bridges between axle and wheel is obtained in 39% yield in a one-step synthesis starting from a [2]rotaxane which contained one sulfonamide group each in both the wheel and the axle. Temperature controlled chemoselective substitution reactions first at these sulfonamide nitrogens and then subsequently at the various other carboxamide nitrogens in the wheel and axle give rise to the formation of an isomeric mixture of three double-bridged [1]rotaxanes which could be separated by HPLC. Structure determination of the main product **3a** was possible by NMR experiments supported by molecular modeling calculations. Using different reaction conditions, a double-substituted but not yet bridged [2]rotaxane **4** could be isolated as an intermediate giving further evidence for the assigned structure of **3a** and the way of its formation. The shape of this double-bridged [1]rotaxane **3a** reminds of a self-intertwining chiral "molecular 8", in which any possible racemization due to deslipping is hindered by the two stoppers originating from the former rotaxane axle. Hence, to the best of our knowledge this is the first example of a molecule in which both concepts, cycloenantiomerism and helical chirality, are realised in one structure. Enantiomer separation of the main product was possible by further HPLC using chiral stationary phases. The Cotton effects of the circular dichrograms are different to those of the already synthesized [1]rotaxanes bearing just one aliphatic bridge between axle and wheel.

**Keywords:** chemoselective substitution · cycloenantiomerism · helical chirality · molecular modeling · rotaxanes

## Introduction

The design of interlocked molecules such as rotaxanes and catenanes and also of intertwined molecular knots gives rise to a whole range of compounds with novel structural and chiroptical properties based on non-classical types of chirality.[1]

Cycloenantiomerism of such molecules was foreseen theoretically by Frisch and Wasserman in 1961.[2] Topological chirality of catenanes can be determined by a difference in the segment sequence of one macrocycle with respect to the other. In order for such a directionality to exist, each ring of a catenane must consist of at least three different segments, even though every segment may appear in both rings.[3] The first topologically chiral catenanes and molecular knots, however, were not synthesized before the late 1980s.[4, 5] In 1971 Schill described the stereochemistry of rotaxanes as being closely related to that of catenanes.[6] Cycloenantiomerism of rotaxanes occurs when both its components, the wheel and the axle, contain a sequence information in their molecular scaffolds. One enantiomer has a clockwise orientation of the wheel with respect to the axle, whereas the other enantiomer is arranged anti-clockwise. In 1996 our group reported the first enantiomer separated, cycloenantiomeric [2]rotaxane (Figure 1).[7]

A covalent bridge between the wheel and the axle of such a chiral rotaxane leads to cycloenantiomeric [1]rotaxanes. We recently described the first synthesis of such mono-bridged [1]rotaxanes and the dependence of their chiroptical properties on the character of the bridges.[8] The covalent connection of the wheel with the axle was possible by the incorporation of sulfonamide units into carboxamide-based [2]rotaxanes, as the sulfonamide nitrogens can be substitued chemoselectively in the presence of carboxamide nitrogens using a mild base and room temperature as reaction conditions.[7] Two such covalent connections between wheel and axle should give rise to double-bridged [1]rotaxanes with a structure resembling a "molecular 8". Compared to other molecules with a figure-eight conformation described in the literature the inversion barrier of this particular "molecular 8" is supposed to be much higher because of the bulky blocking groups of the axle preventing a deslipping.[9] The chirality of such a new double-bridged [1]rotaxane would not only be based on cycloenan-

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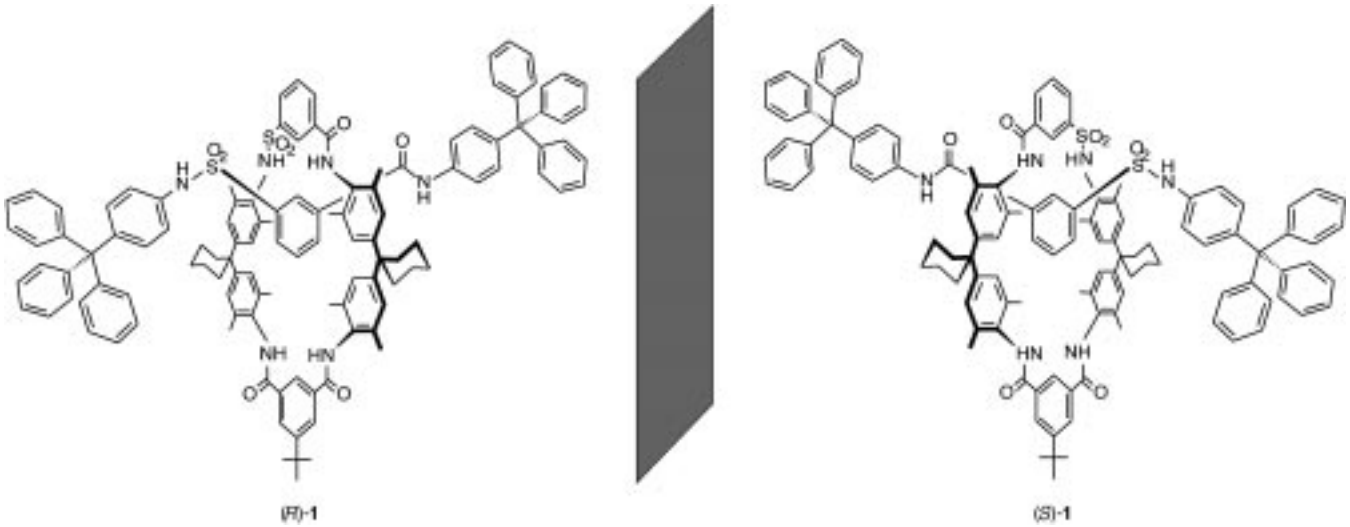



Figure 1. Cycloenantiomers of bissulfonamide[2]rotaxane **1**.

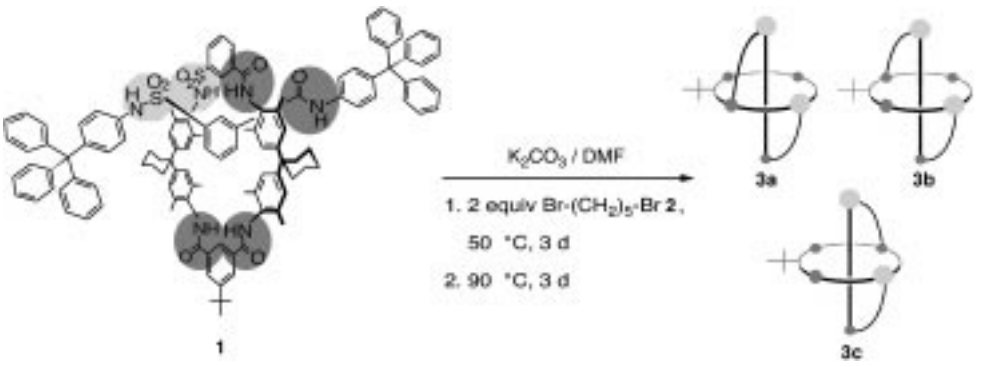
tiomerism but on helical chirality as well. Therefore, segment information of the wheel and the axle should not be necessary anymore for the chirality of such molecules.

Here we set out to investigate the first synthesis of such a [1]rotaxane with two covalent bridges between the wheel and the axle starting from a [2]rotaxane with one sulfonamide unit both in the axle and the wheel.[10]

## Results and Discussion

The synthetic approach for the preparation of a double-bridged [1]rotaxane started from a [2]rotaxane **1** which contains one sulfonamide group each in both its axle and its wheel. Due to the higher acidity of the sulfonamide NH compared with the carboxamide NH a substitution reaction under mild conditions using 1,5-dibromopentane **2** as an alkylating agent should take place first chemoselectively at the sulfonamide nitrogens. Further reaction under more severe conditions should then lead to ring closure of the two bridges through alkylation of the less reactive carboxamide NHs. The racemic mixture of the starting [2]rotaxane **1** was prepared by a chemical threading reaction based on non-ionic templating.[7] Solutions of **1** and the dibromide **2** were then simultaneously added to a suspension of potassium carbonate in DMF first at 50 °C (Scheme 1). After stirring at 50 °C for three days the reaction temperature was raised to 90 °C and the suspension was stirred for another 3 d. The temperature control is important to achieve the desired chemoselectivity. Purification of the reaction mixture on silica gel yielded 39 % of a colorless solid. FAB and MALDI-Tof spectra showed only a single product with $m/z$ 1970.7 as the molecular ion peak $[M]^+$ which clearly proves the presence of two aliphatic pentamethylene bridges in the product. Hence, the desired double-bridged [1]rotaxane was indeed formed in the reaction. However, $^1$H NMR experiments pointed out that not just one compound but a mixture of isomers was present, which could then be separated by HPLC into three isomers of the double-bridged [1]rotaxane in a ratio of 79:13:8.

Using HH-, CH-COSY, and NOE experiments all signals of the pure main isomer could be identified and based on this information the two bridges can be located as follows: Neither any of the sulfonamide NH nor the carboxamide NH of the axle are present in the NMR spectra, which shows that these amides have been substituted and now serve as anchoring points for the two bridges. As the spatial distance of the sulfonamide nitrogen of the axle to the carboxamide nitrogen of the axle is too far, a covalent connection of these two groups by a single bridge consisting of only five methylene groups is not possible.[8] Hence, the carboxamide nitrogen of the axle has to be linked via the first bridge to the sulfonamide nitrogen of the wheel not only in the main isomer but also in




Scheme 1. One-step synthesis of [1]rotaxanes **3a–c** containing two bridges.

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all possible isomers of this particular double-bridged [1]rotaxane **3**.[11] Less clear is the exact location of the second bridge. In principle, the sulfonamide nitrogen of the axle could be connected to any of the three carboxamide nitrogens of the wheel which either leads to structure **3a**, **3b** or **3c**. In **3a** the second bridge is formed to that of the two carboxamides of the 5-*tert*-butylisophthalamide unit which is on the same half of the wheel relative to the sulfonamide group. In **3b** the carboxamide group in the opposite half of the wheel is the anchoring point, whereas in **3c** the second bridge is formed to the carboxamide group in the sulfobenzoyl moiety. In the $^1$H NMR spectrum of the main isomer at least one of the two remaining carboxamide protons could be identified. The signal at $\delta = 7.97$ clearly belongs to the carboxamide NH of the 3-sulfobenzoylamide unit of the wheel. The second signal at $\delta = 8.46$ is one of the two carboxamide NHs of the 5-*tert*-butylisophthalamide moiety, which could not be further differentiated by $^1$H NMR methods. Whereas structure **3c** can therefore be definitely excluded as the main isomer, the NMR spectra do not allow to distinguish between isomer **3a** and **3b**.

To further elucidate the structure of the main isomer we performed a molecular dynamics calculation using the Amber* force field as implemented in the Macromodel 6.5 software package.[12] Even though the absolute energy values of a force field calculation for such highly complex compounds might not be very accurate due to missing data and errors in the force field parametrization, the calculated relative energy differences between various isomers of the same compound should be quite reliable. A conventional Monte Carlo conformational search showed that in water (using the Macromodel GB/SA solvation treatment) the three possible double-bridged isomers **3a**, **3b** and **3c** are indeed quite different in energy. Isomer **3a** in which the second bridge is formed to the proximal carboxamide group of the 5-*tert*-butylisophthalamide unit is the most stable one. Isomer **3b** in which the distal carboxamide group is the anchoring point for the second bridge is less stable by 9 kJ mol$^{-1}$. Isomer **3c** in which the second bridge is formed to the carboxamide group in the 3-sulfobenzoylamide unit is the least stable one and is 24 kJ mol$^{-1}$ higher in energy than **3a** due to unfavorable steric interactions. Therefore, according to the molecular mechanics calculations isomer **3a** is expected to be the main product in the formation of **3**, as the reaction takes place under thermodynamic conditions (high temperature, long reaction times) and the product ratio is hence determined by the relative stabilities of the various isomers. Even though the alkylation reaction at amide groups itself might not be reversible, according to the Hammond postulate product development control still favors, even under kinetic conditions, the formation of the most stable isomer.

However, the experimental reaction takes place under somewhat different conditions than the ones used in the Monte Carlo calculation. The lower polarity of the solvent (DMF) and the higher temperature (90 °C) could have a significant effect especially on the energy difference between **3a** and **3b**. In water, their relative stabilities are mainly caused by a better hydrophobic clustering of the large hydrophobic groups in **3a** compared with **3b**. It is expected that such a clustering effect is less important in a solvent other than water or at higher temperatures, where the mobility of the molecules, especially of such a flexible one as **3**, is much higher. Hence, to check whether the solvent polarity has a significant effect on the relative stabilities of **3a** and **3b**, we performed an analogous Monte Carlo simulation on those two isomers using chloroform as a solvent. Again, **3a** is more stable than **3b**, but the energy difference becomes smaller (4 kJ mol$^{-1}$ instead of 9 kJ mol$^{-1}$ in water). As expected for a solvent of lower polarity, the better hydrophobic clustering for **3a** in water is no longer important and the energy difference in chloroform is mainly due to electrostatic effects. Therefore, it seems quite reasonable to assume that also in DMF, which has a somewhat medium polarity in between water and chloroform, isomer **3a** remains more stable than **3b**.

To account for the reaction temperature of 90 °C and its influence on stability, we performed molecular dynamics calculations on **3a** and **3b** at 360 K over a time period of 100 ps using time steps of 0.5 fs both in water and chloroform. In both cases, isomer **3a** remains the most stable one. However, as expected the energy difference between **3a** and **3b** calculated from the molecular dynamics simulations is smaller than for the Monte Carlo calculations: 5 kJ mol$^{-1}$ in water and 3 kJ mol$^{-1}$ in chloroform.

Although the theoretical calculations do not allow to simulate the experimental conditions exactly, it seems quite clear from the modeling results that isomer **3a**, with both bridges originating from the same half-side of the wheel, is the most stable one of the three double-bridged isomers investigated. The other isomer **3b**, with the bridges attached to opposite sides of the wheel, is slightly less stable than **3a**, whereas the third possible isomer **3c** is much less stable and should therefore only be a minor by-product in the formation of **3**.

The structure of the most stable isomer **3a** as obtained from the molecular dynamics calculation at 360 K is shown in Figure 2. The axle is slightly S-shaped with the wheel sitting more or less in the middle on top of the 3-sulfobenzoylamide

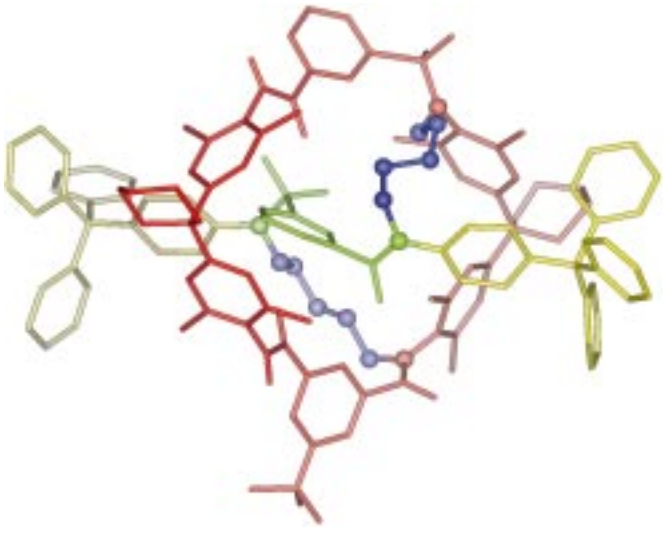

Figure 2. Structure of the isomer **3a** as obtained from a MD calculation at 360 K (cycle: red, axle: green, stoppers: yellow, bridges: blue).



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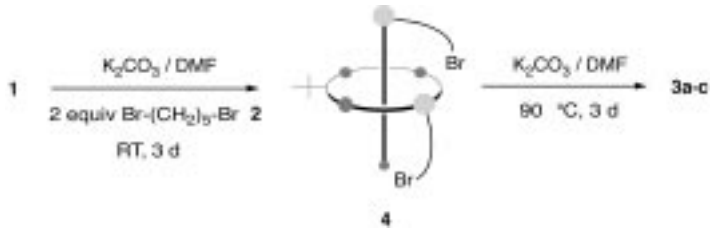
unit. This probably reflects the time averaged flexibility of the molecule, as the static Monte Carlo calculation yields a more compact and clustered structure.

To confirm the above-mentioned hypothesis, that the formation of the double-bridged [1]rotaxane **3** takes place in a two-step sequence, in which first the sulfonamide and then subsequently the carboxamide groups are alkylated (as shown in Scheme 2), we tried to isolate the predicted disubstituted




Scheme 2. Two-step synthesis of [1]rotaxanes **3a–c**.

but not yet bridged intermediate **4**. Indeed, a chemoselective substitution reaction of two equivalents 1,5-dibromopentane (**2**) with one equivalent of the racemic mixture of [2]rotaxane **1** using potassium carbonate as a mild base at room temperature yielded 83 % of the expected disubstituted [2]rotaxane **4**.[11] Using NOE as well as HH-and CH-COSY NMR experiments it was possible to not only show that both sulfonamide NHs are missing but also to assign a signal at $\delta =$ 9.03 to the carboxamide proton of the axle. As already mentioned above, this signal is absent in the spectrum of the main isomer of [1]rotaxane **3**; this proves that one bridge has formed to this group. We could also determine the two singlets of the 5-*tert*-butylisophthalamide NHs at $\delta = 8.87$ and $\delta = 7.90$ though we again could not identify which one belongs to the proximal and which to the distal carboxamide group. All other singlets could be clearly identified. Hence, in **4** both sulfonamide groups have indeed been alkylated, whereas none of the carboxamide groups has reacted so far. When a suspension of this disubstituted [2]rotaxane **4** and potassium carbonate in DMF was heated to 90 °C under dilution conditions a product with the same $R_f = 0.51$ and the same molecular mass of 1970.7 g mol$^{-1}$ as already observed for **3** could be isolated after purification on silica gel. Further analysis using HPLC showed that again all three isomers **3a–c** were formed but in a somewhat different ratio of 56:37:7. This not only supports the structure and the way of formation of the double-bridged [1]rotaxane **3**, but is also in excellent agreement with the modeling results. Based on the calculated energy differences it was expected, that **3a** and **3b** are formed as the two main products while **3c** is formed only in minor amounts. Why the isomer ratios differ for the one-step and the two-step reaction is not quite clear at the moment. This might be due to competing alternative pathways of product formation in the one-step procedure, which possibly do not go via the doubly substituted intermediate **4**.

**Enantiomer separation and chiroptical properties**: In contrast to the already characterized [1]rotaxanes with only one aliphatic or benzylic bridge, the new [1]rotaxane **3a** contains

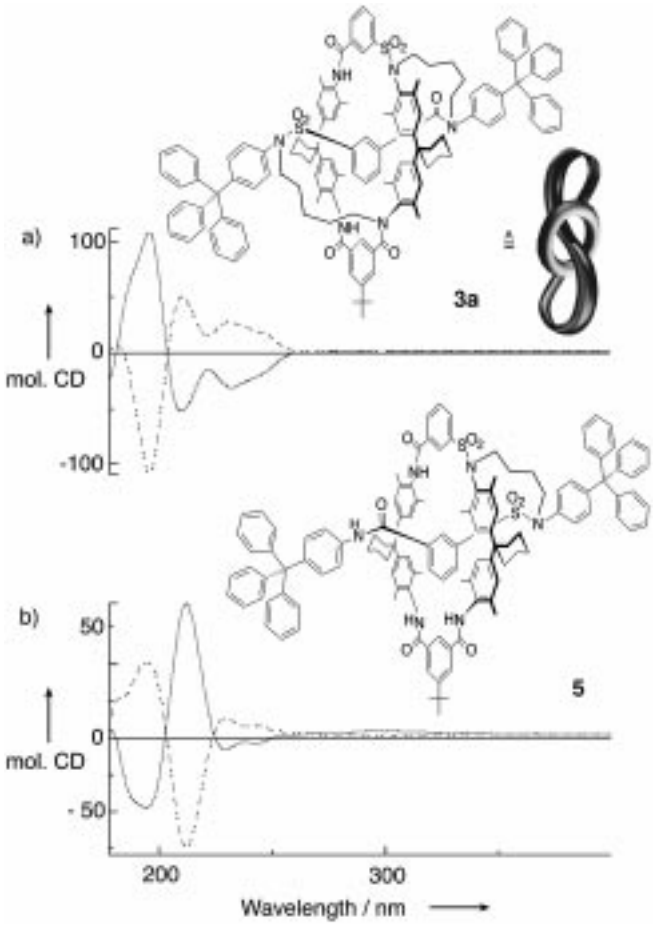



Figure 3. Circular dichrograms of a) **3a** and b) a [1]⟨4⟩rotaxane[8a] **5** in 1,1,1,3,3,3-hexafluoro-2-propanol.

two bridges which leads to helical chirality which is not dependent on a segment information in the wheel or the axle anymore. Moreover, the reduced translatorial mobility of the wheel with respect to the axle could change the chiroptical properties of this new type of [1]rotaxanes compared with the others.[8] These structural differences posed the question if there are any changes in the enantiomeric resolution constants or the chiroptical properties due to the incorporation of a second bridge.

The separation of the racemic mixture of **3a** into its cycloenantiomers was successful with baseline separation by HPLC on a "Chiralcel OD" column with *n*-hexane/ethanol 9:1.[13] The separation factor $\alpha$ of **3a** was found to be 1.41. Compared with the separation factors of the enantiomer separations of [1]rotaxanes with only one bridge $\alpha$ indicates that the reduced flexibility of the axle and the wheel has no appreciable impact on the separation factor.[8] As in all separations of [1]rotaxanes before the (−)-enantiomer of **3a** was eluted first.[8]

The Cotton effects obtained for the pair of enantiomers are mirror images over the entire spectral range. The molar CDs of the [1]rotaxane **3a** reach three extrema in the aromatic region. The comparison of the intensity of the molar CDs of **3a** with that of any previously reported aliphatically monobridged [1]rotaxane, for example compound **5** with one bridge containing four methylene groups, shows that the two bridges

in **3a** increase the intensity of the molar CD at 190 nm and 230 nm whereas the intensity at 210 nm is decreased by at least a factor of two each (Figure 3).[8]

In conclusion, we were able to synthesize the first double-bridged, enantiomer separated chiral [1]rotaxane **3a** by temperature controlled chemoselective substitution reactions starting from the racemic mixture of sulfonamide-based [2]rotaxane **1**. The presence and position of the two bridges could be determined by MS and NMR experiments and were supported by molecular dynamics studies. The chirality of **3a** is not only dependent on cycloenantiomerism but also on helical chirality and its pure enantiomers exhibit Cotton effects in the same order of magnitude known for mono-bridged [1]rotaxanes but different from those of helicenes. The results shown here, not only represent the first example of such a double-bridged [1]rotaxane but also contribute to the understanding of the chiroptical properties of mechanically interlocked molecules in general.

## Experimental Section

All solvents were distilled prior to use and all other chemicals were of the best quality commercially available and used as received. The [2]rotaxane **1** was prepared as reported previously.[7] 1,5-Dibromopentane was purchased from Aldrich. FAB MS: Concept 1H Kratos Analytical, Manchester, matrix: *m*-nitrobenzyl alcohol. MALDI TOF: MALDI-TofSpecE, Micromass, Manchester, matrix: 9-nitroanthracene or 2,5-dihydroxybenzoic acid. $^1$H, $^{13}$C NMR spectroscopy: AM 400 MHz, or DRX 500 MHz, Bruker, Analytische Meßtechnik, Karlsruhe. CD spectrometer: JASCO, J-720 spectrometer, Labor- und Datentechnik GmbH, Deutschland.

The following symbols are used for the characterization of the protons found: ar = aromatic proton of the macrocycle, *t*bu = 5-*tert*-butylisophthaloyl diamide, cyc = cyclohexyl, sb = 3-sulfonylisophthaloyl diamide, trityl = trityl group.

**One-step synthesis of [1]rotaxanes 3a–c**: [2]Rotaxane **1**[7] (100 mg, 0.05 mmol), 1,5-dibromopentane (**2**, 23 mg, 0.10 mmol), and potassium carbonate (35 mg, 0.25 mmol) were suspended in dry DMF (35 mL). The suspension was stirred at 50 °C. After 3 d the temperature was raised to 90 °C and stirring was continued for another 3 d. After the addition of chloroform (100 mL) the solution was extracted three times with water (70 mL each). The organic layer was separated and dried over $Na_2SO_4$. The crude product was then purified by column chromatography (silica gel, 63–100 μm, dichloromethane/ethyl acetate 40:1). The isomeric mixture **3a–c** was isolated as a colorless powder (39 mg, 0.02 mmol, 39 %). The separation of isomer **3a** was achieved by HPLC using a silica gel column (*n*-hexane/ethanol 9:1).

**[1]Rotaxane 3a**: $R_f$ = 0.51 (dichloromethane/ethyl acetate 40:1); $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 8.66 (s, 1H; $sb_{cycle}$), 8.46 (s, 1H; $NH_{cycle}$ (*t*Bu)), 8.38 (s, 1H; *t*bu), 8.29 (s, 1H; *t*Bu), 8.22 (d, $^3J$(H,H) = 7.8 Hz, 1H; $sb_{cycle}$), 8.10 (s, 1H; *t*Bu), 7.97 (s, 1H; $NH_{cycle}$, sb), 7.86 (d, $^3J$(H,H) = 7.8 Hz, 1H; $sb_{cycle}$), 7.67 (d, $^3J$(H,H) = 7.8 Hz, 1H; $sb_{axle}$), 7.65 (dd, $^3J$(H,H) = 7.8 Hz, $^3J$(H,H) = 7.8 Hz, 1H; $sb_{cycle}$), 7.62 (s, 1H; $sb_{axle}$), 7.43 (dd, $^3J$(H,H) = 7.8 Hz, $^3J$(H,H) = 7.8 Hz, 1H; $sb_{axle}$), 7.25–7.12 (m, 44H; trityl, ar, $sb_{axle}$), 6.86 (d, $^3J$(H,H) = 8.2 Hz, 2H; tritylaniline), 5.59 (s, 1H, ar), 4.58–4.45 (m, 2H; $CH_2$N), 3.41–3.28 (m, 2H; $CH_2$), 3.09–3.00 (m, 2H; $CH_2$), 2.95–2.81 (m, 2H; $CH_2$), 2.50–2.19 (m, 2H; $CH_2$), 2.33 (br, 8H; cyc $CH_2$), 2.16 (s, 4H; cyc $CH_2$), 2.05 (br, 8H; cyc $CH_2$), 1.95–1.62 (m, 4H; $CH_2$), 1.65 (s, 12H; $CH_3$), 1.52 (s, 12H; $CH_3$), 1.39 (s, 9H; *t*Bu $CH_3$), 1.48–1.12 (m, 6H; $CH_2$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta$ = 172.2 (amide Cq), 165.2, 164.9, 163.7, 153.4 (Cq), 150.9, 149.2, 146.6, 146.5, 146.3, 144.6, 142.2, 139.4, 136.2, 135.4, 134.2, 134.1, 133.9, 133.7, 132.0, 131.9 (CH), 131.3, 131.1, 131.0, 130.5, 130.4, 129.2, 129.1, 128.9, 128.3, 127.6, 127.5, 127.4, 126.2, 126.1, 125.8, 123.3, 122.1, 67.1 (trityl Cq), 64.7, 52.2 ($CH_2$), 49.5, 47.4 (cyc Cq), 44.6, 40.8, 35.3 (*t*Bu Cq), 31.9, 31.5 (*t*Bu $CH_3$), 31.3, 30.7, 29.7, 29.4, 27.8, 26.5, 26.2, 25.2, 22.9, 22.7, 22.4, 20.2 ($CH_3$), 19.8, 18.5, 18.4; FAB MS: *m*/*z*: 1970.7 $[M]^+$ (calcd 1970.7); MALDI Tof MS: *m*/*z*: 2009.4 $[M+K]^+$.

**Two-step synthesis of [1]rotaxanes 3a–c**

**Synthesis of the disubstituted [1]rotaxane 4**: [2]Rotaxane **1**[7] (200 mg, 0.10 mmol), dissolved in DMF (50 mL), was added over a period of 3 h to a stirred suspension of 1,5-dibromopentane (**2**, 46 mg, 0.20 mmol) and potassium carbonate (69 mg, 0.50 mmol) in dry DMF (20 mL). The suspension was stirred at room temperature for 3 d. After the addition of chloroform (100 mL) the solution was extracted three times with water (70 mL each). The organic layer was separated and dried over $Na_2SO_4$. The crude product was then purified by column chromatography (silica gel, 63–100 μm, dichloromethane/ethyl acetate 40:1). The disubstituted [2]rotaxane **4** was isolated as a colorless powder (177 mg, 0.08 mmol, 83 %). $R_f$ = 0.41 (dichloromethane/ethyl acetate 40:1); m.p. 195 °C; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ = 9.03 (s, 1H; $NH_{axle}$), 8.87 (s, 1H; $NH_{cycle}$ (*t*Bu)), 8.69 (s, 1H; *t*bu), 8.35 (s, 1H; *t*bu), 8.20 (s, 1H; *t*bu), 8.19–8.16 (br, 2H; $NH_{cycle}$ (sb), $sb_{cycle}$), 8.13 (d, $^3J$(H,H) = 8.0 Hz, 1H; $sb_{cycle}$), 8.02 (d, $^3J$(H,H) = 8.0 Hz, 1H; $sb_{cycle}$), 7.90 (s, 1H; $NH_{cycle}$ (*t*bu)), 7.55 (dd, $^3J$(H,H) = 8.0 Hz, $^3J$(H,H) = 8.0 Hz, 1H; $sb_{cycle}$), 7.25–7.12 (m, 40H; trityl, ar, $sb_{axle}$), 7.03 (dd, $^3J$(H,H) = 7.7 Hz, $^3J$(H,H) = 7.7 Hz, 1H; $sb_{axle}$), 6.98 (d, $^3J$(H,H) = 8.2 Hz, 2H; tritylaniline), 6.86 (d, $^3J$(H,H) = 8.2 Hz, 2H; tritylaniline), 6.84 (s, 2H, ar), 6.52 (d, $^3J$(H,H) = 7.7 Hz, 1H; $sb_{axle}$), 6.16 (d, $^3J$(H,H) = 8.2 Hz, 2H; tritylaniline), 4.06 (d, $^3J$(H,H) = 6.4 Hz, 1H; Br-$CH_2$), 3.42 (d, $^3J$(H,H) = 6.4 Hz, 1H; Br-$CH_2$), 3.32–3.23 (m, 8H; $CH_2$), 2.33 (br, 8H; cyc $CH_2$), 2.16 (s, 4H; cyc $CH_2$), 2.05 (br, 8H; cyc $CH_2$), 1.95–1.62 (m, 4H; $CH_2$), 1.65 (s, 12H; $CH_3$), 1.52 (s, 12H; $CH_3$), 1.39 (s, 9H; *t*Bu $CH_3$), 1.48–1.12 (m, 6H; $CH_2$); $^{13}$C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta$ = 166.9 (amide Cq), 165.2, 164.9, 163.7, 153.4 (Cq), 150.9, 149.2, 146.6, 146.5, 146.3, 144.6, 142.2, 139.4, 136.2, 135.4, 134.2, 134.1, 133.9, 133.7, 132.0, 131.9 (CH), 131.3, 131.1, 131.0, 130.5, 130.4, 129.2, 129.1, 128.9, 128.3, 127.6, 127.4, 126.2, 126.1, 125.8, 123.3, 122.1, 64.8 (trityl Cq), 64.7, 50.5 ($CH_2$), 49.9, 45.3 (cyc Cq), 44.9, 35.3 (*t*Bu Cq), 33.6, 33.5, 32.2, 32.0, 31.0 (*t*Bu $CH_3$), 27.2, 26.4, 25.6, 24.6, 22.9, 22.8, 18.8 ($CH_3$), 18.4; MALDI Tof MS: *m*/*z*: 2132.7 $[M]^+$ (calcd 2132.5).

**Bridging reaction of 4 to 3a–c**: [2]Rotaxane **4** (145 mg, 0.07 mmol) and potassium carbonate (25 mg, 0.18 mmol) were suspended in dry DMF (250 mL). The suspension was stirred for 3 d at 90 °C. After the addition of chloroform (100 mL) the solution was extracted three times with water (70 mL each). The organic layer was separated and dried over $Na_2SO_4$. The crude product was then purified by column chromatography (silica gel, 63–100 μm, dichloromethane/ethyl acetate 40:1). The separation of the main isomer **3a** was achieved by HPLC using a silica gel column (*n*-hexane/ethanol 9:1) and **3a** was isolated as a colorless powder (20 mg, 0.01 mmol, 15 %).[11]

**Enantiomer separation of the [1]rotaxane 3a**: Column: Chiralcel OD (25 × 0.46 cm i.d.); eluent: *n*-hexane/ethanol 9:1; flow rate: 1.0 mL min$^{-1}$; sample: 10 mL (5 mg mL$^{-1}$, dichloromethane/methanol 8:1).

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