Chiral [1]Rotaxanes: X-Ray Structures and Chiroptical Properties

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New chiral [1]rotaxanes with aromatic bridges were prepared in yields up to 72% starting from a [2]rotaxane with sulfonamide groups in wheel and axle. The X-ray structures of the parent [2]rotaxane **1** and of the three [1]rotaxanes **3e**,**g**,**h** were solved which show networks of H-bonds between wheel and axle. The separation of the racemic mixtures of four of the [1]rotaxanes, *i.e.*, of **3a**,**b**,**d**,**e**, was possible with HPLC on *Chiralcel OD*. The aromatic chromophores in the bridges lead to a considerable enhancement of the intensities of the molar CD as compared to the analogues with aliphatic bridges. In one case (**3d**), the *Cotton* effects are as strong as those usually found in helicenes.

1. Introduction. – The design of mechanically interlocked molecules such as rotaxanes, catenanes, and knots present a range of novel structural and chiroptical properties and nonclassical types of chiralities [1]. Cycloenantiomerism of such molecules was foreseen theoretically by *Frisch* and *Wassermann* in 1961 [2], and *Schill* described in 1971 the stereochemistry of rotaxanes as being closely related to that of catenanes (for chiral rotaxanes, see [3]). The first topologically chiral catenane [4] and molecular knot [5], however, were not synthesized before the late 1980s. Our group reported in 1996 the first enantiomer-separated, cycloenantiomeric [2]rotaxane **1** [6].

Cycloenantiomerism of rotaxanes occurs when both its components, the wheel and the axle, contain a sequence information in their molecular scaffolds [7]. One enantiomer has a clockwise orientation of the wheel with respect to the axle, whereas the other enantiomer is arranged anticlockwise. The covalent connection of the wheel and the axle of such a chiral rotaxane with suitable bridges leads to cycloenantiomeric [1]rotaxanes[1]) as shown in *Fig. 1*. We recently described the first synthesis of

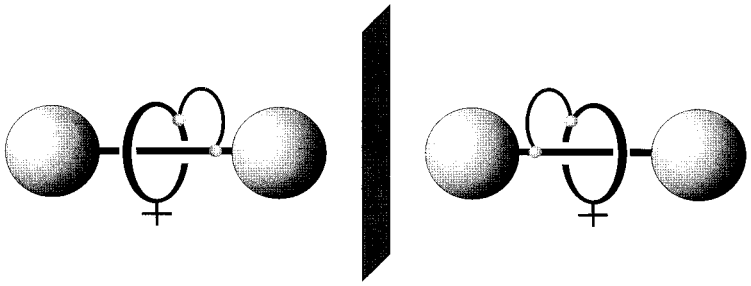

Fig. 1. *Object and mirror image of the cycloenantiomeric [1]rotaxanes* **3**

[1]) In a [1]rotaxane, the wheel and the axle of a [2]rotaxane are connected covalently.

[1]rotaxanes such as **3g** and **3h** and the dependence of the chiroptical properties on the length of their aliphatic bridges [7].

Here we set out to investigate the influences of the incorporation of aromatic groups as chromophores into the bridges on the CD spectra. Furthermore, crystal structures of [1]rotaxanes were obtained for the first time as well as of the parent [2]rotaxane **1**.

2. Results. – 2.1. *Synthesis.* [1]Rotaxanes **3a**–**f** were prepared by chemoselectively bridging the racemic mixture of [2]rotaxane **1** between the sulfonamide groups in both its axle and its wheel with the bis(bromomethyl)arenes **2a**–**f** in the presence of potassium carbonate in DMF at room temperature under dilution conditions (*Scheme*). Yields turned out to be remarkably high (50–72%) in most cases. With the short 2,3-disubstituted quinoxaline **2f** and the rather rigid 2,6-disubstituted naphthalene **2c**, the yields were somewhat lower, while in general the chain length did not seem to have a significant effect (see *Table 1*). By-products were identified as the unbridged mono- and disubstituted [2]rotaxanes[2]). These results show that [2]rotaxane **1** is flexible enough, especially with respect to the translational mobility of the axle, to adjust to the spatial needs of a multitude of bridging units to allow the covalent linkage of wheel and axle.

Scheme. *Synthesis of the Chiral [1]Rotaxanes* **3a**–**h**

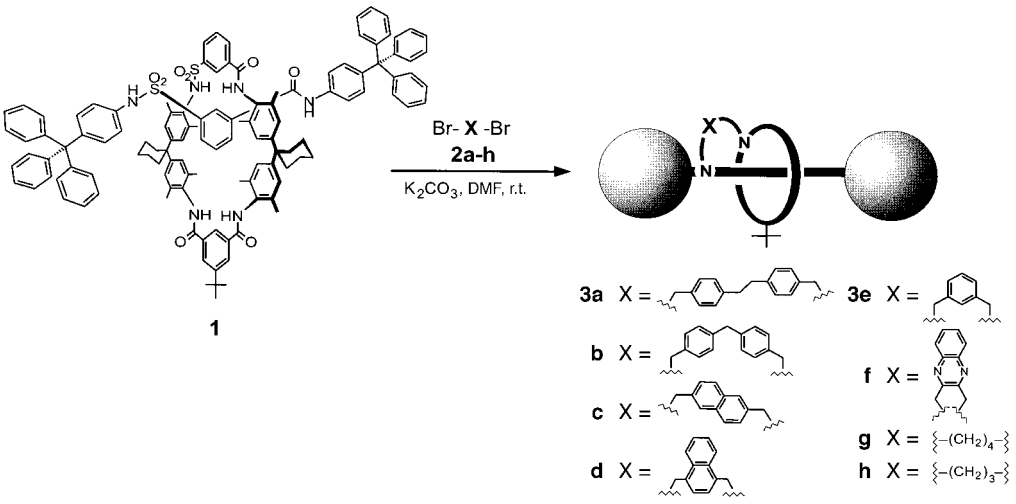

Table 1. *Yields of the [1]Rotaxanes* **3a**–**f**

[1]Rotaxane	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**
Bridge length[a])	12	11	8	6	5	4
Yield [%]	60	68	24	50	72	33

[a]) Number of atoms in the shortest possible chain between bridgehead N-atoms.

[2]) The mono- and disubstituted [2]rotaxanes that were formed as by-products of the intramolecular substitution reaction were analyzed by FAB or MALDI-TOF mass spectrometry but not fully characterized.

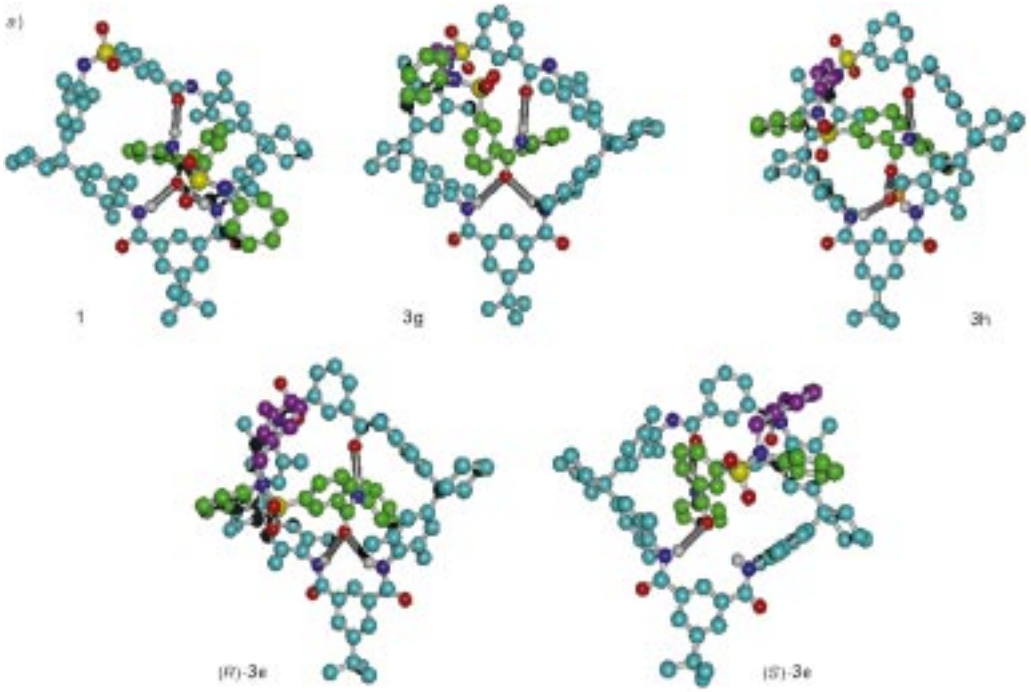

Fig. 2. *Two views of the crystal structures of the (*R*)-enantiomers of [2]rotaxane* **1** *and the [1]rotaxanes* **3g** *and* **3h**, *and the pair of enantiomers of* **3e**, *the conformations of which are not the mirror images in the crystal* (perspectives in all cases are such that the sulfonamide group of the axle is above the wheel and the wheel is positioned with the sulfonamide group at '11 o'clock' in *a*) with the exception of (*S*)-**3e** ('1 o'clock')): a) *View from above, the trityl stoppers are not shown*, *and* b) *view from the side, the diphenylcyclohexane groups of the wheels are not shown*. C-Atoms of the wheels in cyan, C-atoms of the axles in green, C-atoms of the bridges in violet, C-atom of MeOH in the structure of **3h** in orange, O-atoms in red, N-atoms in blue, S-atoms in yellow, H-atoms involved in H-bonds in grey (others not shown), H-bonds represented as dark grey cylinders.

2.2. *Crystal Structures.* For the first time, X-ray crystal structures of [1]rotaxanes were obtained, *i.e.*, of **3e**, **3g**, and **3h**, and also of the cycloenantiomeric [2]rotaxane **1** from which they were derived (*Fig. 2*). Unlike in the three other cases, different conformations were found for the two enantiomers of **3e** in the racemic crystals. Those two structures differ mostly in the orientation of the 1,3-phenylenebis(methylene) bridge with respect to the wheel ('*endo*' for (*R*)-**3e** and '*exo*' for (*S*)-**3e**). In all five structures, the carbonyl O-atom of the sulfobenzoyl group of the wheel is pointing toward the center of the macrocyle (*Fig. 2,a*). This '*cisoid*' conformation enables the formation of a H-bond with the amide proton of the axle. In the [2]rotaxane **1**, the carbonyl O-atom of the axle is H-bonded in a bifurcated manner with the two amide H-atoms of the isophthalamide moiety. This pattern is reminiscent of that of [2]catenanes and [2]rotaxanes of the same type [8]. The '*cisoid*' structure of the sulfobenzoyl group is also found in the axles causing a curved shape. An exception is **3g**, where it is *transoid* and rather linear.

In the [1]rotaxanes, the two sulfonamide groups are pulled together by the bridges, which leads to a different position of the axles relative to the wheels as compared to the

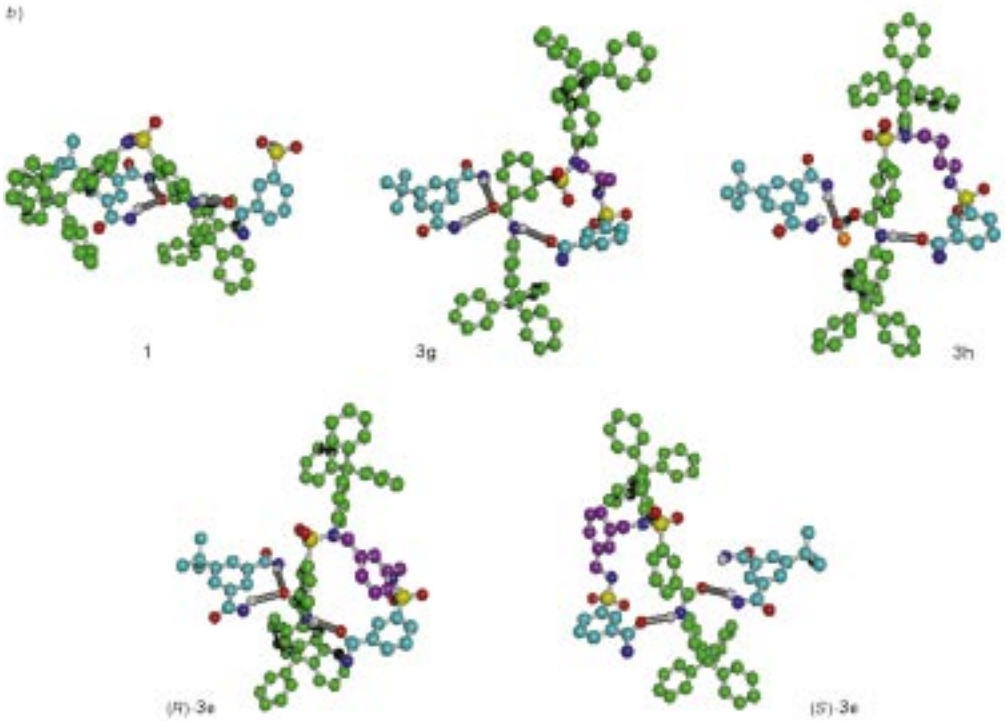

Fig. 2 (cont.)

[2]rotaxane **1**. The bifurcated H-bonds of **3g** and (*R*)-**3e** are longer, *i.e.*, weaker than those of **1**. In the structure of (*S*)-**3e**, one of each is entirely missing.

For **3h**, the pattern of the H-bonds in the crystal differs from that of the other molecules: a methanol OH group is inserted between one of the isophthalamide H-atoms of the wheel and the carbonyl O-atom of the axle under formation of two short H-bonds. Here, also, the wheel is nearly planar. In the other structures, the H-bonds induce a distortion of the wheel. This is especially pronounced for the [2]rotaxane **1**, which, on the other hand, has the three shortest wheel-to-axle H-bonds. This pattern of three intercomponent H-bonds furthermore supports the selectivity of binding for secondary amides in solution found for macrocyclic lactams like the wheel used here [9]. The lengths and bond angles of the intramolecular H-bonds are listed in *Table 2*.

2.3. *Enantiomer Resolution and Chiroptical Properties.* In contrast to the already characterized [1]rotaxanes such as **3g** and **3h** with aliphatic bridges [7], the new [1]rotaxanes **3a**–**f** contain rigid aromatic units in the bridges that, in addition to their contribution as stronger chromophores, lead to a reduced translational mobility of their axles. These structural differences opened up the question if any changes in the enantiomer-resolution constants or of the chiroptical properties come along with the variation of the nature of the bridge. Especially the circular dichrograms of the enantiomers of **3c**, **3d**, and **3f** with naphthalene and quinoxaline groups incorporated in their bridges were of special interest because of the resulting low-energy $\pi\pi^*$-transfers upon UV absorption.

Table 2. *Lengths* (*d*) *and Angles* (*a*) *of the Intramolecular H-Bonds Found in the Crystal Structures of* **1**, *(*R*)- and (*S*)-***3e***, ***3g***, *and* ***3h***. The values for strong H-bonds are printed bold. Italic values are not in accordance with H-bonds. NH_l and NF_r refer to the left and right isophthalamide amide H-atoms, respectively, in *Fig. 2,a*. W stands for wheel and A for axle

	W-NH_l···A–CO		W-NH_r···A–CO		W-CO···A–NH			
	d [Å]	*a* [°]	*d* [Å]	*a* [°]	*d* [Å]	*a* [°]		
1	**2.09**	**160**	**2.13**	**154**	**1.95**	**158**		
(*R*)-**3e**	2.35	158	2.41	148	**2.02**	**157**		
(*S*)-**3e**	2.34	151	*2.84*	*144*	**2.09**	**152**		
3g	2.35	154	2.31	161	2.17	142		
	W-NH_l···Me–O		W-NH_r···A–CO				Me–OH···A–CO	
	d [Å]	*a* [°]	*d* [Å]	*a* [°]			*d* [Å]	*a* [°]
3h	**1.99**	**164**	*2.43*	*141*	**1.96**	**155**	**1.92**	**156**

The baseline separation of the racemic mixtures of **3b** and **3e** into their cycloenantiomers was possible by HPLC on *Chiralcel OD* (hexane/EtOH 90:10) [10]. The enantiomer separation of **3a** and **3d** was more difficult and had to be repeated several times. However, no enantiomer resolution of **3c** and **3f** was obtained, neither on *Chiralcel OD* nor on *Chiralpak AD* [10b]. The separation factors α of **3a**,**b**,**e** increase with decreasing length of the bridges and were found to range between 1.45 and 2.30 (*Table 3*). In all separations, the (–)-enantiomer was eluted first.

The *Cotton* effects obtained for each pair of enantiomers are mirror images over the entire spectra in all cases (*Fig. 3*). The molar CDs of the [1]rotaxanes **3b**, **3d**, and **3e** reach three extrema in the aromatic region. Additionally, in the CD spectrum of **3d**, a shoulder at both the first and at the second extremum appears (*Table 3*).

The comparison of the intensity of the molar CDs of **3b**, **3d**, and **3e** with that of any aliphatically bridged [1]rotaxane described before [7], *e.g.*, **3g** and **3h**, shows that chromophore bridges increase the intensity of the molar CD by at least a factor of 2. This is probably caused by the chromophoric character of the bridges and the reduced flexibility of the new rotaxanes. The circular dichrogram of the naphthalenediyl-bridged [1]rotaxane **3d** showed remarkably high molar CDs, up to 550 M^{-1} cm^{-1}. *Cotton* effects of this high intensity are usually only found in helicenes with their large

Table 3. *Separation Factors* α *in Hexane/EtOH 90:10, and Location and Intensity of the Extrema of the Molar CDs*

	Bridge length	α	Extrema: λ_{max} [nm] (intensity) [$M^{-1}cm^{-1}$]		
			1st	2nd	3rd
1	–	1.48[a])	–	203 (114)	235 (34)
3a	12	1.45	–	–	–
3b	11	1.74	183.0 (112)	198.9 (183)	245.1 (48)
3d	6	1.32	188.1 (550)	212.6 (400)	238.7 (75)
			192.6 (421)	222.8 (350)	–
3e	5	1.98	192.0 (146)	210.9 (138)	242.8 (19)
3g	4	2.30	187.3 (66)	211.1 (75)	245.5 (14)
3h	3	1.79	186.4 (48)	238.0 (90)	251.1 (13)

[a]) *Chiralpak AD* (hexane/i-PrOH 82:18) [6].

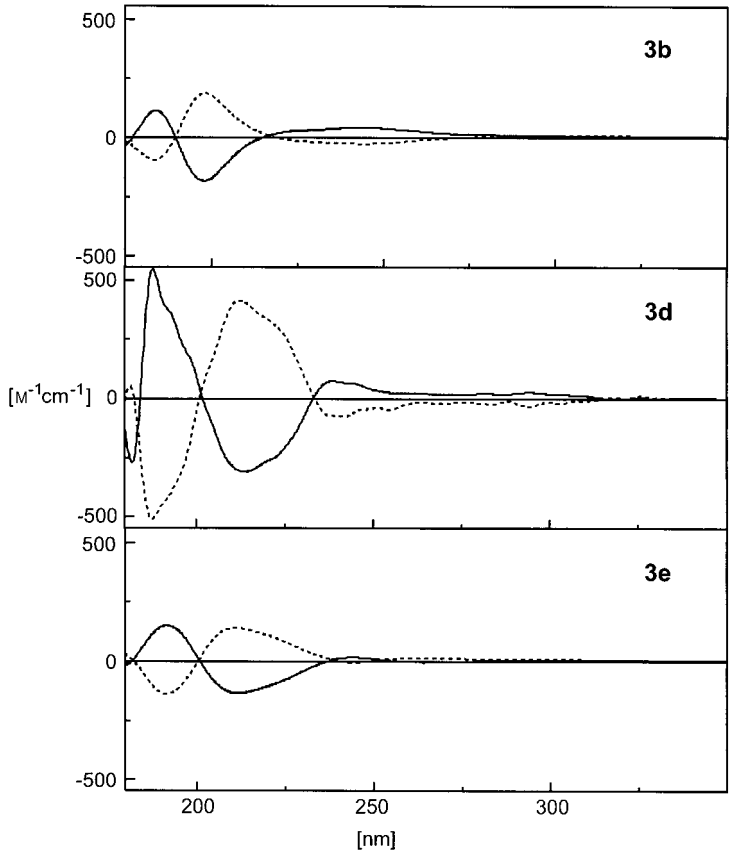

Fig. 3. *Circular dichrograms of* **3b**, **3d**, *and* **3e** *in 1,1,1,3,3,3-hexafluoropropan-2-ol*

delocalized π-systems [11]. Possibly, the nature of the bridge induces a certain helicity into the structure of the rotaxane.

3. Conclusion. – The pure enantiomers of the new cycloenantiomeric [1]rotaxanes presented here exhibited in some cases *Cotton* effects in the order of magnitude known for helicenes. These results contribute to the understanding of cycloenantiomerism, the chirality of which is determined by segment sequence information. The X-ray analyses of the [1]rotaxanes obtained for the first time and that of the parent [2]rotaxane showed the influence of the nature of the bridge on the length and pattern of the H-bonds.

The non-classical chirality of mechanically interlocked molecules is one of the fields of current interest in supramolecular chemistry. Especially with regard to the construction of molecular devices, cycloenantiomers might in the future allow opposite directional motions of molecular motors. The translational and rotational processes of the wheel on the axle might be tuned by incorporating the appropriate bridges.

Experimental Part

General. All solvents were distilled prior to use, and all other chemicals were of the best commercial quality available and were used as received (2,3-bis(bromomethyl)quinoxaline (**2f**) from *Aldrich*), *Chiracel OD* = cellulose tris[(3,5-dimethylphenyl)carbamate]. The [2]rotaxane **1** [6a], the [1]rotaxanes **3g** and **3h** [7], 1,1′-(ethane-1,2-diyl)bis[4-(bromomethyl)benzene] (**2a**) [12], 1,1′-methylenebis[4-(bromomethyl)benzene] (**2b**) [12], 2,7-bis(bromomethyl)naphthalene (**2c**) and 1,4-bis(bromomethyl)naphthalene **2d** [13], and 1,3-bis(bromomethyl)benzene (**2e**) [14] were prepared as reported previously. CD Spectra: *JASCO-J-720* spectrometer, *Labor- und Datentechnik GmbH*, Germany. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AM-400-MHz* or *DRX-500-MHz* instrument, *Analytische Messtechnik GmbH*, Karlsruhe, Germany; δ in ppm with solvent peak as reference, J in Hz; abbrevations used for the assignments: anil = aniline of axle, bib = bibenzyl, qux = quinoxaline, cyh = cyclohexanediyl, dma = 2,6-dimethylaniline, dpm = diphenylmethane, grp = signal group, iso = isophthaloyl, sb = 3-sulfobenzoyl, *t*bi = 5-*t*bu-isophthaloyl, trt = trityl, xyl = *m*-xylylene (= 1,3-phenylenebis(methylene)). FAB-MS: *Concept-1 H* instrument, *Kratos Analytical Ltd.*, Manchester; matrix: 3-nitrobenzyl alcohol. MALDI-TOF-MS: *MALDI-TofSpecE* instrument, *Micromass*, Manchester, UK; matrix: 9-nitroanthracene or 2,5-dihydroxybenzoic acid. Elemental analysis: analytical facilities of the Kekulé-Institut für Organische Chemie und Biochemie of the University of Bonn.

[1]Rotaxanes **3a**–**f**: *General Procedure.* [2]Rotaxane **1** (100 mg, 0.05 mmol) and dibromide **2a**–**f** (0.05 mmol) are dissolved in dry DMF (50 ml) each. At r.t., both solns. are simultaneously added within 2 h to a stirred suspension of K_2CO_3 (25 mg, 0.18 mmol) in DMF (100 ml). Stirring is continued for another 3 d. After the addition of $CHCl_3$ (100 ml), the soln. is extracted with H_2O (3 × 70 ml). The org. layer is dried (Na_2SO_4) and evaporated. The crude product is then purified by column chromatography (SiO_2, 63–100 μm).

General Conditions for the Enantiomer Separation of the [1]Rotaxanes **3a**, **3b**, **3d**, *and* **3e**. Column: *Chiralcel OD* (25 × 0.46 cm i.d.), elution with hexane/EtOH 90:10, flow rate 0.5 ml/min; samples: 1 ml (5 mg/ml, CH_2Cl_2/MeOH 8:1).

*[1]⟨N′,7′-[(Ethane-1,2-diyl)bis(4,1-phenylenemethylene)]⟩{N-[4-(triphenylmethyl)phenyl]-3-{[[4-(triphenylmethyl)phenyl]amino}sulfonyl}benzamide}-{29′-(*tert*-butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyldispiro[cyclohexane-1,2′-[8]thia[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.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]-14′-26′-32′-trione 8′,8′-Dioxide} Rotaxane*[3]) *(=29′-(*tert*-Butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyl-7′-{[4-{2-[4-{[[4-(triphenylmethyl)phenyl]ethyl}phenyl]methyl}phenyl]{[3-{[[4-(triphenylmethyl)phenyl]amino}carbonyl]phenyl}sulfonyl}amino}methyl]phenyl}ethyl]phenyl}methyl]dispiro[cyclohexane-1,2′-[8]thia[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.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]-14′,26′,32′-trione 8′,8′-Dioxide Inner Rotaxane*; **3a**): 61 mg (60%). Colorless powder. R_f 0.65 (CH_2Cl_2/AcOEt 25:1). M.p. 203°. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.48 (*s*, Me); 1.39 (*s*, Me_3C); 1.60 (*s*, 2 Me); 1.67 (br., 8 H, cyh); 1.82 (*s*, 2 Me); 1.91 (*s*, 2 Me); 2.25 (*s*, 8 H, cyh, bib-CH_2); 2.41 (*s*, Me); 2.80 (br., 8 H, cyh); 4.03 (*d*, ^2J = 15.1, 1 H, CH_2N); 4.21 (*d*, ^2J = 13.6, 1 H, CH_2N); 4.50 (*d*, ^2J = 15.1, 1 H, CH_2N); 4.90 (*d*, ^2J = 13.6, 1 H, CH_2N); 6.34–6.61 (grp, 15 H, dma, bib, sb); 6.89–7.31 (grp, 42 H, anil, NH, sb, trt); 7.41 (*d*, ^3J = 7.8, 1 H, sb); 7.04 (*dd*, ^3J = 7.8, ^3J = 7.8, 1 H, sb); 7.69 (*s*, 2 H, dma); 7.84 (*d*, ^3J = 7.8, 1 H, sb); 7.70 (*s*, 1 H, NH); 8.11 (*s*, 1 H, sb); 8.12 (*s*, 1 H, NH); 8.26 (*s*, 1 H, NH); 8.38 (*s*, 1 H, *t*bi); 8.53 (*s*, 1 H, *t*bi); 8.88 (*s*, 1 H, *t*bi). ^{13}C-NMR: (100.6 MHz, $CDCl_3$): 18.3, 18.7, 19.0, 19.6 (Me); 22.7, 22.9, 26.3, 34.8, 35.2, 35.9, 36.1 (CH_2); 31.3 (Me); 35.3 (quat. C); 38.0 (CH_2); 44.9, 45.3 (quat. C); 53.4, 54.7 (CH_2N); 64.7, 64.8 (quat. C); 122.8, 122.3, 125.6, 125.9, 126.1, 126.2, 127.2, 127.5, 127.6, 127.7, 128.4, 128.5, 128.7, 128.8, 128.9, 129.1, 129.6, 130.0, 130.3, 131.0, 131.1, 131.5, 131.7, 131.3, 131.7 (CH); 132.3, 133.6, 133.8, 133.9, 134.0, 134.9, 135.1, 136.6, 137.0, 138.5, 138.8, 139.6, 140.3, 143.5, 144.6, 146.3, 146.6, 146.8, 148.2, 152.4, 153.4 (quat. C); 164.7, 164.8, 164.9, 167.9 (CO). FAB-MS: 2040.9 (M^+).

*[1]⟨N′,7′-[Methylenebis(4,1-phenylenemethylene)]⟩{N-[4-(triphenylmethyl)phenyl]-3-{[[4-(triphenylmethyl)-phenyl]amino}sulfonyl}benzamide}-{29′-(*tert*-butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyldispiro[cyclohexane-1,2′-[8]thia[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.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]-14′,26′,32′-trione 8′,8′-Dioxide} Rotaxane (=29′-(*tert*-Butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyl-7′-{[4-{[4-{[[4-(triphenylmethyl)phenyl]{[3-{[[4-(triphenylmethyl)phenyl]amino}carbonyl]phenyl}sulfonyl]amino}methyl]phenyl}methyl]phenyl}methyl]dispiro[cyclohexane-1,2′-[8]thia[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,*

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[3]) The nomenclature of [1]rotaxanes has not yet been defined. Here we set the bridge into angular brackets before the conventional name of the parent [2]rotaxane, *i.e.*, [1]⟨bridge⟩{axle}-{wheel} rotaxane. The first locant given is the bridgehead atom on the axle (*N′*), the second that on the wheel (7′); see also [7].

18,21,23,27,29,31(39),34,36,37,40,42,45]octadecaene-20′,1″-cyclohexane]-14′,26′,32′-trione 8′,8′-Dioxide Inner Rotaxane; **3b**): 69 mg (68%). Colorless powder. R_f 0.78 (CH_2Cl_2/AcOEt 25:1). M.p. 193°. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.59 (*s*, Me); 1.40 (*s*, Me_3C); 1.48 (br., 8 H, cyh); 1.56 (*s*, 2 Me); 1.57 (*s*, 2 Me); 1.62 (*s*, 2 Me); 1.86 (*s*, 4 H, cyh); 2.35 (br., 8 H, cyh); 2.66 (*s*, Me); 3.72 (*s*, 2 H, dpm-CH_2); 4.23 (*d*, ^2J = 13.4, 1 H, CH_2N); 4.52 (*d*, ^2J = 14.6, 1 H, CH_2N); 4.71 (*d*, ^2J = 13.4, 1 H, CH_2N); 4.74 (*d*, ^2J = 14.6, 1 H, CH_2N); 5.71 (*s*, 1 H, dma); 6.23 (*d*, ^3J = 7.8, 2 H, dpm); 6.32 (*d*, ^3J = 7.7, 1 H, sb); 6.46 (*d*, ^3J = 8.0, 2 H, dpm); 6.48 (*d*, ^3J = 8.0, 2 H, dpm); 6.60 (*d*, ^3J = 7.8, 2 H, dpm); 6.78 (*s*, 2 H, dma); 6.85 (*d*, ^3J = 8.5, 2 H, anil); 6.95 (*d*, ^3J = 8.5, 2 H, anil); 7.04 (*dd*, ^3J = 7.7, ^3J = 7.7, 1 H, sb); 7.08–7.28 (grp, 41 H, anil, dma, sb, trt); 7.31 (*s*, 1 H, sb); 7.52 (*s*, 1 H, NH); 7.52 (*d*, ^3J = 7.7, 1 H, sb); 7.64 (*d*, ^3J = 7.7, 1 H, sb); 7.91 (*s*, 1 H, NH); 7.99 (*d*, ^3J = 7.7, 1 H, sb); 8.20 (*s*, 1 H, NH); 8.26 (*s*, 1 H, NH); 8.32 (*s*, 1 H, *t*bi); 8.53 (*s*, 1 H, *t*bi); 8.88 (*s*, 1 H, *t*bi). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 18.1, 18.4, 19.1, 20.0 (Me); 22.6, 22.7, 26.7, 26.9, 29.1, 29.2 (CH_2); 31.0 (Me); 32.6, 33.9 (quat. C); 35.0 (quat. C); 26.1, 26.2, 27.8, 27.9, 44.7, 45.2, 45.8, 46.6, 49.8, 49.9 (CH_2); 64.2, 64.5 (quat. C); 120.6, 120.8, 120.9, 122.5, 122.8, 123.2, 125.3, 125.6, 125.8, 126.0, 126.1, 126.2, 127.4, 127.5, 127.6, 128.0, 128.2, 128.6, 128.9, 130.7, 130.9, 131.0, 131.1, 131.3, 131.7 (CH); 132.4, 133.8, 134.1, 135.1, 135.4, 136.4, 139.1, 139.6, 141.3, 145.7, 146.1, 146.4, 152.4, 153.4 (quat. C); 165.0, 165.1, 165.4, 165.8 (CO). FAB-MS: 2026.7 (M^+). Anal. calc. for $C_{135}H_{128}N_6O_8S_2 \cdot CH_2Cl_2$: C 77.36, H 6.21, N 3.98, S 3.04; found: C 77.30, H 6.34, N 3.94, S 3.26.

[1]⟨N′,7′-[(Naphthalene-2,6-diyl)bis(methylene)]⟩{N-[4-(triphenylmethyl)phenyl]-3-{[[4-(triphenylmethyl)-phenyl]amino}sulfonyl}benzamide}-[29′-(tert-*butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyldispiro[cyclohexane-1,2′-[8]thia[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.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]-14′,26′,32′-trione 8′,8′-Dioxide} Rotaxane* (=*29′-*(tert-*Butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyl-7′-{[6-{[[4-(triphenylmethyl)phenyl]{[3-{[[4-(triphenyl-methyl)phenyl]amino}carbonyl}phenyl]sulfonyl}amino}methyl]naphthalen-2-yl}methyl}dispiro[cyclohexane-1,2′-[8]thia[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.1^{27,31}]hexatetraconta[3,5,9,11,13(44),16,18,21,23,27,29,31(39),34,36,37,40,41,45]octadecaene-20′,1″-cyclohexane]-14′,26′,32′-trione 8′,8′-Dioxide Inner Rotaxane*; **3c**): 24 mg (24%). Colorless powder. R_f 0.68 (CH_2Cl_2/AcOEt 40:1). M.p. 207°. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.45 (*s*, Me); 1.33 (*s*, 2 Me); 1.42 (*s*, Me_3C); 1.61 (*s*, 2 Me); 1.70 (br., 8 H, cyh); 1.95 (*s*, Me); 2.10 (*s*, Me); 2.12 (*s*, 8 H, cyh); 2.61 (br., 4 H, cyh); 2.64 (*s*, Me); 4.11 (*d*, ^2J = 13.9, 1 H, CH_2N); 4.39 (*d*, ^2J = 13.9, 1 H, CH_2N); 4.76 (*s*, 1 H, dma); 4.91 (*d*, ^2J = 17.8, 1 H, CH_2N); 5.30 (*d*, ^2J = 17.8, 1 H, CH_2N); 5.85 (*d*, ^3J = 7.4, 1 H, sb); 6.22 (*s*, 1 H, sb); 6.30 (br., 1 H, NH); 6.58 (*d*, ^3J = 7.4, 1 H, sb); 6.63–6.78 (grp, 4 H, anil, dma); 6.80–6.92 (grp, 3 H, anil, dma); 6.99–7.40 (grp, 42 H, anil, dma, naph, sb, trt); 7.43 (*dd*, ^3J = 7.4, 7.4, 1 H, sb); 7.72 (*d*, ^3J = 7.4, 1 H, sb); 8.05–8.10 (grp, 4 H, naph); 7.84 (*d*, ^3J = 7.8, 1 H, sb); 8.30 (*s*, 1 H, *t*bi); 8.42 (*s*, 2 H, NH, *t*bi); 8.53 (*s*, 2 H, NH, *t*bi); 8.64 (*s*, 1 H, NH). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 18.0, 18.3, 19.2, 19.5 (Me); 22.9, 23.0, 23.1, 26.3, 26.6, 35.3, 36.5, 37.7 (CH_2); 31.3 (Me); 33.9, 35.3 (quat. C); 53.1, 56.2 (CH_2N); 64.5, 64.7 (quat. C); 120.8, 121.6, 124.0, 125.0, 126.0, 126.6, 127.0, 127.2, 127.5, 127.6, 128.5, 128.8, 129.0, 129.1, 129.2, 129.3, 130.9, 131.0, 131.1, 131.3, 131.4, 131.8 (CH); 132.2, 132.3, 133.6, 134.1, 134.4, 135.3, 135.4, 135.5, 137.4, 139.3, 142.9, 143.4, 144.6, 146.2, 146.3, 146.8, 153.1, 153.4 (quat. C); 162.6, 164.3, 165.1, 165.4 (CO). MALDI-TOF-MS: 1985.5 (M^+).

[1]⟨N′,7′-[(Naphthalene-1,4-diyl)bis(methylene)]⟩{N-[4-(triphenylmethyl)phenyl]-3-{[[4-(triphenylmethyl)-phenyl]amino}sulfonyl}benzamide}-[29′-(tert-*butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyldispiro[cyclohexane-1,2′-[8]thia[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.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]-14′,26′,32′-trione 8′,8′-Dioxide} Rotaxane* (=*29′-*(tert-*Butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyl-7′-{[4-{[[4-(triphenylmethyl)phenyl]{[3-{[4-(triphenyl-methyl)phenyl]amino}carbonyl]phenyl}sulfonyl]amino}methyl]naphthalen-1-yl}methyl}dispiro[cyclohexane-1,2′-[8]thia[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.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]-14′,26′,32′-trione 8′,8′-Dioxide Inner Rotaxane*; **3d**): 49 mg (50%). Colorless powder. R_f 0.58 (CH_2Cl_2/AcOEt 25:1). M.p. 189°. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.49 (*s*, 2 Me); 1.30 (*s*, Me_3C); 1.59 (*s*, 2 Me); 1.60 (br., 8 H, cyh); 1.78 (*s*, 4 H, cyh); 2.01 (*s*, 2 Me); 2.31 (br., 8 H, cyh); 2.68 (*s*, 2 Me); 4.45 (*d*, ^2J = 14.0, 1 H, CH_2N); 4.02 (*s*, 1 H, dma); 4.74 (*d*, ^2J = 14.0, 1 H, CH_2N); 5.12 (*d*, ^2J = 17.7, 1 H, CH_2N); 5.19 (*s*, 1 H, dma); 5.24 (*d*, ^2J = 17.7, 1 H, CH_2N); 5.90 (*d*, ^3J = 7.4, 1 H, sb); 6.27–6.45 (grp, 8 H, anil, naph); 6.69 (*s*, 4 H, dma); 6.88–7.15 (grp, 42 H, anil, dma, sb, trt); 7.46–7.57 (grp, 5 H, naph, sb); 7.72 (*d*, ^3J = 7.4, 1 H, sb); 8.05–8.10 (grp, 4 H, naph); 7.80 (*s*, 1 H, sb); 7.88 (*d*, ^3J = 7.4, 1 H, sb); 8.00 (*d*, ^3J = 7.9, 1 H, sb); 8.18 (*s*, 1 H, *t*bi); 8.22 (*s*, 1 H, *t*bi); 8.28 (*s*, 1 H, *t*bi); 8.29 (*d*, ^3J = 7.9, 1 H, sb); 8.38 (*s*, 1 H, NH); 8.42 (*s*, 1 H, NH); 8.78 (*s*, 1 H, NH). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 18.3, 18.5, 19.6, 19.9 (Me); 22.8, 22.9, 23.0, 26.4, 26.6, 34.2, 34.6, 35.9, 37.7 (CH_2); 31.3 (Me); 35.3, 44.9, 47.3 (quat. C); 53.1, 56.2 (CH_2N); 64.7 (quat. C); 121.4, 121.8, 122.7, 123.2, 123.6, 125.3, 126.0, 126.2, 126.5, 127.5, 127.6, 127.7, 128.2, 128.4, 128.7, 129.2, 129.3, 129.4, 129.7, 130.0, 131.0, 131.1, 131.5, 131.8, 132.2 (CH); 132.1, 132.2, 132.3, 132.4, 133.6, 133.7, 134.0, 135.3, 135.5, 136.1, 137.7, 138.1, 138.8, 144.7, 146.2, 146.5, 147.0, 152.9, 153.4 (quat. C); 164.5, 164.9, 165.3, 166.4 (CO). MALDI-TOF-MS:

1984.0 (M^+). Anal. calc. for $C_{132}H_{124}N_6O_8S_2 \cdot C_4H_8O_2 \cdot CH_2Cl_2$: C 76.19, H 6.23, N 3.89; found: C 76.34, H 6.23, N 3.85.

*[1]⟨N′,7′-[1,3-Phenylenebis(methylene)]⟩{N-[4-(triphenylmethyl)phenyl]-3-{{[4-(triphenylmethyl)phenyl]-amino}sulfonyl}benzamide}-{29′-(*tert*-butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyldispiro[cyclohexane-1,2′-[8]thia-[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.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]-14′,26′,32′-trione 8′,8′-Dioxide} Rotaxane* (=*29′-(*tert*-Butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyl-7′-{{3-{{[4-(triphenylmethyl)phenyl]{{3-{{[4-(triphenylmethyl)phenyl]amino}carbonyl}phenyl}sulfonyl}amino}methyl}phenyl}methyl}dispiro[cyclohexane-1,2′-[8]thia[7,15,25,33]tetraaza-heptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.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]-14′,26′,32′-trione 8′,8′-Dioxide Inner Rotaxane*; **3e**): 70 mg (72%). Colorless powder. R_f 0.65 (CH_2Cl_2/AcOEt 40:1). M.p. 189°. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.42 (*s*, Me_3C); 1.53 (br., 17 H, cyh, Me); 1.67 (*s*, 2 Me); 1.69 (*s*, 4 H, cyh); 1.91 (*s*, Me); 2.22 (*s*, Me); 2.32 (br., 8 H, cyh); 2.61 (*s*, Me); 4.03 (*d*, ^2J = 14.6, 1 H, CH_2N); 4.14 (*d*, ^2J = 14.6, 1 H, CH_2N); 4.50 (*d*, ^2J = 14.6, 1 H, CH_2N); 4.78 (*d*, ^2J = 14.6, 1 H, CH_2N); 5.19 (*s*, 1 H, dma); 6.21 (*s*, 1 H, dma); 6.27 (*s*, 1 H, xyl); 6.51 (*d*, ^3J = 7.5, 1 H, xyl); 6.76 (*s*, 4 H, dma); 6.80 (*s*, 2 H, dma); 6.82 (*s*, 2 H, dma); 6.92 (*s*, 1 H, sb); 6.96 (*s*, 1 H, sb); 7.00–7.59 (grp, 41 H, NH, anil, sb, trt); 7.66 (*s*, 1 H, sb); 7.83 (br., 1 H, sb); 8.01 (br., 1 H, sb); 8.08 (*s*, 1 H, NH); 8.29 (br., 1 H, sb); 8.32 (*s*, 1 H, NH); 8.43 (*s*, 1 H, *t*bi); 8.56 (*s*, 1 H, *t*bi); 8.88 (*s*, 1 H, *t*bi); 9.42 (*s*, 1 H, NH). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 18.5, 18.8, 18.9, 19.8 (Me); 22.9, 23.1, 26.4, 26.6, 34.4, 35.3, 35.8 (CH_2); 31.3 (Me); 38.0 (quat. C); 45.0, 47.6 (quat. C); 53.4, 54.7 (CH_2N); 64.7, 64.8 (quat. C); 121.4, 124.0, 125.6, 126.1, 126.2, 126.7, 127.4, 127.5, 127.6, 128.3, 128.4, 128.5, 128.7, 129.0, 129.2, 129.4, 130.4, 131.0, 131.2, 131.7, 131.8, 132.0, 138.1 (CH); 132.4, 133.7, 133.9, 134.8, 134.9, 135.1, 135.5, 135.6, 136.0, 142.2, 142.6, 145.2, 146.2, 146.6, 147.2, 152.7, 153.4 (quat. C); 164.7, 165.0, 165.3, 165.9 (CO). MALDI-TOF-MS: 1936.0 (M^+).

*[1]⟨N′,7′-[(Quinoxaline-2,3-diyl)bis(methylene)]⟩{N-[4-(triphenylmethyl)phenyl]-3-{{[(4-(triphenylmethyl)-phenyl]amino}sulfonyl}benzamide}-{29′-(*tert*-butyl)-[5′,17′,23′,35′,38′,40′,43′,45′-octamethyldispiro[cyclohexane-*

Table 4. *Crystallographic Data of Compounds* **1**, **3g**, **3h**, *and* **3e**

	1	**3g**	**3h**	**3e**
Empirical formula	$C_{57}H_{44}N_2O_3S \cdot C_{63}H_{72}N_4O_5S \cdot 1.5\ CH_2Cl_2 \cdot 1\ CH_3OH$	$C_{123}H_{120}N_6O_8S_2 \cdot 3\ CH_2Cl_2 \cdot 3\ CH_3OH \cdot 1.5\ H_2O$	$C_{124}H_{122}N_6O_8S_2 \cdot 4\ CH_3OH \cdot 5\ H_2O$	$C_{128}H_{122}N_6O_8S_2 \cdot 5\ CH_2Cl_2 \cdot 2.5\ CH_3OH \cdot 2.5\ H_2O$
Formula weight	1993.74	2252.30	2106.64	2486.21
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c* (no. 15)	*P*2(1)/*c* (no. 14)	*C*2/*c* (no. 15)	*P*2(1)/*c* (no. 14)
Unit-cell dimensions *a* [Å]	34.6914(12)	21.5996(3)	64.008(3)	38.3352(10)
b [Å]	30.4423(10)	23.8227(3)	17.9135(6)	25.2610(9)
c [Å]	24.6104(7)	25.4520(2)	22.4082(8)	27.9598(14)
β [°]	116.559(2)	114.196(1)	94.856(3)	107.476(2)
Volume [Å^3], *Z*	23248.0(13), 8	11946.0(2), 4	25601.2(16), 8	25826.1(17), 8
Calculated density [g·cm^{-3}]	1.139	1.252	1.093	1.279
Absorption coeff. [mm^{-1}]	0.172	0.242	0.103	0.311
F(000)	8440	4764	9008	10464
Crystal size [mm]	0.15 × 0.15 × 0.15	0.70 × 0.50 × 0.15	0.25 × 0.15 × 0.10	0.30 × 0.25 × 0.10
$2\theta_{max}$ [°]	25.0	25.0	22.5	22.5
Limiting indices	$-41 \le h \le 33$ $-33 \le k \le 36$ $-29 \le l \le 29$	$-25 \le h \le 25$ $-28 \le k \le 28$ $-26 \le l \le 30$	$-68 \le h \le 68$ $-12 \le k \le 19$ $-21 \le l \le 24$	$-40 \le h \le 41$ $-21 \le k \le 27$ $-30 \le l \le 27$
Reflections collected/unique	76009/20239	144528/21004	66556/16714	73140/33580
R_{int}	0.0953	0.0513	0.0705	0.0625
Data/restraints/parameters	20239/1370/1264	21004/250/1370	16714/1356/1366	33580/3357/2884
Goodness-of-fit on F^2	0.968	1.062	1.043	0.994
Final R_1, wR_2 ($I > 2\sigma(I)$)	0.0994, 0.2621	0.0872, 0.2385	0.1021, 0.2805	0.1452, 0.3916
Final R_1, wR_2 (all data)	0.1951, 0.3074	0.1135, 0.2586	0.1453, 0.3194	0.1945, 0.4354
Max. diffr. peak/hole [e·Å^{-3}]	1.121, −1.446	1.760, −1.409	1.671, −0.580	1.904, −1.274

1,2′-[8]thia[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.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]-14′,26′,32′-trione 8′,8′-Dioxide} Rotaxane (= *29′-(*tert*-Butyl)-5′,17′,23′,35′,38′,40′,43′,45′-octamethyl-7′-{{3-{{[4-(triphenylmethyl)phenyl]{{3-{{[4-(triphenylmethyl)-phenyl]amino}carbonyl}phenyl}sulfonyl}amino}methyl}quinoxalin-2-yl}methyl}dispiro[cyclohexane-1,2′-[8]thia-[7,15,25,33]tetraazaheptacyclo[32.2.2.2^{3,6}.2^{16,19}.2^{21,24}.1^{9,13}.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]-14′,26′,32′-trione 8′,8′-Dioxide Inner Rotaxane*; **3f**): 33 mg (33%). Colorless powder. R_f 0.65 (CH_2Cl_2/AcOEt 40:1). M.p. 197°. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.04 (*s*, 2 Me); 1.43 (*s*, Me_3C); 1.50 (br., 8 H, cyh); 1.62 (*s*, 2 Me); 1.79 (*s*, 2 Me); 1.82 (*s*, 2 Me); 2.30 (*s*, 4 H, cyh); 2.41 (br., 8 H, cyh); 4.01 (*d*, ^2J = 18.6, 1 H, CH_2N); 4.16 (*d*, ^2J = 18.6, 1 H, CH_2N); 4.38 (*s*, 1 H, dma); 4.42 (*d*, ^2J = 12.3, 1 H, CH_2N); 4.61 (*d*, ^2J = 12.3, 1 H, CH_2N); 5.87 (*d*, ^3J = 7.9, 1 H, sb); 6.11 (*s*, 1 H, dma); 6.69 (*s*, 1 H, NH); 6.84 (*s*, 1 H, dma); 7.01 (*d*, ^3J = 8.6, 2 H, anil); 7.03–7.20 (grp, 42 H, anil, dma, sb, trt); 7.32 (*s*, 1 H, dma); 7.48 (*d*, ^3J = 7.9, 1 H, sb); 7.53 (*d*, ^3J = 7.9, 1 H, sb); 7.58–7.68 (grp, 5 H, chx, sb); 7.83 (*s*, 1 H, NH); 8.10–8.19 (grp, 2 H, chx); 8.30 (*s*, 1 H, NH); 8.38 (*s*, 1 H, *t*bi); 8.49 (*s*, 1 H, *t*bi); 8.67 (*s*, 1 H, *t*bi); 9.12 (*s*, 1 H, NH). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 18.2, 18.7, 20.0, 21.0 (Me); 22.9, 23.0, 26.4, 26.6, 34.2, 35.3, 37.3 (CH_2); 31.3 (Me); 35.6, 44.9, 47.5 (quat. C); 50.1, 52.1 (CH_2N); 64.6, 64.7 (quat. C); 121.2, 124.4, 125.5, 126.0, 126.1, 126.6, 127.5, 127.8, 128.2, 128.3, 128.6, 128.7, 129.0, 129.1, 129.3, 129.4, 129.6, 130.4, 131.0, 131.1, 131.7, 132.0, 132.8 (CH); 132.2, 133.4, 135.5, 135.8, 138.0, 139.6, 140.1, 140.2, 141.6, 145.1, 145.9, 146.2, 146.4, 147.3, 148.2, 152.9, 153.2, 152.9 (quat. C); 164.5, 164.8, 165.2, 165.4 (CO). MALDI-TOF-MS: 1988.4 ($[M+2H]^+$). Anal. calc. for $C_{130}H_{122}N_8O_8S_2$: C 78.52, H 6.18, N 5.63, S 3.22; found: C 78.34, H 6.43, N 5.36, S 3.40.

X-Ray Crystal Structures. Crystals were obtained by slow evaporation of CH_2Cl_2/MeOH solns. For crystallographic data of compounds **1**, **3e**, **3g**, and **3h**, see *Table 4*. Intensities were measured with a *Nonius Kappa CCD* diffractometer (MoK_λ, λ 0.71073 Å), T 123(2) K. The structures were solved by direct methods; refinement (full-matrix least-squares on F^2): non-H-atoms were refined anisotropically, H-atoms with a 'riding' model. For computer programs used, see [15]. The crystallographic data have been deposited at the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-138317 (**1**), CCDC-138318 (**3g**), CCDC-138319 (**3h**), and CCDC-138320 (**3e**). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223336033; e-mail: deposit@ccdc.cam.ac.uk).

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