Topologically Chiral Covalent Assemblies of Molecular Knots with Linear, Branched, and Cyclic Architectures

Oleg Lukin,[a] Takateru Kubota,[b] Yoshio Okamoto,[b] Astrid Kaufmann,[a] and Fritz Vögtle*[a]

Dedicated to Professor J. Bargon on the occasion of his 65th birthday

Abstract: Selectively functionalized molecular knots (*knotanes*) of the amide-type have been used as building blocks in syntheses of higher covalent assemblies composed of up to four knotane units. Preparation of linear and branched tetraknotanes consisted of the consecutive selective removal of allyl groups followed by linking of the intermediate hydroxyknotanes with biphenyl-4,4′-disulfonyl chloride. Macrocyclic knotane oligomers involving two, three, and four knotane moieties were obtained by high-dilution cyclization of dihydroxyknotane and biphenyl-4,4′-disulfonyl chloride. Due to their relation with cyclophanes, the latter class of oligomeric knotanes was termed "*knotanophanes*". Chiral resolution analysis of new oligoknotanes has been attempted on chemically bonded Chiralpak AD stationary phases, however met severe difficulties due to their complex isomeric compositions, and in most cases a significant overlap of the isomer fractions was observed. In spite of the limits of presently available chiral stationary phases that allowed only partial resolution of the synthesized topologies, oligoknotanes have been shown to be of high fundamental interest due to their unprecedented chirality. The chirality descriptions of topologically chiral unsymmetrical dumbbell **4**, and the linear tetraknotane **5** are analogous to the Fischer projections of erythrose/threose and hexaric acid, respectively, while the isomeric composition of the branched tetraknotane **8** is completely unique. Moreover, the linear and branched tetraknotanes are constitutional isomers. Chirality of knotanophanes represents, in turn, analogies to known cyclic forms of peptides or sugars with multiple stereogenic centers.

Keywords: chiral resolution · molecular knots · nanostructures · supramolecular chemistry · topological chirality

Introduction

Extending the complexity of intertwined molecular assemblies, which involve molecular catenanes, rotaxanes, and knots[1] pursues many fundamental and practical goals, such as the search for novel templation techniques[2] and unprecedented examples of topological isomerism and chirality,[1,3,4] utilization of large-amplitude molecular movements of the intertwined molecular parts in molecular machinery,[5] and the elucidation of biochemical functions of diverse nontrivial tangles in the structure of DNA and proteins.[6] Another important aspect in this connection is the construction of new macromolecules from interlocked monomers in the quest for new functional polymeric materials.[7]

Our long-standing interests in the chemistry and topological chirality of diverse intertwined species including catenanes,[8] rotaxanes,[8,9] and molecular knots (knotanes)[4a,b,10] on the one hand, and the chemistry of dendritic molecules[11] on the other have emerged to formulate a more general concept of iterative construction of unprecedented perfect macromolecular linear, branched, and cyclic topologies from intertwined and interlocked monomers.

Apart from polydisperse polymeric catenanes and rotaxanes,[7] previous reports on nanosized oligomeric topologies, which possess well-defined structures encompass the preparation of linear polycatenanes,[12] and linear and dendritic polyrotaxanes.[13] The drawbacks of these species are both

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  DOI: 10.1002/chem.200400110

extremely low yields and relatively low molecular weight. Our recent reports on the syntheses of topologically chiral molecular dumbbells[4a] and rotaxanes with knotted stoppers (*knotaxanes*)[4b] involve covalently linked knotanes of type **1** which have been shown to be promising and readily obtainable intertwined building blocks for diverse nanoassemblies. In this paper we demonstrate the advantages of covalent chemistry of knotanes, which are used here as building blocks in the first synthesis of linear, branched, and even macrocyclic 'knotted' oligomers.

Results and Discussion

Synthesis: The overall strategy towards linear knotane oligomers is illustrated in Scheme 1. It consists of the iterative selective removal of allyl groups followed by linking with biphenyl-4,4′-disulfonyl chloride. Thus, two moieties of monohydroxyknotane **1** available in up to gram quantities by selective deprotection of tris(allyloxy)knotane[4a] can be linked by reaction with biphenyl-4,4′-disulfonyl chloride **2** to yield dumbbell **3**. Consequently, the selective removal of one allyl group from **3** gives rise to monohydroxy-dumbbell **4**, sulfonylation of which with **2** yields 55% of linear tetraknotane **5**.

This synthetic strategy can be altered for the preparation of branched oligoknotanes, which necessitate a multifunctional core and monofunctional branching units (dendrons). Reaction of monohydroxyknotane **1** with excess biphenyl-4,4′-disulfonyl chloride **2** readily gives sulfonylated knotane **6**, which contains one reactive sulfonyl chloride unit. The latter is in turn converted by reaction with trihydroxyknotane **7** to yield the branched tetraknotane **8**. The structures of the unsymmetrical dumbbell **4** and both tetraknotanes **5** and **8** were proved by means of MALDI-TOF (matrix-assisted laser desorption ionization time-of-fight) mass spectrometry and ^{1}H NMR spectroscopy. With the aid of the latter method we have recently demonstrated that in [D_6]DMSO solution at room temperature knotanes adopt a rigid unsymmetrical conformation similar to that found in the solid state, while faster conformational exchange leading to the average D_3-symmetric structure was detected in a number of other solvents. Amide proton signals of 2,6-pyridinedicarbamide units have been shown to be especially sensitive with respect to the 4-substituent in the pyridine ring. ^{1}H NMR spectra of **4**, **5**, and **8** recorded in DMSO solutions are in line with their substitution patterns, showing intensities in amide proton signals of 2,6-pyridinedicarbamide characteristic of four allyloxy-, two arylsulfonyloxy-, and one hydroxyl-substituted pyridine subunits.[10c] Additionaly, the ^{1}H NMR spectrum of **4** reveals signals at 11.38, 11.48, and 11.57 ppm pertaining to the hydroxyl group that is in line with the simultaneous existence of hydroxyknotane subunit conformers that have different kinetic stabilities on the ^{1}H NMR timescale. Applying different ionization conditions in the MALDI-TOF measurements experiment we could observe either preferential presence of molecular ion peaks of compounds **4**, **5**, and **8** or their characteristic fragmentation patterns similar to those formerly detected for dumbbell **3**,[4a] and knotaxanes[4b] brought about by the destruction of sulfonic acid esters.

Preparation of macrocyclic knotane oligomers implies the availability of a selectively bifunctionalized knotane such as dihydroxyknotane **9**, the preparation of which we have recently described.[10c] As illustrated in Scheme 2, the reaction of **9** with an equivalent amount of biphenyl-4,4′-disulfonyl dichloride in high-dilution conditions results in a mixture of the oligomeric macrocycles composed of two (**10**), three (**11**), and four (**12**) knotane moieties in an overall yield of 65%. We suggest the term "*knotanophanes*" for the latter class of oligomeric knotanes according to the rules of cyclophane nomenclature.[14] A MALDI-TOF spectrum of the isolated mixture of knotanophanes **10**–**12** depicted in Figure 1 reveals that no appreciable amounts of higher

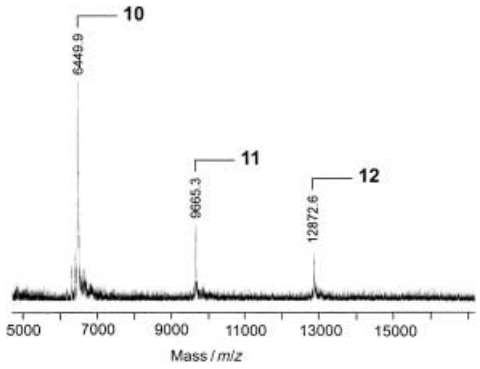
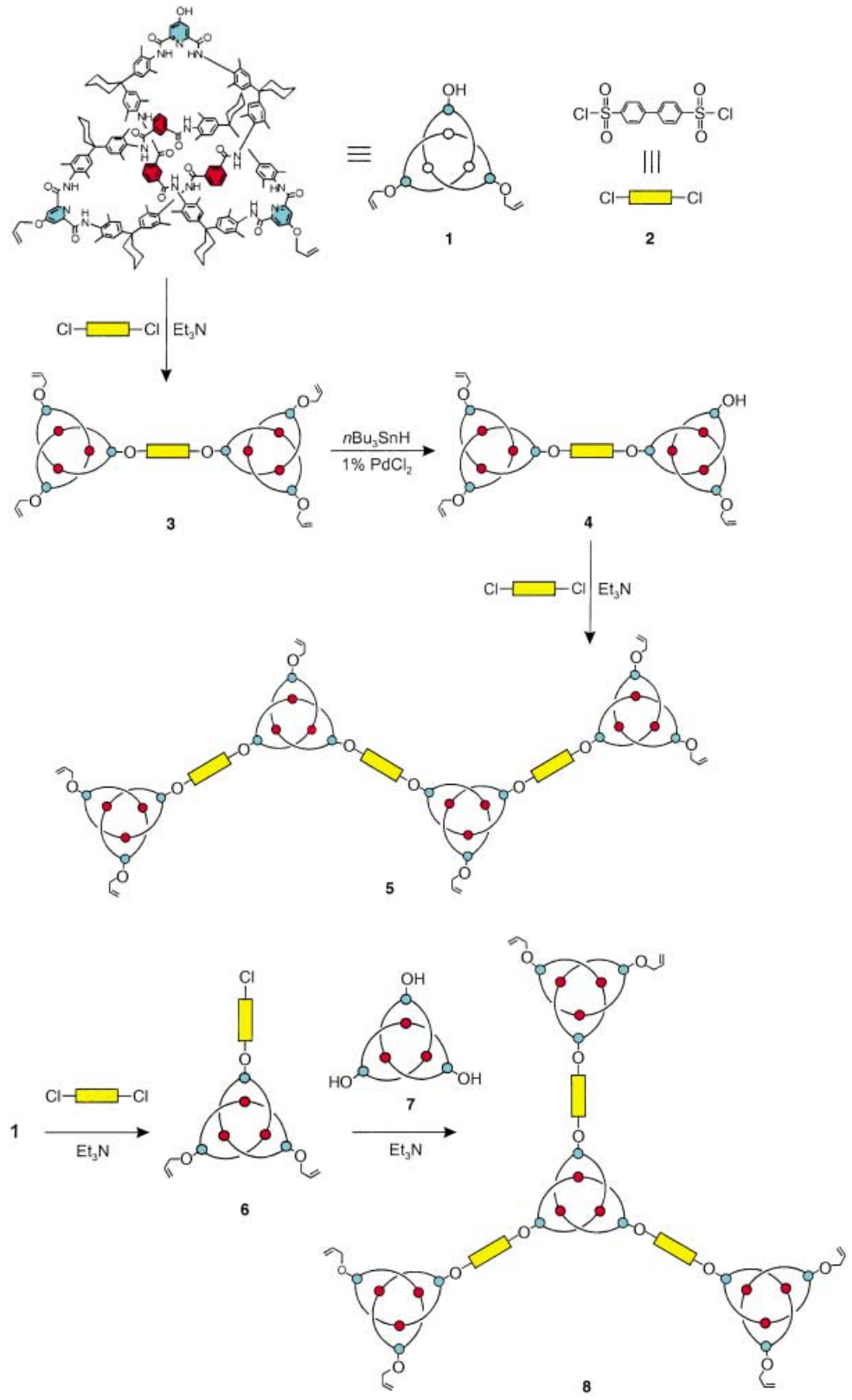


Figure 1. Fragment of a MALDI-TOF mass spectrum of the isolated mixture **10**–**12**.

oligomers were formed in the macrocyclization reaction. The preparative isolation of the individual components **10**–**12** from their mixture was afforded by using a usual silica gel HPLC (high performance liquid chromatography) column. The HPLC analysis also allowed us to estimate the relative amount of each oligomer in the initial mixture; this gave the ratio of 30:35:35 for **10**, **11**, and **12**, respectively.

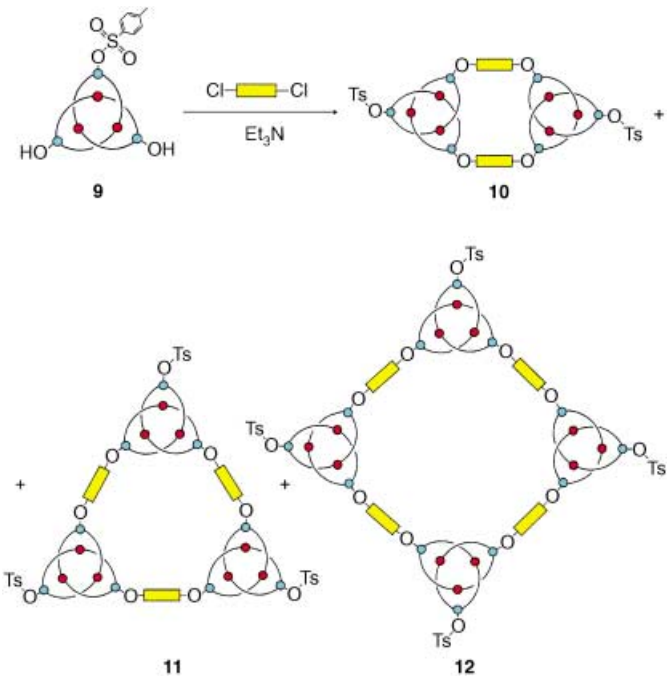
Interestingly, ^{1}H NMR spectra of knotanophanes **10**–**12** are identical as follows from a comparison of the ^{1}H NMR spectrum of the initially isolated mixture of **10**–**12** with that of a pure sample of **10** obtained after HPLC separation. Furthermore, the ^{1}H NMR spectral pattern of knotanophanes is characteristic of knotanes that bear three equivalent *para*-substituents at the outer 2,6-pyridinedicarbamide units. The latter observation can be rationalized by very close steric and electronic effects of *p*toluenesulfonyloxy- and biphenyl-4,4′-disulfonyloxy groups in influencing ^{1}H NMR chemical shifts.

Topological chirality: Scheme 3 shows the expected isomeric composition of the novel oligomeric knotanes involving **4**, **5**, **8**, and **10**–**12**. Recently we mentioned[4a,b] that chirality designation of topologically chiral knotane assemblies composed of two knotanes, such as dumbbell **3**[4a] and knotaxanes[4b] were analogous to the Fischer projections of tartaric and trihydroxyglutaric acids, respectively. Therefore, further modification or growth of the knotane chain should expand the



Scheme 1. Synthesis of linear and branched knotane oligomers.

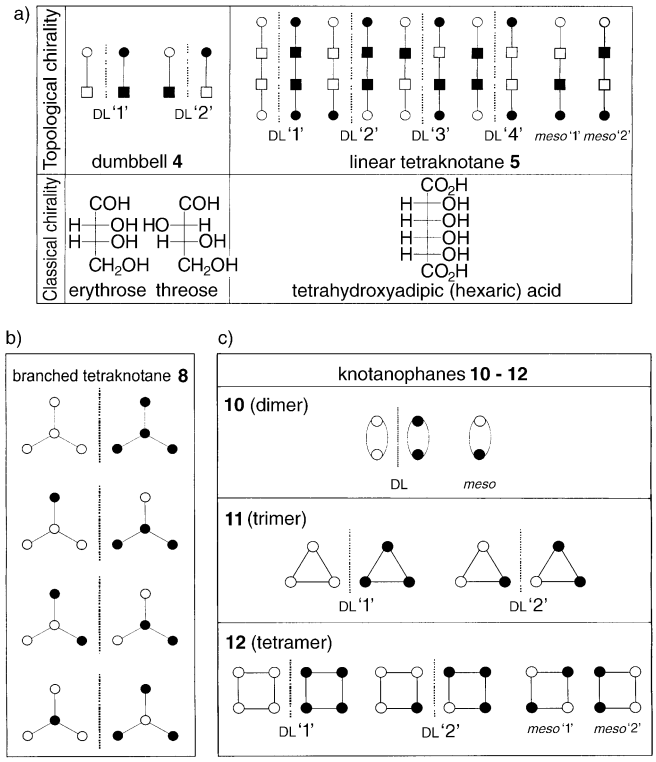
isomeric possibilities similarly to the open chain sugars. Scheme 3 illustrates the relationship between the chirality designation of unsymmetrical dumbbell **4**, the linear tetraknotane **5**, and the Fischer projections of erythrose/threose, which bear two classical stereocenters and hexaric acid containing four stereocenters, respectively.[15] The isomeric composition of the branched tetraknotane **8** depicted in Scheme 3 is entirely unique, since no centrochiral analogues



Scheme 2. Synthesis of "knotanophanes".

same as dumbbell **3** previously reported by us.[4a] This implies the existence of one D,L-pair and one *meso*-form. The trimer **11** composed of three knotanes in the cycle should consist of two D,L-pairs, whilst the largest isolated member of the knotanophane family, tetramer **12**, should exhibit an even more complex isomeric composition as shown in Scheme 3. Despite the similarity of the arrangements of the stereogenic units in **11** and **12** to those in chiral trisubstituted cyclopropanes and tetrasubstituted cyclobutanes, respectively,[15d] the chirality scheme of the former knotanophanes is essentially different; this is due to the inability to draw additional symmetry planes cutting the topological stereogenic centers. The chirality scheme of **11** and **12** can only be compared to the known chiral cyclopeptides[15c,d,16] composed of three and four equal amino acid moieties, respectively. The isomerism of **12** is also analogous to that of cyclic forms of pentoses,[17] differing however due to the higher symmetry of **12**.

The chiral resolution of the novel oligomeric knotanes **4**, **5**, **8**, and **10**–**12** was analysed by using noncommercial "Chiralpak AD" column material,[18] which contained tris(3,5-dimethylphenylcarbamate) amylose covalently linked to a silica gel support. The resolution chromatograms are summarized in Figure 2. All samples of the oligomeric knotanes



Scheme 3. Isomerism of oligomeric knotanes: a) analogy of topological descriptors in unsymmetrical dumbbell **4** and linear tetraknotane **5** with the Fischer projections of known open-chain sugars; b) expected isomeric composition of branched tetraknotane **8**, and c) expected isomeric composition of knotanophanes **10**–**12**. ● or ■ = (+) knots, ○ or □ = (−) knots.

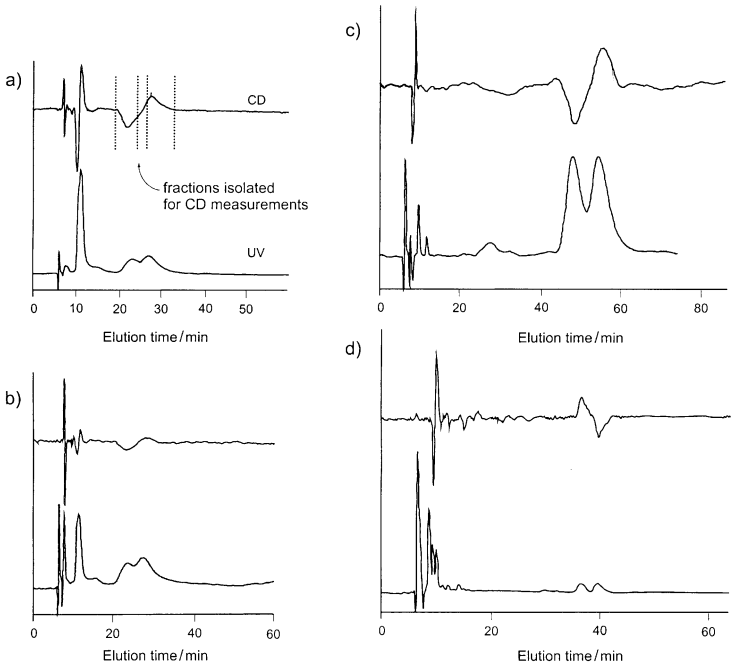


Figure 2. a) Partial chiral resolution of **4** (eluent: hexane/chloroform = 30:70); b) resolution of **5** (eluent: hexane/chloroform/isopropanol = 60:40:3); c) resolution of **8** (eluent: hexane/chloroform/isopropanol = 60:40:3); d) resolution of **10** (eluent: hexane/chloroform = 70:30). In all of the above cases: Chiralpak AD material was used; CD-detection at 254 nm.

with such constitution can exist. The isomerism of knotanophanes **10**–**12** depends on the number of knotanes that form the cycle (Scheme 3). Thus, the isomerism of dimer **10** is the

were shown to be quite pure. As follows from the chromatogram of unsymmetrical dumbbell **4**, instead of its four expected isomers constituting two D,L-pairs, only two optically active fractions could be resolved. After the separation, all fractions were additionally checked by MALDI-TOF mass

spectrometry. The circular dichrograms of the separated fractions of **4** are shown in Figure 3. Experimental identification of all isomers of both **5** and **8** was difficult, as seen from their chromatograms in Figure 2. Thus, two instead of eight isomers of **5**, and only one instead of four enantiomer-

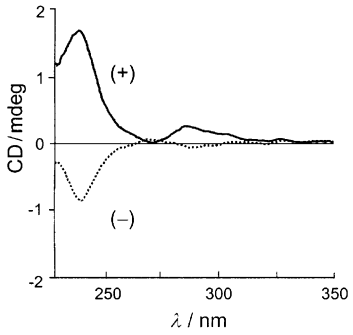


Figure 3. Circular dichrograms of optically active fractions of **4** (d = 0.1 mm, THF).

ic pairs of **8** could be detected. Chiral resolution of knotanophanes was only successful in the case of their simplest member, dimer **10**. However, solely enantiomeric peaks could be seen on the chromatogram of **10**, whereas its *meso*-form could not be detected. The difficulties in detecting the *meso*-forms were due to their overlap with fractions of enantiomers; this has already been discussed by us in the course of chiral resolutions of knotaxanes.[4b] We have obviously reached the limit of complexity for the separation on chiral stationary phases available today. Therefore, the chiral resolution of the oligomeric knotanes should challenge the development of new chiral stationary phases.

Conclusion

The successful synthesis of oligomeric knotanes possessing linear, branched, and cyclic architectures highlights the advance in synthetic chemistry for such macromolecular topological compounds. For the first time, we have four covalently linked topological stereogenic units arranged in three different ways. The topological chirality of the tetraknotanes combined with their sizes and masses, which exceed 10 nm and 12000 Da, respectively defines a new class of artificial macromolecules beyond polymers and dendritic species, yet perfect in shape and dispersity. Despite the limits of modern chiral separation science, which do not allow for complete isolation of all isomers of synthesized topologies, oligomeric knotanes have been shown to be of high fundamental value in developing new knowledge about chirality. The chirality designations of topologically chiral nonsymmetrical dumbbell **4**, and the linear tetraknotane **5** are analogous to the Fischer projections of erythrose/threose and hexaric acid, respectively,[15] while the isomeric composition of the branched tetraknotane is completely unique, since no centrochiral analogues with such constitution can exist. Chirality of knotanophanes represents, in turn, analogies to known cyclic forms of peptides or sugars with chiral centers. Additionally, knotanophanes are topologically chiral cycles of several nanometers in size (nanocycles),[19] which are of the pyridinophane type and related to 'phanophanes',[14] in which the knotane that is a phane itself acts as the core and the biphenyl-4,4′-disulfonate unit as the bridge. Our vision is to use knotanophanes and linear oligomeric knotanes as a chiral wheel and axle components, respectively, in future giant rotaxanes with functions close to the naturally occurring enzyme complexes.[5,20] The fascinating action of these natural complex molecular topologies can be the source of future inspiration to assemble nanosized macrocycles in which the knots are not just covalently implemented, but involved as intertwined parts of a macrocycle.[21]

Experimental Section

General remarks: We have previously described the preparation of hydroxyknotanes **1** and **7**, and molecular dumbbell **3**.[4a,10c] Reactions were monitored by thin-layer chromatography by using DC-Alufolien silica gel $60F_{254}$ (Merck). Melting points were determined in a Reichert Thermovar microscope and were uncorrected. ^{1}H NMR spectra were recorded by using 400 and 500 MHz Bruker instruments; the solvent signals were used for internal calibration. For a detailed discussion on the NMR spectra of knotanes see ref. [10c]. Mass spectra were recorded by means of a MALDI-TofSpec-E from MICROMASS, GB (MALDI) and Voyager-DE from PE Biosystems (MALDI).

HPLC separations: The separation of knotanophanes **10**–**12** was performed at 25 °C on a line consisting of an analytical pump model 590 (Waters), a Rheodyne injector 7125, and a LCD 2084 UV-Detector (Techlab). The separation was achieved on a preparative Kromasil column (material: silica gel, particle size 5 micron). Chiral resolutions of all samples were carried out on a noncommercial chemically bonded Chiralpak AD column.[18]

Monohydroxy-dumbbell 4: Bu_3SnH (4 mg, 0.014 mmol) was injected (by using a syringe) into a vigorously stirred solution of tetra(allyloxy)dumbbell **3** (100 mg, 0.017 mmol) and $PdCl_2(PPh_3)_2$ (0.5 mg) in wet dichloromethane (50 mL), and the reaction mixture was allowed to stir for four hours at room temperature. The solvent was evaporated under reduced pressure, and the crude product was purified by chromatography on silica gel with $CH_2Cl_2/CH_3OH/Et_3N$ (20:1:0.3); this yielded the starting material tetra(allyloxy)dumbbell **3** (35 mg, R_f = 0.95) and the desired monohydroxy-derivative **4** (52 mg, 55%) as a colorless solid. R_f = 0.33; m.p. 273 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = [0.06, 0.86, 0.95] (ArCH$_3$), 1.24, 1.36, 1.48, 1.56, 1.82, 1.99, 2.18, 2.24, 2.28, 2.32, 4.88 (m, 6H; OCH2), 4.99 (m, 2H; ArH), 5.31–5.46 (m, 6H, *CH*$_2$=CH), 5.83 (br, 2H; ArH), 6.06 (m, 3H; *CH*=CH$_2$), [6.41, 6.43, 6.51, 6.63, 6.65, 6.79, 6.90, 6.95, 6.98, 7.16, 7.33, 7.43, 7.50, 7.52, 7.56, 7.59, 7.63, 7.67, 7.69, 7.72, 7.76, 7.77, 7.79, 7.82, 7.87, 7.90, 7.92, 8.02, 8.09, 8.11, 8.19] (ArH), [8.27, 8.58, 9.05, 9.13, 9.38, 9.56, 9.81, 10.17, 10.21, 10.43, 10.46, 10.50, 10.54, 10.59, 10.93, 10.94, 10.99, 11.00, 11.04, 11.06] (NH), 11.38, 11.48, 11.57 ppm (OH); MALDI-TOF: m/z: calcd for $C_{375}H_{396}N_{30}O_{34}S_2$ 5931.2; found: 5932.4 [M^++H], 5954.2 [M+Na$^+$].

Linear tetraknotane 5: Triethylamine (10 mg, 0.1 mmol) and dry dichloromethane (2 mL) were added to a stirred suspension of monohydroxy-dumbbell **4** (45 mg, 0.07 mmol) in dry acetonitrile (8 mL). After the suspension became a homogenous solution, biphenyl-4,4′-disulfonyl chloride (1.5 mg, 0.004 mmol) dissolved in dry acetonitrile (0.5 mL) was infused into it. The reaction mixture was allowed to stir for 30 min at reflux and then at room temperature overnight. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (4:1) resulting in a colorless solid (38 mg) in 82% yield. R_f = 0.73; m.p. 210 °C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = [0.05, 0.86, 0.95] (ArCH$_3$), 1.24, 1.36, 1.47, 1.56, 1.81, 1.99, 2.17, 2.24, 2.28, 2.31, 4.87 (brs, 12H; OCH$_2$), 4.98 (br, 4H; ArH), 5.29–5.45 (m, 12H; *CH*$_2$=CH), 5.83 (br, 4H; ArH), 6.06 (br, 6H; *CH*=CH$_2$), [6.41, 6.49, 6.63, 6.78, 6.89, 6.95, 7.15, 7.33, 7.43, 7.50,

7.55, 7.77, 7.79, 7.82, 7.86, 7.89, 8.02, 8.09, 8.19] (ArH), [8.27, 8.58, 9.06, 9.13, 9.33 (br.), 9.47, 9.56, 9.78, 10.20, 10.48, 10.52, 10.57, 10.99, 11.03, 11.06 ppm] (NH); MALDI-TOF: *m/z*: calcd for $C_{762}H_{798}N_{60}O_{72}S_6$: 12141.6 [$M^+$]; found: 12219.8.

Compound 6: Monohydroxyknotane **1** (100 mg, 0.035 mmol) dissolved in dry dichloromethane (3 mL) containing triethylamine (20 mg, 0.2 mmol) was added to a stirred solution of biphenyl-4,4′-disulfonyl chloride **2** (250 mg, 0.70 mmol) in dry dichloromethane (10 mL). The reaction mixture was stirred for two hours and the solvent was then evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel. First the excess of biphenyl-4,4′-disulfonyl chloride **2** was eluted with CH_2Cl_2/ethyl acetate (50:1), then the product was eluted with the second fraction CH_2Cl_2/ethyl acetate (5:1). Yield 90 mg (81%); m.p. 180°C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = {0.06, 0.86, 0.95, 1.24, 1.36, 1.47, 1.48, 1.57, 1.60, 1.82, 1.99, 2.19, 2.25, 2.28, 2.32} (CH_2 and $ArCH_3$), 4.88 (m, 4H; O*CH*$_2$), 4.99 (t, J = 7 Hz, 1H; ArH), 5.31–5.47 (m, 4H; *CH*$_2$=CH), 5.83 (d, J = 7 Hz, 1H; ArH), 6.07 (m, 2H; *CH*=CH$_2$), {6.41, 6.44, 6.51, 6.63, 6.80, 6.90, 6.95, 6.98, 7.16, 7.35, 7.44, 7.50, 7.52, 7.56, 7.70, 7.72, 7.77, 7.79, 7.82, 7.87, 7.90, 7.93, 7.97, 8.02, 8.04, 8.05, 8.07, 8.09, 8.11, 8.14, 8.19, 8.20} (ArH), {8.27, 8.58, 9.05, 9.13, 9.36, 9.47, 9.57, 9.80, 10.21, 10.49, 10.53, 10.58, 10.99, 11.00, 11.03, 11.06 ppm} (NH); MALDI-TOF: *m/z*: calcd for $C_{195}H_{204}N_{15}O_{19}S_2Cl$: 3161.5; found: 3160.2 [M^+].

Branched tetraknotane 8: Triethylamine (10 mg, 0.1 mmol) and dry dichloromethane (2 mL) were added to a stirred suspension of trihydroxyknotane **7** (20 mg, 0.007 mmol) in dry acetonitrile (8 mL). After the suspension became a homogenous solution, (*p*-biphenylsulfonyl chloride)sulfonyloxy(bis)alyloxy knotane **6** (68 mg, 0.021 mmol) dissolved in dry dichloromethane (2 mL) was added. The reaction mixture was allowed to stir at room temperature overnight. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (4:1); this yielded a colorless solid (42 mg, 48%). R_f = 0.70; m.p. >300°C; ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = [0.05, 0.86, 0.95] ($ArCH_3$), 1.24, 1.36, 1.48, 1.56, 1.82, 1.99, 2.17, 2.19, 2.24, 2.28, 2.32, 4.88 (m, 12H; OCH_2), 4.99 (m, 4H; ArH), 5.31–5.47 (m, 12H; *CH*$_2$=CH), 5.83 (br s, 4H; ArH), 6.06 (m, 6H; *CH*=CH$_2$), [6.42, 6.50, 6.63, 6.79, 6.89, 6.95, 6.98, 7.16, 7.34, 7.43, 7.50, 7.52, 7.56, 7.77, 7.79, 7.82, 7.87, 7.90, 7.92, 7.99, 8.02, 8.05, 8.09, 8.19] (ArH), [8.27, 8.58, 9.06, 9.13, 9.32, 9.36, 9.47, 9.57, 9.78, 10.21, 10.48, 10.52, 10.57, 10.99, 11.00, 11.04, 11.06 ppm] (NH); MALDI-TOF: *m/z*: calcd for $C_{762}H_{798}N_{60}O_{72}S_6$: 12141.6 [$M^+$]; found: 12243.0.

Knotanophanes 10–12: A solution of *p*-toluenesulfonyloxydihydroxy-knotane **9** (60 mg, 0.02 mmol) in absolute dichloromethane (5 mL) containing triethyamine (10 mg, 0.10 mmol), and a solution of biphenyl-4,4′-disulfonychloride **2** (7 mg, 0.02 mmol) in dry acetonitrile (5 mL) were added simultaneously into a stirred flask containing dry acetonitrile (40 mL). After two hours, the addition was complete and the reaction mixture was stirred for three more hours. The solvent was evaporated under reduced pressure, and the products were purified by chromatography on silica gel with CH_2Cl_2/ethyl acetate (4:1), R_f = 0.80, giving a colorless solid. As described in a preceding section, the product represented a mixture of **10–12**, which was later separated by using HPLC. Overall yield of **10–12** (40 mg, 65%); m.p. 213–216°C; ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = [0.02, 0.85, 0.92] ($ArCH_3$), 1.23, 1.35, 1.44, 1.54, 1.81, 1.96, 2.17, 2.21, 2.26, 2.29, 2.42, [4.95, 5.27, 5.81, 6.41, 6.47, 6.62, 6.80, 6.86, 6.94, 7.15, 7.33, 7.43, 7.52, 7.53, 7.77, 7.91–8.17] (ArH), [8.25, 8.60, 9.06, 9.16, 9.34, 9.47, 9.80, 9.18, 10.53, 10.57, 11.04, 11.09 ppm] (NH); MALDI-TOF: *m/z*: found: 6400.9 (calcd for dimer **10**: $C_{392}H_{402}N_{30}O_{42}S_6$: 6398.1 [$M^+$]), found: 9607.3 (calcd for trimer **11**: $C_{588}H_{603}N_{45}O_{63}S_9$: 9597.2 [$M^+$]), found: 12822.6 (calcd for tetramer **12**: $C_{784}H_{804}N_{60}O_{84}S_{12}$: 12796.3 [$M^+$]).

Acknowledgement

Financial assistance by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 624) and the Fonds der Chemische Industrie is gratefully acknowledged. O.L. thanks Alexander von Humboldt Foundation for the fellowship.

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Received: February 4, 2004

Published online: April 26, 2004

