Non-Rusty [2]Catenanes with Huge Rings and Their Polymers

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We describe the design and synthetic realisation of [2]catenanes characterised by having huge rings that can rotate freely and shift laterally within the constraints of concatenation. The synthetic strategy, which is based on using a carbonate group as a covalent template and oxidative dimerization of alkynes to achieve ring formation, is versatile with respect to ring size and the presence of functional groups. The monocyclic constitutional isomer of the catenane is available by a simple exchange of steps in the sequence. EPR spectroscopy revealed that in solution the catenanes adopt all possible co-conformations in equal abundances. The thermotropic liquid crystallinity of the [2]catenanes and their corresponding non-intertwined macrocycles proves intermolecular ordering in the bulk phase. The [2]catenanes were polymerized through ester formation and through acyclic diene metathesis. All of the poly[2]catenanes have rather low degrees of polymerisation ($<P_n> \approx 10$), possibly because cyclisation occurs. For the preparation of [*n*]catenanes having $n > 3$, we propose fusing the rings of [2]catenanes so that the crucial steps of threading and cyclisation need only occur during the synthesis of the smallest catenane.

1. Introduction

Catenanes have been the topic of discussion about 90 years[1] ago and, as the growing number of groups involved in this research area indicates, there is still much interest in them today. The current attraction has developed to a good extent because of the associated, and possibly useful, properties that originate from the unique phenomenon of independent motion − rotation and translation − of a ring that is part of a larger molecule (Figure 1).

At present, one central topic of research is the externally triggered switching of the catenane's rings between two defined co-conformations[2] to allow catenanes to be used as molecular machines.[3−5] Another topic is the relationship between topology and material properties,[6] such as the elasticity, reptation, friction, and impact resistance of polycatenanes. One may expect a contribution from the translational freedom of the rings to the entropy term of the elasticity. The rotation of the rings may be thermally addressable and, as such, may result in a special mode of energy uptake and may provide a unique method for energy

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Adelheid Godt received her training in chemistry at the Ludwig-Maximilians-University in Munich. After her diploma work on propellanes and bicyclobutanes in the group of Professor Dr. G. Szeimies, she joined the Max Planck Institute for Polymer Research in Mainz where she received her PhD for her work on the synthesis of double-stranded polymers in the group of Professors Dr. A. D. Schlüter and Dr. G. Wegner. A fellowship from the DFG allowed her to undertake research on NLO polymers at Cornell University in Ithaca, N. Y., in collaboration with the Kodak Research Laboratories, Rochester, N. Y. She then returned to the MPI in Mainz to continue experiments on NLO polymers, and to start research on catenanes and phenylene ethynylenes. In 2001 she received her habilitation degree from the Free University Berlin, to which she has been associated as a teacher. In 2003 she was appointed visiting professor of chemistry at the International University Bremen and recently joined the University of Bielefeld. Her present research interests are catenanes, macrocycles, oligo(phenylene ethynylene)s, and coupling chemistry.

MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

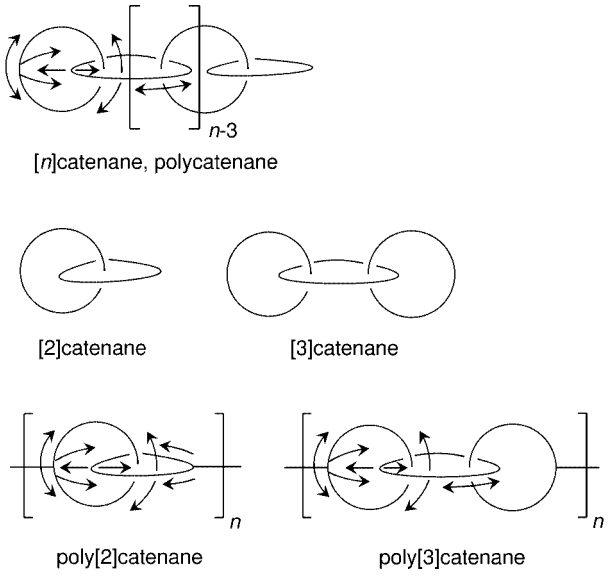


Figure 1. Polycatenanes, representative cut-outs, and poly[*n*]catenanes. The arrows indicate some of the possible rotations and translational displacements

dissipation. Additionally, this rotation may have an effect on the friction between polycatenanes, or between a polycatenane and a surface, and, thus, it may influence the relaxation after mechanical deformation of the material.[7] No doubt, this list of possible effects of the topology on the properties of catenanes can be extended. It is very unsatisfying, however, to have to rely on speculations that are only occasionally supported by theoretical calculations.[8] Experimental investigations are urgently required, which raises the question of the availability of the materials. Despite remarkable successes in the synthesis of [*n*]catenanes with up to seven intertwined rings,[9–11] these materials cannot be considered as readily available for studies of their properties because they have been obtained only in very small amounts (< 50 mg when $n > 3$). These small amounts have been obtained not only because of the small scale at which the experiments have been performed but also because of principal limitations in forming polymers by using reactions such as threading and cyclisation that are not quantitative and are accompanied by side reactions. Consequently, the idea arose to use representative cut-outs of the polycatenane — such as the much more synthetically accessible [2]catenane, which is the smallest representative unit of a polycatenane — as the building blocks for polymers having the catenane unit in the main chain.[12–17] The rings of the resulting poly[2]catenane have similar degrees of freedom as those of a polycatenane with the major difference that the bond that connects the [2]catenanes impedes full rotation of the rings (Figure 1). Full ring rotation, such as that which occurs in polycatenanes, is possible, at least for one of the three rings, when the second smallest cut-out of a polycatenane, a [3]catenane, is used as a building block to give a poly[3]catenane. Thus, poly[2]catenanes and poly[3]catenanes could be useful models to provide insight into the relationship between topology and the material properties of polycatenanes.

The specific designs of the catenanes will definitely influence the properties of their polymers, which makes it highly desirable to undertake comparative studies of poly[*n*]catenanes derived from very different [*n*]catenanes. For example, one can distinguish between catenanes (Figure 2) that have built-in rotation barriers, as represented by the Stoddart-[18] and Hunter–Vögtle–Leigh type[19–21] catenanes **1** and **2**

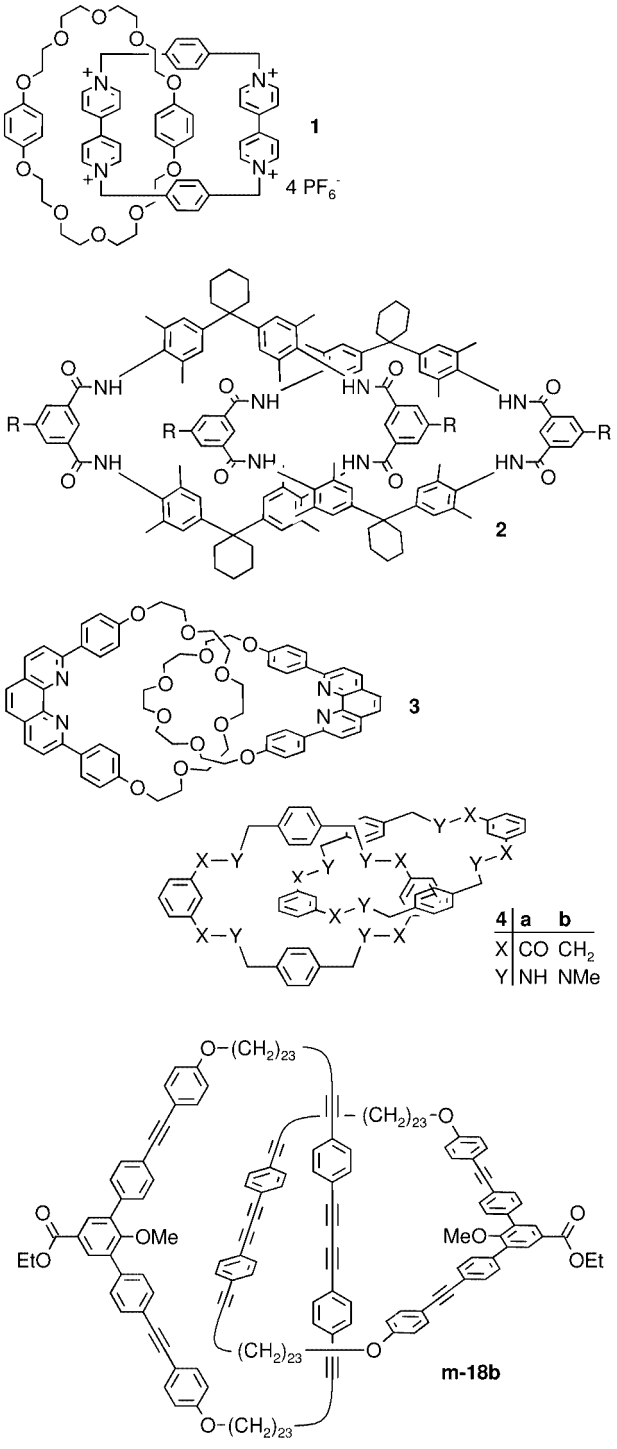


Figure 2. [2]Catenanes prepared by Stoddart (catenane **1**), Hunter (R = H) and Vögtle (R = OMe) (catenane **2**), Sauvage (catenane **3**), Leigh (catenane **4a**; reduced and methylated form: **4b**), and our group (catenane **m-18b**)

("rusty" catenanes), catenanes with freely rotating rings ("non-rusty" catenanes), such as the Sauvage type catenane[22] **3** or the reduced and N-methylated Leigh type catenane **4b**,[23] and catenanes **18**[24] from our group consisting of rings that not only can rotate freely but also have a considerable degree of freedom for lateral displacement. The latter catenanes are the focus of this review. Their design was guided by our interest in systems for which we could most readily determine the contribution that the topology makes towards the properties of the material. Therefore, the main aspects were negligible interactions between the intertwined rings, a substantially modifiable ring size, and a synthesis that is both flexible in regard to its tolerance of functional groups and can be performed on large scale.

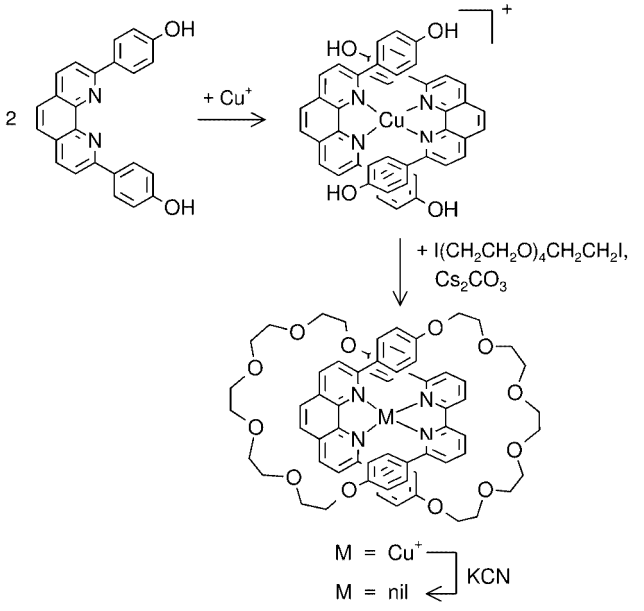
In the following discussion, I outline our rational design for the synthesis of a catenane and its successful realisation, as well as a general limitation of our strategy. Investigations on the mobility of the rings by EPR spectroscopy experiments are presented. I report the preparation of poly[2]catenanes and, finally, suggest a new concept for the synthesis of polycatenanes.

2. Synthesis of Functionalized Catenanes with Rings of Variable Size

2.1 The Synthetic Strategy and Its Realisation

The strategically most simple approach to [2]catenanes relies on the chance that a cyclic molecule can be threaded by another molecule. Therefore, catenanes are expected to form when molecules are cyclised in the presence of a high concentration of cyclic molecules. Around 1960, Wasserman used this method to prepare the first deliberately made [2]catenane from diethyl tetratriacontanedioate and cyclotetratriacontane.[1,25] More recently, Hogen-Esch[26] used this method to prepare a [2]catenane consisting of a polystyrene and a poly(2-vinylpyridine) macrocycle.[26–29] The yields of isolated catenanes have been extremely low in all such experiments.[30] Already Wasserman mentioned in one of his papers that a more efficient strategy would require preorganisation of the two building blocks: the ring and the ring precursor.[1] This concept was realized for the first time by Lüttringhaus and Schill[31] and has displayed its potential clearly in the elegant routes to [2]catenanes developed, or found by chance, by Dietrich-Buchecker and Sauvage,[22,32] Stoddart,[18,33] Hunter,[19] and Vögtle[20,34] and their co-workers who have employed either metal-complex formation[22,32] or a combination of π–π stacking and hydrogen bonding[35,36] as the driving forces for preorganisation. Nowadays, these routes are well established[37] and have been the subject of substantial variations by the groups of Leigh,[5a,38] Sanders and Hamilton,[39] and others.[40,41] Besides these mainstream approaches, routes that rely completely on self-assembly, not only for the preorganisation of the building blocks but also for the ring formation, have been explored by Fujita,[42] Puddephatt,[43] Sauvage,[44] and Beer[45] and their co-workers. A unique route to a [2]catenane, which was reported recently, uses the spontaneous assembly of two once-folded protein molecules into a bisecting U-shaped motif, followed by cyclisation of the two intertwined protein strands through native chemical ligation.[46] Several reviews have been published that are either comprehensive[33,39a,47] or focus[32,34,42b,48] on one of the routes.

Perusing the numerous, different recipes for the preparation of catenanes with respect to flexibility in the ring size and the type of functional groups employed, and keeping in mind our desire for free rotation of the rings, my attention was attracted by the elegant route employed by Dietrich-Buchecker and Sauvage[32,48a] (Scheme 1). This approach uses the complexation of Cu^{I} by phenanthroline to organise the two building blocks — either two ring precursors or one ring and one ring precursor — geometrically in such a way that after the cyclisation step the two rings are intertwined. Finally the copper ions are removed to allow the rings to rotate freely.

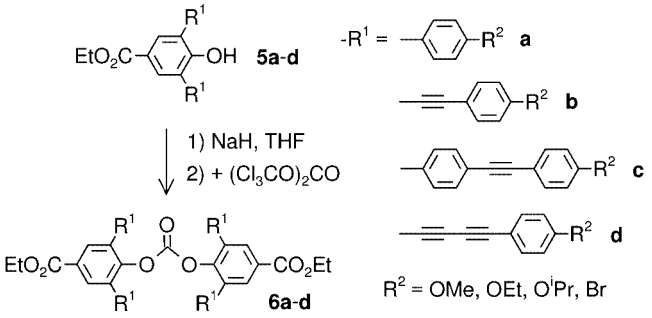


Scheme 1

Inspired by this work, we developed a strategy based on a carbonate linkage between appropriately substituted phenols as the templating unit.[24] Using a covalent bond to arrange the building blocks during a catenane synthesis may appear to be a step backwards in development. There is no disadvantage, however, as long as both the bond formation, i.e., the templating process, and the bond cleavage after both cycles have been formed are clean, quantitative, and easily performed reactions. Moreover, a covalent template may allow larger variabilities in structures and functionalities, considering that subtle changes in structures can influence the efficiency of self-assembly dramatically and, most often, unpredictably.

The assumption that a carbonate linkage between 2,6-disubstituted phenols can act as a template for a catenane synthesis was at first speculative. It was simply based on the consideration of the steric demand of long, stiff substituents

in combination with the W-shaped conformation of the $C_{aryl}-O-CO-O-C_{aryl}$ moiety that has been observed for diarylcarbonates in the crystalline state[49] and had been predicted by calculations to be the preferred conformation in the glassy state of polycarbonates and for isolated molecules.[50] Therefore, our first step was to synthesize the diphenylcarbonates **6a**–**d** with phenyl, tolane, phenylethynyl, and phenylbutadiynyl substituents at both *ortho* positions of the phenolic oxygen atom (Scheme 2) and to determine their structure in the solid state as well as to study their conformational dynamics in solution by NMR spectroscopy.[51]



Scheme 2

Single-crystal X-ray structural analysis revealed that, indeed, all of the carbonates **6a**–**d** display a W-shaped conformation of the $C_{aryl}-O-CO-O-C_{aryl}$ moiety and intersection of the two angular phenolic moieties (Figure 3). Roughly speaking, the carbonates in the crystal have C_2 symmetry, with the C=O bond as the C_2 axis, and occur in two enantiomeric forms. For the carbonates in solution at room temperature, however, NMR spectra indicate that the four substituents are magnetically equivalent. NMR spectroscopic investigations at lower temperatures disclosed this discrepancy to be the result of the rotation about the $O-C_{aryl}$ axis of the two angular moieties around the carbonate group. Whereas the short substituents of carbonate **6a** can pass each other, as sketched in Figure 4 (in which, for reasons of demonstration, a chiral carbonate is depicted),[52] the substituents of the carbonates **6b**–**d** are sufficiently long to inhibit the interconversion of the two enantiomeric forms. Instead, in the case of the latter, the rotations of the two angular moieties around the carbonate group are coupled with the consequence that, in spite of the conformational freedom, these two angular moieties are always intersecting and, thus, are in the arrangement that we sought for use the carbonate unit as a template for catenane synthesis. The carbonate linkage is just one out of a number of conceivable templates. Oxalate may be another because, in the crystalline state, the two angular moieties of oxalate **7** are arranged akin to those of the carbonates **6** (Figure 5).[53]

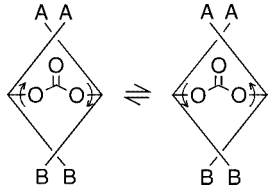


Figure 4. Rotation around the $C_{aryl}-OCO$ bond that results in interconversion of the two enantiomeric carbonates. A chiral carbonate is depicted for the purpose of demonstration. Such rotation is possible for **6a**, but not for **6b**–**d**

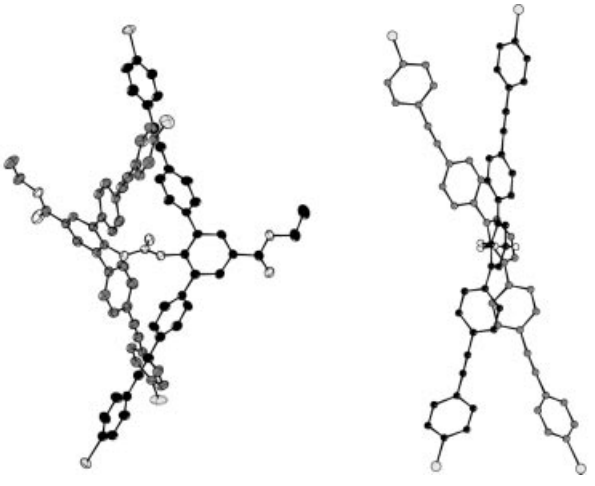


Figure 3. Structure of carbonate **6c** with R^2 = Br in the crystal (free of solvent). *Left*: Ortep plot (50% probability). *Right*: View along the connecting line between the two carbon atoms of the $C_{aryl}O$ group. The ester groups have been omitted for clarity

The synthesis of the model carbonates not only fulfilled the purpose of elucidating their structures but also the need to develop a reliable synthetic route to the carbonates[51] and the underlying building blocks **5**,[54] to learn about their reactivity, and to find conditions for their cleavage. One surprising finding is outlined here to illustrate the relevance that studying model compounds has for avoiding dead ends at a late step of a synthesis. Side products obtained during the synthesis of the phenols **5b**,**d**, which are the starting materials for carbonates **6b**,**d**, made me suspicious regarding the stability of the carbonates in pyridine in the presence of copper salts, i.e., under conditions of an oxidative alkyne dimerization, which we had chosen for ring formation. Indeed, the carbonates **6b**,**d** are labile in neat pyridine (e.g., 38% of **6d** was cleaved within 24 h at room temperature) and, after aqueous workup, we obtained a mixture of carbonate and the corresponding phenols **5b** and **5d**, respectively. A dramatic acceleration of the rate of carbonate cleavage occurred in the presence of copper salts. A solution of carbonate **6d** in pyridine was converted quantitatively into a mixture of benzofuran **8d** and bisbenzofuran **9d** (Scheme 3) within 30 min of the addition of CuCl (4 mol equiv.). In contrast to this observation, diphenylcarbonates that carry tolane substituents, such as **6a**,**c**, proved to be sufficiently stable under the conditions of the oxidative dimerization of alkynes and, thus, they turned out to be the structural motif of choice.

Besides the structure of the template, efficient cylisation is the other key issue to address when designing a new catenane synthesis. We chose the oxidative dimerization of

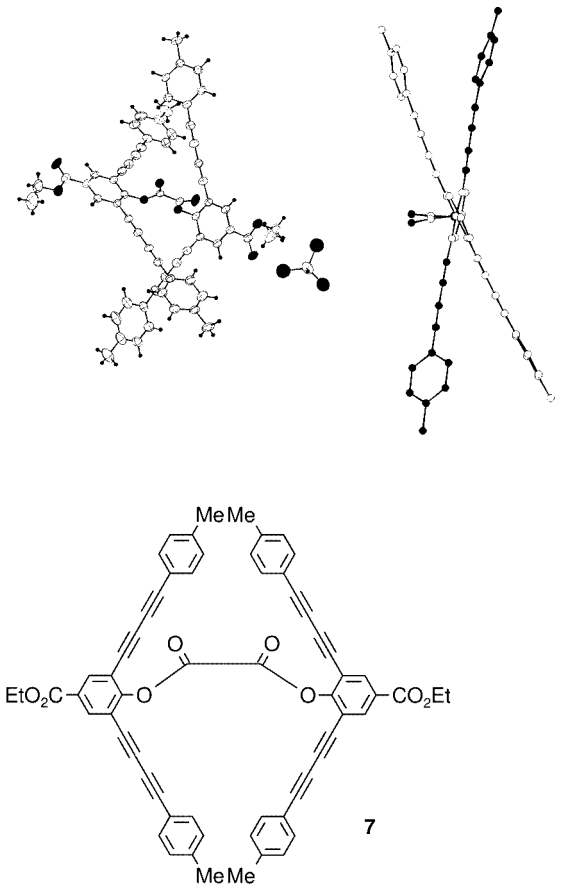
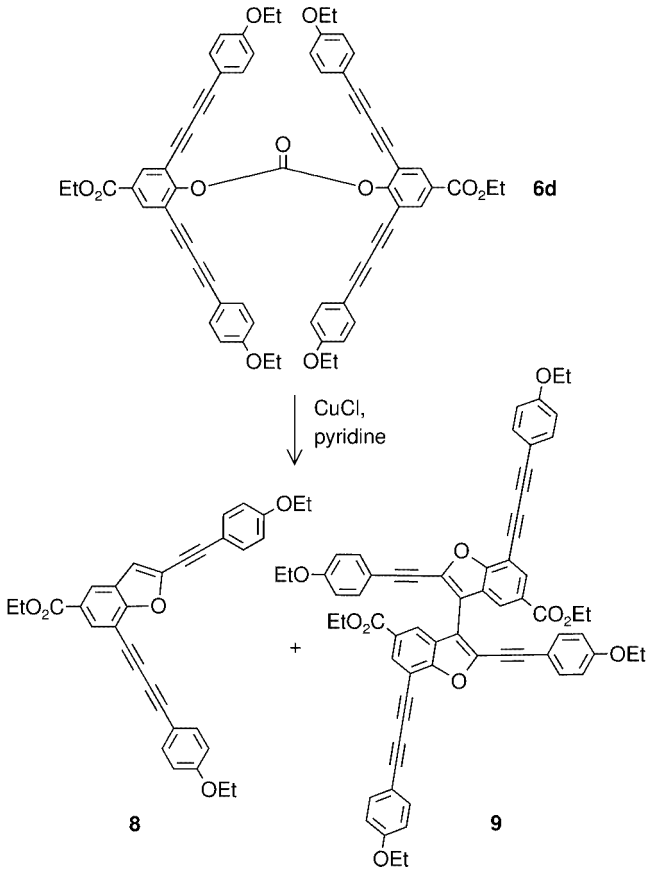
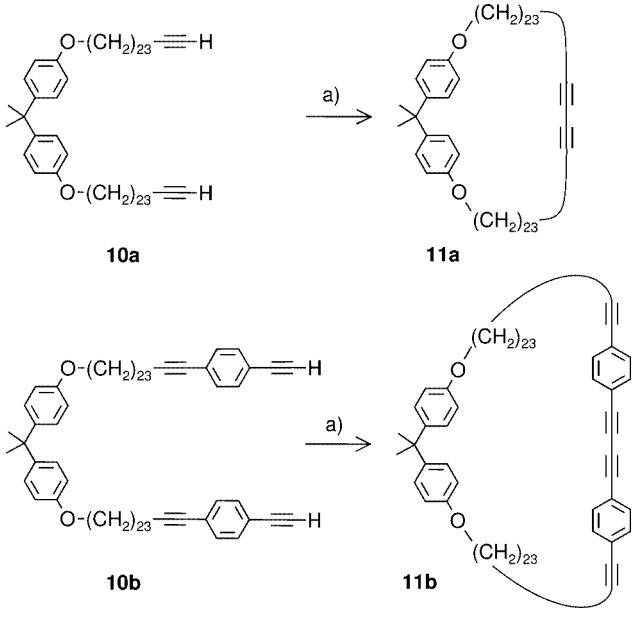


Figure 5. Structure of oxalate **7** in the crystal. *Left*: Ortep plot (50% probability). *Right*: View along the connecting line between the two carbon atoms of the $C_{aryl}O$ group. The ester groups have been omitted for clarity



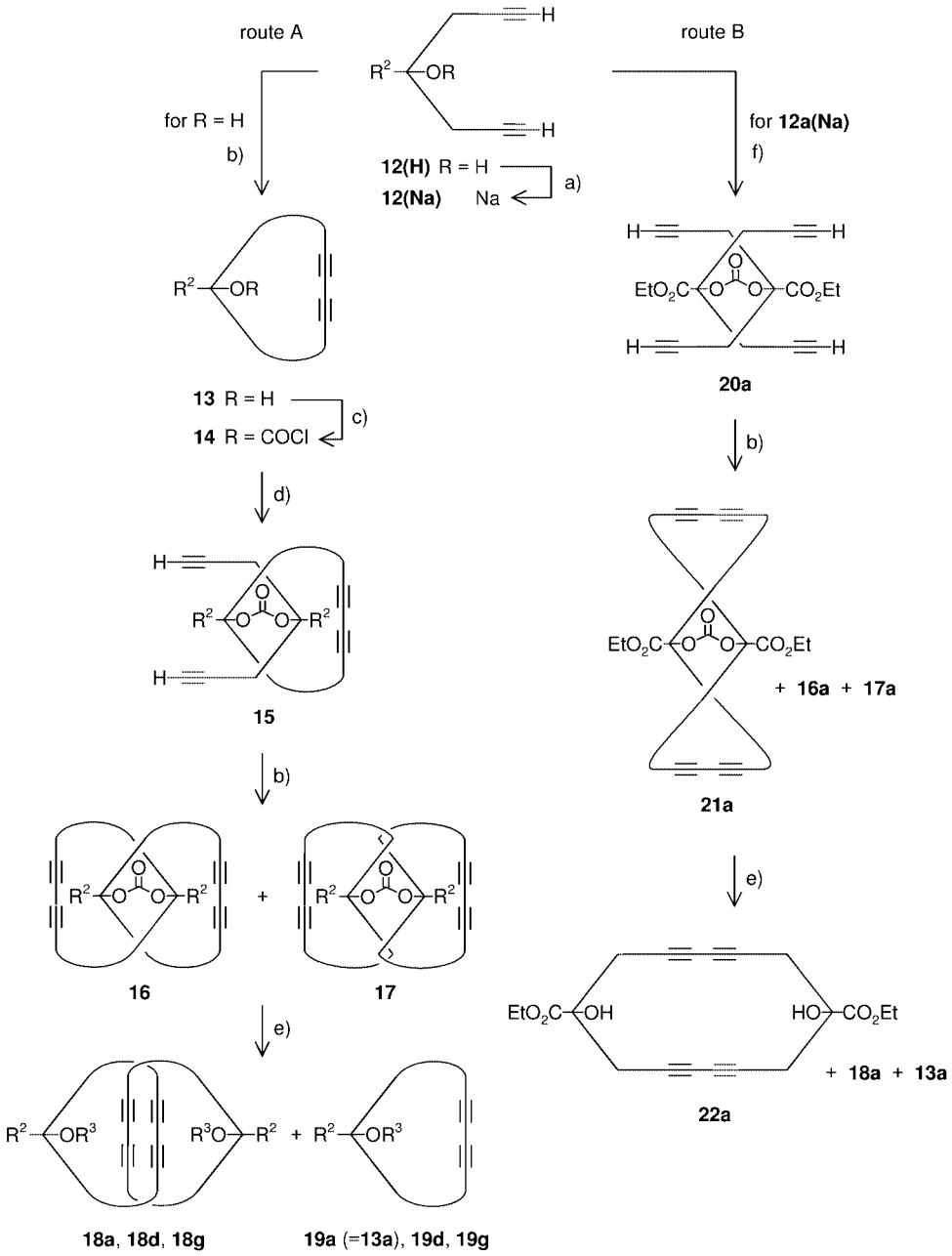
Scheme 3



Scheme 4. a) CuCl, $CuCl_2$, pyridine, pseudo-high dilution

alkynes because it has been demonstrated to give high yields of cyclic compounds in numerous cases, including those forming ultra-large cycles.[55] Several protocols for the oxidative dimerization of alkynes exist,[56] yet choosing suitable reaction conditions is a matter of trial and error because of the vague understanding of the reaction mechanism and the lack of comparative studies, even though this reaction has been known for a very long time.[56] This situation demonstrates clearly the requirement of undertaking model studies that are as simple as possible.[57] We chose to use CuCl and $CuCl_2$ in pyridine, conditions that have been described by Breslow et al. for the preparation of a molecular cage.[58] Slow addition of the simple α,ω-bisalkyne **10a** using a syringe pump (conditions of pseudo-high dilution) gave mainly oligomers as a mixture with the starting material and the target macrocycle **11a**, while the addition of the α,ω-bisalkyne **10b** gave predominantly (85% isolated yield) macrocycle **11b** (Scheme 4). It appears that arylalkynes are better suited to the reaction than are alkylalkynes under our chosen conditions. Under different conditions, the reverse result might be found.

We took our findings on the carbonates and the cyclisation as a guide for the design of the final structure of the ring precursors **12(H)**. Although in a multistep synthesis, the ring precursors can be prepared on multigram scales (4−10 g) by a partially convergent route.[57] Altogether, transferring the reaction conditions that we had elaborated using the model compounds went smoothly and the catenanes **18** were obtained as depicted in Scheme 5 through route A comprising the following steps:[24] (1) cyclisation of



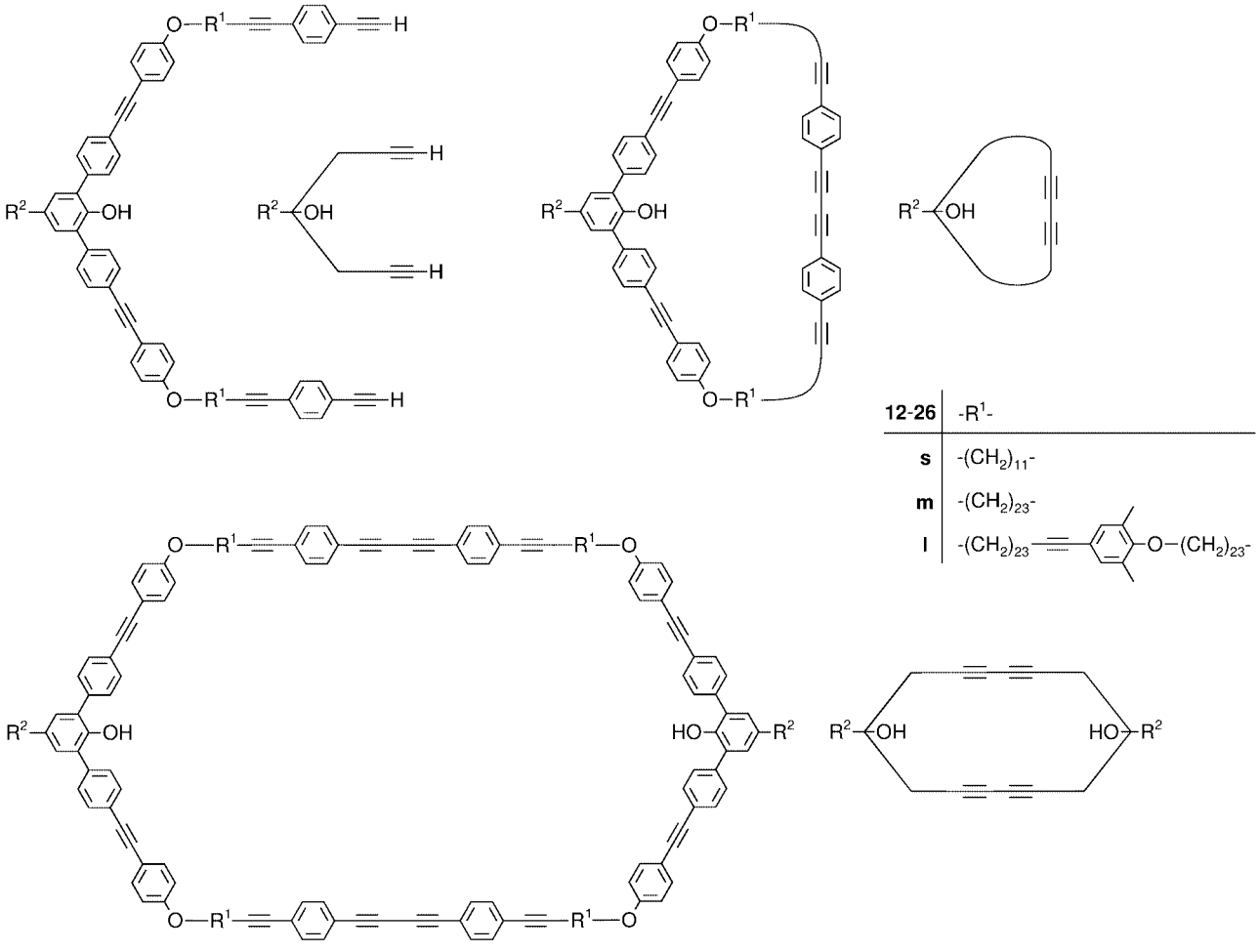
12-17	R^2-
a	EtO_2C-
b	EtO_2C-$(CH_2)_2$-
c	MeO-C$_6$H$_4$-CH_2O-$(CH_2)_3$-

18,19	a	b	c	d	e	f	g	h
R^2-	EtO_2C-	EtO_2C-	HO_2C-	$HO_2C(CH_2)_2$-	$MeO_2C(CH_2)_2$-	$HO_2C(CH_2)_2$-	$HO(CH_2)_3$-	$HO(CH_2)_3$-
R^3	OH	OMe	OMe	OH	OMe	OMe	OH	OMe

Scheme 5. a) NaH, THF; b) CuCl, $CuCl_2$, pyridine, pseudo-high dilution; c) Cl_2CO, iPr$_2$NEt, THF or CH_2Cl_2; d) for **15a**: + **12a(Na)**, THF; for **15b**: + **12b(H)**, DMAP, THF; for **15c**: + **12c(H)**, DMAP, THF; e) for hydrolysis of **16a**, **17a**, and **21a**: nBu$_4$NF, THF, 50 °C; for hydrolysis of **16b**,**c** and **17b**,**c**: 10 N NaOH, THF, EtOH, 50 °C; f) $(Cl_3CO)_2CO$, THF; g) MeI, K_2CO_3, DMF, 35−40 °C; h) 10 N NaOH, THF, EtOH, 20−45 °C. See the index for precise structures

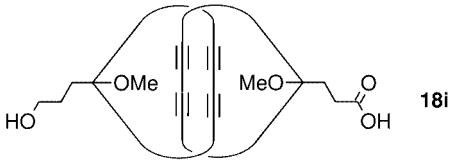
ring precursors **12a(H)** to obtain macrocycles **13a** by employing the oxidative dimerization of alkynes under conditions of pseudo-high dilution by slow addition of **12a(H)** to a suspension of CuCl and $CuCl_2$ in pyridine, (2) conversion of macrocycles **13a** into the corresponding chloroformates **14a** through reaction with phosgene in the presence of iPr$_2$NEt, (3) threading of these macrocycles onto **12a(Na)**, the sodium salts of the ring precursors, with the formation of the carbonates **15a**, (4) cyclisation by oxidative dimerization of the alkynes as in the first step to give the precatenanes **16a**, and finally (5) carbonate cleavage with nBu$_4$NF in THF to obtain the catenanes **18a**. In addition to the catenanes, the macrocycles **13a** are formed in the last step. They derive from the dumbbell-shaped products **17a** that accompany the precatenanes **16a**. Both compounds **16a** and **17a** result from an intramolecular alkyne dimerization. Whereas the two rings of precatenanes **16a** are intertwined, however, those of **17a** are not. The origin of the dumbbells **17a** is discussed below. The separation of precatenanes **16a** and dumbbells **17a** is tedious because they have very similar chromatographic behaviour. In contrast, chromatographic separation of catenanes **18a** and macrocycles **19a** (=**13a**), as well as of the methylated derivatives **18b** and **19b**, is easy to achieve.

The successful preparation of catenanes **s-18a**, **m-18a**, and **l-18a** having substantially different ring sizes — 63-, 87-, or 147-membered rings — clearly demonstrates one of the potentials of our approach. This new synthetic route also suits our goal of flexibility regarding the functional groups, as is shown by the synthesis of the [2]catenanes **m-18d** and ***m*-18g** (Scheme 5).[59] Not unexpectedly, substitution of the ester group by an ω-functionalised alkyl substituent influences the reactivity of the phenolic OH group, which allowed simplification of the carbonate-formation step and demanded changes in the procedure for ester cleavage. The formation of carbonates **15b**,**c** no longer requires the sodium salt of the ring precursors; it is sufficient merely to add DMAP to a solution of the chloroformates **14b**,**c** and the ring precursors **12b**,**c(H)** to obtain these carbonates quantitatively.[60] Applying the carbonate-cleavage procedure (nBu$_4$NF in THF at 50 °C), which we had used for the precatenanes **16a**, to the carbonates **16b**,**c** resulted in slow carbonate cleavage accompanied by a substantial degree of decomposition. Instead, hydrolysis with aqueous NaOH in THF, conditions that we found to be unsuitable for **16a**, worked well for **16b**,**c**. The successful syntheses of the catenanes **m-18d** and **m-18g** prove that other functional groups can be introduced; they need not



necessarily be attached to the phenolic moiety, but may be attached to another site of the molecule, e.g., to the dimethylphenol unit of catenane **l-18a** or somewhere on the alkyl chains.

The unsymmetrical intermediates, the carbonates **15**, suggest the option of preparing catenanes consisting of different rings. This challenge was realized by the synthesis of catenane **m-18i**, whose two rings are substituted differently, starting from **m-12b** and **m-12c**.[59] Such catenanes are highly valuable for the preparation of monodisperse oligo-[2]catenanes and are ideal monomers for poly[2]catenanes because no further, complementary monomer is needed, which disburdens the demand of stringent mass balance in polycondensation and polyaddition reactions.

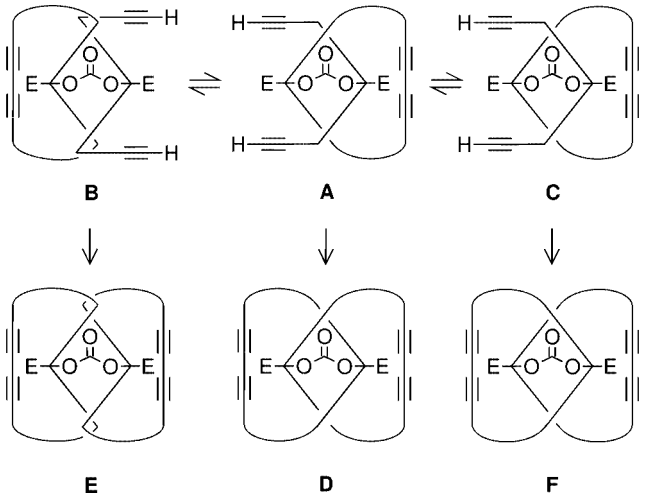


18i

2.2 The Origin of the Dumbbells 17

As mentioned above, the reaction of **15** with the copper salts in pyridine not only gave the precatenanes **16** but also dumbbell-shaped compounds **17** (Scheme 5). At first glance, dumbbells **17** may appear to be topological isomers of precatenanes **16**, but this situation is true only as long as we take the chemical reality into account that atoms cannot be fused easily. If we look at the molecular graph[61] and apply a strict and simple topological rule to find out whether two molecules are topologically isomeric — that any deformation is allowed, but no cutting — **16** and **17** turn out to be interconvertable. This interconversion is possible because the tether (i.e., the carbonate linkage) between the two rings of the precatenane can collapse to a point that is common to the two rings. Finally, elongation of this common point gives the dumbbell-shaped compound. Thus, **16** and **17** can be interconverted and are, therefore, not topological isomers in the strict sense. For this and related cases, Vögtle has suggested the term "residual topology".[62]

What is the origin of **17**? According to NMR spectra, TLC, and size-exclusion chromatography (SEC), the reaction of macrocycles **14** and ring precursors **12** gave a uniform material (**15**) for which the underlying structure was proposed to be a ring precursor threaded through a ring (structure **A** in Scheme 6). The formation of precatenanes **16** in the next step provided proof for this threading process. The by-products **17**, however, indicate an equilibrium between **A** and another conformer in which the ring and ring precursor are not intertwined. In principle, the two conformers **B** and **C** must be considered, but **C** can be excluded because of the results of NMR spectroscopy studies on model carbonates **6c** (see above).[51] This finding leads us to assume an equilibrium exists between **A** and **B** in which the ring changes its conformation. The rings appear to be



Scheme 6

sufficiently large and, because of its long aliphatic parts, sufficiently flexible to enable folding of the angular moiety into the ring, whereupon the ring precursor unthreads. Cyclisation of **B** will result in formation of **E**, which is one of the conceivable conformers of dumbbells **17**. This explanation is supported strongly by the finding that the ratio of precatenane **16**:dumbbell **17** decreases upon increasing the ring size (6:1, 2.7:1, and 1.6:1 for the rings with 63, 87, and 147 ring atoms, respectively).[24a] It would be interesting to find out whether, upon further increase of the ring size, the ratio of precatenane:dumbbell approaches or exceeds a ratio of 1:1.

The dumbbell-formation process is expected to be largely independent of the type of template and will, therefore, occur whenever huge rings having some degree of conformational flexibility are used as building blocks. This kind of conformational flexibility will take an additional toll in approaches, such as the Sauvage type and the Hunter–Vögtle type, in which not only are the ring and ring precursor complementary to one another but also the two rings or two ring precursors. In these cases, the templating step already will give a product mixture consisting of the targeted threaded species and of complexes formed from two rings or two ring precursors by ligand exchange of copper phenanthroline complexes or the reversibility of the formation of hydrogen bonds.

2.3 Reconsidering the Synthetic Strategy

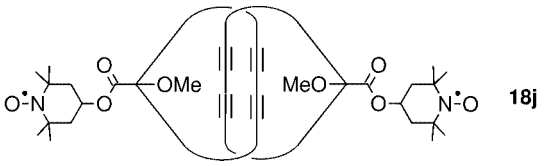
We wondered what would happen if we began with the ring precursors **12** and changed the sequence of the cyclisation and threading steps in such a manner that first the carbonates **20** are prepared and then the alkyne dimerization is carried out (Scheme 5, route B). Possible products of an intramolecular alkyne dimerization are precatenanes **16**, dumbbells **17**, and the dimer precursors **21**. We chose the descriptive name of the latter compounds because they are the cyclic dimers of the ring precursors **12**. Unexpectedly, the reaction of the carbonates **20a** gave predominantly the dimer precursors **21a**.[63] The product selectivity

increases as the length of the chain decreases. The ratio of precatenane **l-16a**:dumbbell **l-17a**:dimer precursor **l-21a** is ca. 1:1:4, whereas only traces of **s-16a** and **s-17a** were formed alongside **s-21a**. This simple switching of a catenane synthesis to a synthesis of a constitutionally isomeric cyclic dimer by interchanging two steps (cyclisation and templating) is unique among other conceptionally related routes.[38b,40,64] Comparative investigations by Sauvage using 2,9-diphenyl-1,10-phenanthroline−Cu^{I} complex as the templating unit and alkene metathesis as the ring-forming reaction gave the catenanes (ca. 90% isolated yield) no matter which route[40a,40b] was taken. Only upon changing the type of template[65] or the chain size[66] were the cyclic dimers obtained instead of the [2]catenanes.

The cyclic dimers **22a** are constitutional isomers of the [2]catenanes **18a**. Both compounds present the same functional groups and are composed of the same building blocks, but the cyclic dimers **22a** lack a topological bond. This feature makes the cyclic dimers valuable reference materials when studying the properties of the catenanes.

3. The Co-Conformation of the Catenanes 18

The special features of catenanes are the options for independent rotation and lateral displacement of the rings. These features are the reason why one would expect specific material properties of catenanes. Freely rotating rings and a sufficient degree of freedom for lateral displacement were the leading aspects when designing the catenanes **18**. Having the catenanes at hand, we took a closer look at their properties to see whether they met our expectations. Because of the huge ring sizes and the lack of strongly interacting functional groups, we expected the two rings to have a random orientation relative to one another; in other words, we expected the catenanes to adopt all possible co-conformations[2] in equal abundances. In agreement with this assumption, the ^{1}H and ^{13}C NMR spectra of catenanes **18** in $CDCl_3$ are very similar to those of the corresponding rings **13** and **19**. Despite the presence of numerous magnetically anisotropic moieties, the proton signals are only marginally shifted to higher field by 0.02−0.05 ppm upon conversion of the smallest ring **s-13a** into the catenane **s-18a**.[24a] Differences in this narrow range have been reported previously for the aliphatic [2]catenane consisting of the two rings, cyclooctacosane and *N*-acetylazacyclohexacosane.[67] Even smaller shifts (0.00−0.03 ppm) were found between the spectra of the larger ring compounds **m-13a**, **m-19e**, **m-19h**, and **l-13a** and the corresponding catenanes **m-18a**, **m-18e**, **m-18h**, and **l-18a**.[24] Moreover, the ^{1}H NMR spectroscopic data of the catenanes **s-18a**, **m-18a**, and **l-18a**, which vary in ring size, differ by 0.03 ppm at most. The NOE spectra of the medium-sized catenane **m-18e** and macrocycle **m-19e** exhibit no significant differences. Obviously, NMR spectroscopy, which has proven to be a very valuable tool in the analysis of other catenanes,[5a,22a,39b,34,68] fails to reveal information on both, the co-conformation adopted and the dynamics of the catenanes **18**. Therefore, in cooperation with G. Jeschke, we applied an EPR-based method that allows the distances between spin labels to be determined very precisely,[69a] as well as distance distributions.[69b]



18j

The question of co-conformation distribution can be translated into a question regarding the distance distribution of the two stable nitroxyl radicals of catenanes **18j**. Four-pulse double-electron electron resonance (DEER) measurements of the dipole−dipole coupling between the two spins allows the label-to-label separation to be deduced.[70] The dipolar time-evolution data we obtained were directly transformed to the pair correlation function, which was also simulated from first principles for a geometric model consisting of two interlocked, infinitely thin, circular rings that can adopt any relative orientation within the constraints given by their intertwinement. The experimental data and theoretical predictions based on this model fit well for the medium- and large-sized catenanes **m-18j** and **l-18j** in chloroform. Thus, in chloroform, the macrocycles of **m-18j** and **l-18j** are nearly fully expanded and have no preferred co-conformation; i.e., as we anticipated, the macrocycles exhibit unimpeded rotation and their lateral displacements are restricted only by their intertwinement. The experimental data of the smallest catenane **s-18j** in chloroform differ significantly from the theoretical ones. This phenomenon may be due to the simplicity of our model. Deviation from a perfect circle for the shape of the macrocycles of **s-18j** may be more significant than in the case of **m-18j** and **l-18j** and the thickness of the torus may no longer be negligible. A skewed co-conformational distribution, however, cannot be ruled out as the reason for this discrepancy. As expected, the solvent influences the rings' conformations. Whereas the macrocycles of **18j** are fully expanded in chloroform, they are collapsed in *o*-terphenyl. Unfortunately, this collapse prevents us from deriving information about the co-conformational distribution in *o*-terphenyl, which might be different from that in chloroform.

EPR spectroscopy also offers access to diffusion constants and, therefore, to information on the dynamics of the rings. Presently, we are pursuing a comparative study of a macrocycle and a [2]catenane, each substituted with one spin label, to learn about the similarities and differences in ring rotations and lateral displacements of intertwined and non-intertwined rings.

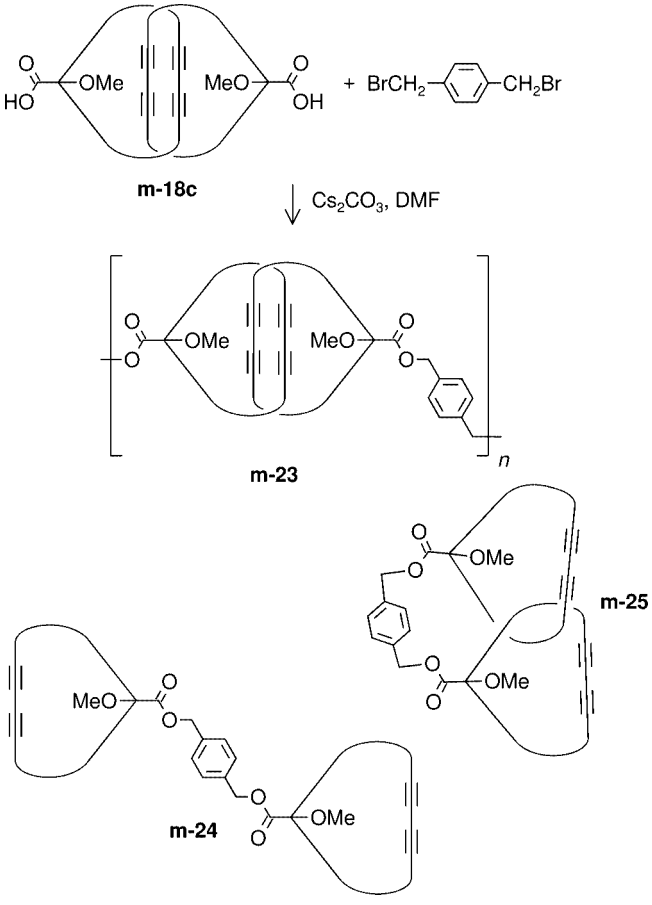
When checking the thermal behaviour, we were surprised to find that the catenanes **18a**,**b** and the corresponding macrocycles **19a**,**b**[57] are thermotropic liquid-crystalline materials. This behaviour probably originates from the banana-shaped and rod-like mesogens and their integration into a ring because, among other reasons, the compounds derived from catenane **m-18b** and macrocycle **m-19b** by full hydrogenation of all their triple bonds do not show liquid-

crystalline phases. Interestingly, the thermal behaviour of a catenane resembles that of the corresponding macrocycle: e.g., **s-18b** and **s-19b** are both monotropic nematic, **m-18b** and **m-19b** are both enantiotropic nematic, and **l-18b** and **l-19b** both show an SmC and an SmA phase in addition to a nematic phase. The transition temperatures of these pairs exhibit differences of as much as 17 °C and as little as 1 °C.[71] The smallest differences were found for the phase transitions of **l-18b** and **l-19b**, i.e., for the largest rings. Obviously, intertwinement of the macrocycles in these catenanes still allows them to align in a manner similar to that exhibited by the non-interlocked rings. This result might indicate that intermolecular interactions govern the spatial arrangement and that, in the bulk also, the directing forces between the two intertwined rings that would lead to preferred specific co-conformations are of little importance. Of course, more experimental data are needed to support this assumption and to reveal how the macrocycles of the catenanes are arranged in the LC phases. Unfortunately, X-ray diffraction studies of the smectic phases of **l-18b** failed to give a detectable signal and, in addition, EPR spectroscopic measurements on samples of spin-labelled catenanes **18j** dissolved in a matrix of the corresponding unlabelled catenanes **18b** were unsuccessful because of thermal degradation.

4. Polymerisation of the [2]Catenanes

The carboxyl groups of **18a**,**d**,**i** and the hydroxyalkyl substituents of **18g**,**i** were incorporated for the purpose of polymerising the [2]catenanes. The site of attachment was deliberately chosen to be the thickest and, therefore, the most space-consuming part of the ring to allow the rings of a poly[2]catenane as much freedom for lateral shift and rotation as possible within a given ring size. For the same reason, we did not attempt to use the phenolic OH groups — a relict of the carbonate template — for polymer formation. Instead, the phenolic OH groups were methylated to make them essentially inert. In most cases, an ester saponification following the methylation provided us with the monomers, the catenane diacids **s-18c**, **m-18c**, **l-18c**, and **m-18f**, the catenane diol **m-18h**, and the AB-type catenane **m-18i** (Scheme 5).

With these derivatized catenanes in hand, a broad range of different procedures can be applied to realise polycondensation or polyaddition. Of course, the choice is confined to reaction conditions that are compatible with all of the functional groups present in the monomers. One attempt, which gave the polyester **m-23**, was the reaction of catenane diacid **m-18c** with 1,4-bis(bromomethyl)benzene in the presence of Cs_2CO_3 in DMF (Scheme 7).[72] Proving the structure of the product by NMR spectroscopy was achieved rather easily with the help of model compound **m-24** because the intertwinement has nearly no effect on the shift of the signal (see above). Size-exclusion chromatography (SEC; Figure 6) revealed a broad molecular mass distribution, which is typical for a step-growth polymerisation, and that the cyclic 1:1 product **m-25**, a molecular pretzel,[73] made up a considerable part of the crude product.[74] Cyclic products are common in step-growth polymerisations. Under conditions of higher dilution, even more of the molecular pretzel **m-25** was formed, which allowed it to be isolated and to have its structure elucidated. Analysis of the SEC trace displayed in Figure 6, using polystyrene as the calibration standard, gave a number-average molecular mass ($<M_n>$) of 11400 and a weight average molecular mass ($<M_w>$) of 74600. If we disregard the signal of the pretzel **m-25**, then $<M_n>$ amounts to 28900 and $<M_w>$ to 95200. Of course, polystyrene is not an adequate calibration standard for catenanes, but it is used as the common standard. Nevertheless, it gives at least a rough idea of the molecular mass and also the degree of polymerisation. Because of the high molar mass of the repeating unit (M = 2970), the value of $<M_n>$ of 28900 translates into the rather low average polymerisation degree ($<P_n>$) of ca. 10. As detected by differential scanning calorimetry, the polymer **m-23**, which is more appropriately termed, oligomer **m-23**, decomposed at 80 °C in a strongly exothermic reaction. Therefore, we turned to other polymerisation reactions.



Scheme 7

Moore and Stupp described the in situ activation of carboxylic acids using carbodiimide in the presence of DMAP and toluenesulfonic acid as a valuable route to polyesters.[75] We applied this rather simple procedure to a

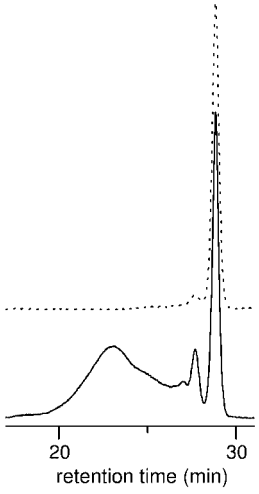
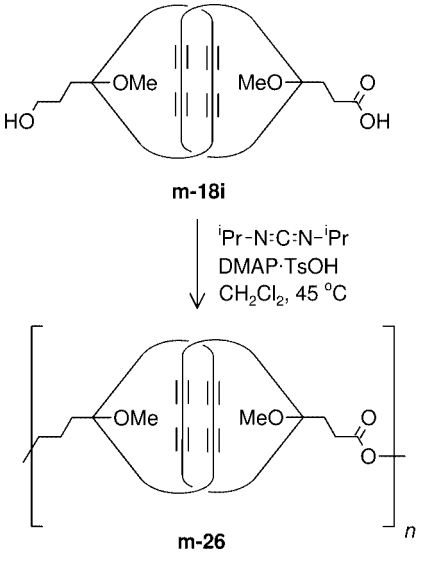
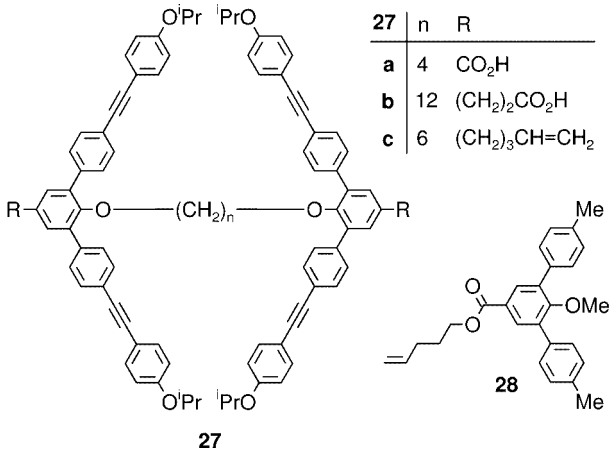


Figure 6. SEC traces (THF, room temperature) of **m-23** (solid line) and **m-25** (dashed line; this compound was contaminated slightly with a species of larger size)

combination of catenane diacid **m-18c** and decanediol,[16] as well as to the AB-type catenane **m-18i** (Scheme 8).[17] The resulting products gave SEC traces that are very similar to that of **m-23** in Figure 6 and indicate a broad molecular mass distribution and a significant amount of the molecular pretzel and other cyclic products. Ignoring the pretzel, we calculated a value for $<P_n>$ of 7 for product **m-26** ($<M_n>$ = 20900, $<M_w>$ = 56400). Even very long reaction times of ca. 1 week did not increase the value of $<P_n>$. This observation may indicate that side reactions occur, such as the well-documented O−N acyl transfer. Although the conditions elaborated by Moore and Stupp disfavour O−N acyl transfer, this intramolecular reaction may still compete efficiently in the case of a slow intermolecular reaction. Experiments with model compounds, such as **27a** and **27b**, pointed to a low reactivity of the carboxyl groups in these polyesterification reactions and, additionally, some of our model studies raised our suspicion with respect to the occurrence of side reactions.

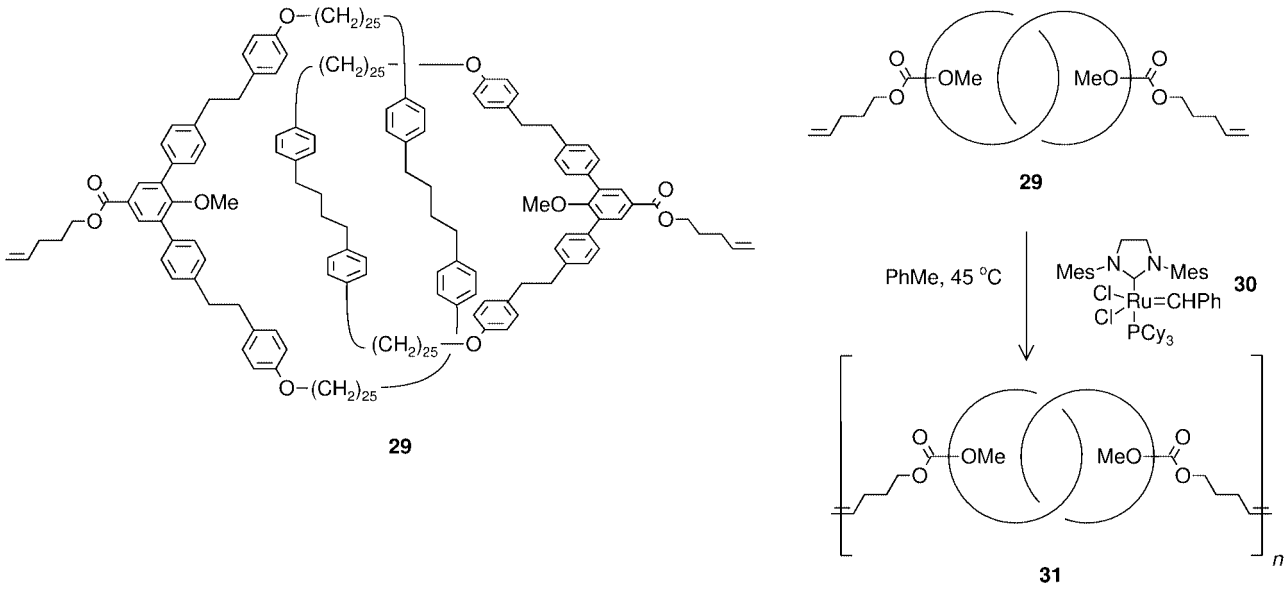


Scheme 8



Seeking a very different type of chemistry to use in the polymerisation, we became interested in acyclic diene metathesis (ADMET).[76a] As Wagener has demonstrated, the second-generation Grubbs catalyst makes ADMET a very convenient, readily proceeding reaction.[76b] Thus, it was very surprising to us that no reaction occurred when this catalyst was added to a solution of model compound **27c** in CH_2Cl_2. Our finding that this compound also inhibited the metathesis of 1,9-decadiene, which readily polymerised in the absence of **27c**, suggested that the alkyne units deactivate the catalyst. Indeed, the model compound **28**, which is similar to **27** but has no alkyne units, underwent the metathesis reaction readily. Thus, our monomer of choice was **29**, which we obtained through Pd-catalyzed hydrogenolysis of the catenane diacid **m-18c** and subsequent alkylation with 5-bromopentene (Scheme 9). The reaction of **29** with the second-generation Grubbs catalyst **30** in toluene at 45 °C gave the polymer **31**. Again, SEC was used to provide an idea of the degree of polymerisation of the crude material obtained after distilling off the solvent. Values of $<M_n>$ = 13000 and $<M_w>$ = 59300 and, when disregarding the molecular pretzel, $<M_n>$ = 33000 and $<M_w>$ = 69300, were determined to correspond to values of $<P_n>$ = 5 and $<P_n>$ = 12, respectively. Surprisingly, the ^{1}H NMR spectrum of **31** exhibits no signals for the terminal olefinic protons, although one would expect to detect them easily for a polymer having a polymerization degree of ca. 12.[77] Whether this result is due to a dominant formation of cyclic oligomers is not yet clear. A detailed mass spectrometric analysis may provide an answer. Cyclic oligomers might be the favored products over linear oligomers because of the dilution of the functional groups by the large backbones of the catenane in combination with a highly flexible polymer backbone. This concept would explain why quite similar values of $<P_n>$ were obtained in all of our rather different polymerisation experiments.

The polymerisation of catenanes of the Stoddart-,[12] Sauvage-,[13a,14] and Vögtle-type[13b] of [2]catenanes has



Scheme 9

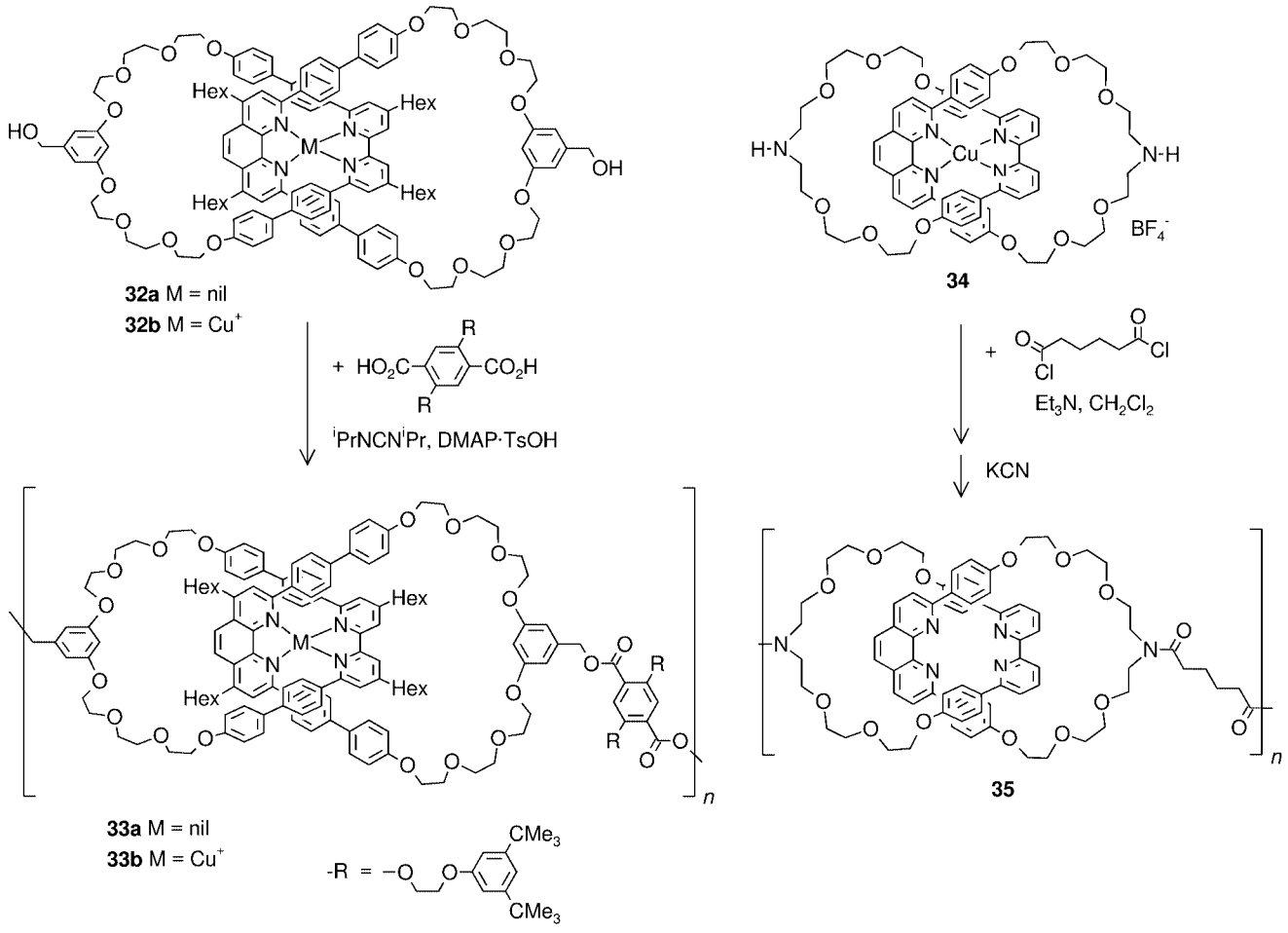
been pursued by other groups. A comparative discussion of the results of the preparation of poly[2]catenanes appears to be too premature, considering the paucity of data available. The most-reliable data can be found for the polymerisation of the Sauvage type [2]catenand **32a** and the Cu−[2]catenate **32b** employing Moore and Stupp's carbodiimide method (Scheme 10).[13a] Using the former, mainly cyclic oligomers were obtained, including a large portion of the molecular pretzel, whereas, when the stiffer catenate **32b** was used, higher-order oligomers were obtained. Demetallation of the product **33b** gave **33a** having a value of $<M_n>$ of 22000, which corresponds to $<P_n> \approx 9$ and is a result very similar to ours. MALDI-TOF spectra indicate the presence of cyclic oligomers. A remarkable value of $<M_n>$ of $8.1 \cdot 10^5$ (determined with SEC) has been reported by Shimada for the poly[2]catenane **35** obtained by the reaction of catenate **34** with adipic acid dichloride and subsequent removal of the copper ions (Scheme 10).[14] This high molecular mass, however, must be considered with a grain of salt because the reported yield of 66% may imply that material of low molecular mass was lost upon workup.

A very different approach to poly[2]catenanes was employed successfully by Fustin and Bailly.[15] They used [2]catenanes in a solid-state copolymerisation with an oligocarbonate to obtain a polymer having polycarbonate segments of different statistical lengths connected by [2]catenane units (Scheme 11). This approach is a clever strategy for the preparation of sufficient amounts of polymers despite a rather limited amount of functionalized catenane. Furthermore, such polymers may be better suited for studies on material properties than are oligomers that possibly contain quite high amounts of cyclic species.

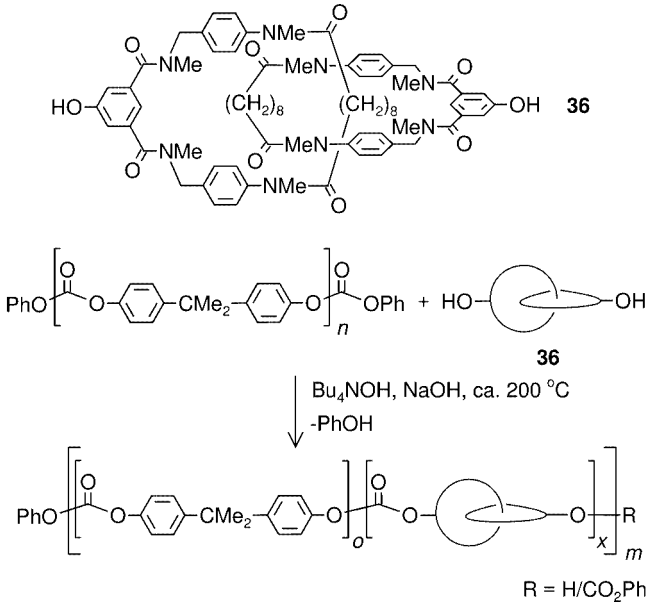
5. A Strategic Outline for the Synthesis of [*n*]Catenanes

Even though poly[2]- and poly[3]catenanes may already be sufficient for studying the effect of the topological bond on a material's properties, the aesthetically appealing structure of polycatenanes ([*n*]catenanes having a large number for *n*) and their synthetic challenge makes one keep dreaming of their realisation. We are asked frequently whether we want or are able to apply our route also to the preparation of [3]catenanes, [4]catenanes, and so on. I think our approach can be extended to obtain a [3]catenane in a useful amount, but, very generally, going beyond a [3]catenane using a stepwise approach consisting of recurring threading and cyclisation steps (Scheme 12, a), will be tedious and will result only in small amounts of [*n*]catenanes, no matter whether the synthesis is performed as a single-pot experiment[11] or as a series of separate reactions.[9] Furthermore, the isolation of structurally well-defined [*n*]catenanes, as well as unambiguous proof of their structures, will become increasingly difficult — if not impossible — with increasing values of n.

No doubt, the synthesis and isolation of a [5]- and a [7]catenane by Stoddart's group is a very remarkable achievement.[9] Both compounds were obtained, however, only in very small amounts, such as 5−30 mg of the [5]catenane[9a,9c,9d] and 8 mg of the [7]catenane.[9a] Later experiments demonstrated that separation of the [5]catenane from a topological isomer failed on larger scales (e.g., 59 mg).[9b] The other strategies for catenane synthesis have also been employed to prepare [*n*]catenanes. Using the Hunter−Vögtle route, catenanes with up to four rings have



Scheme 10

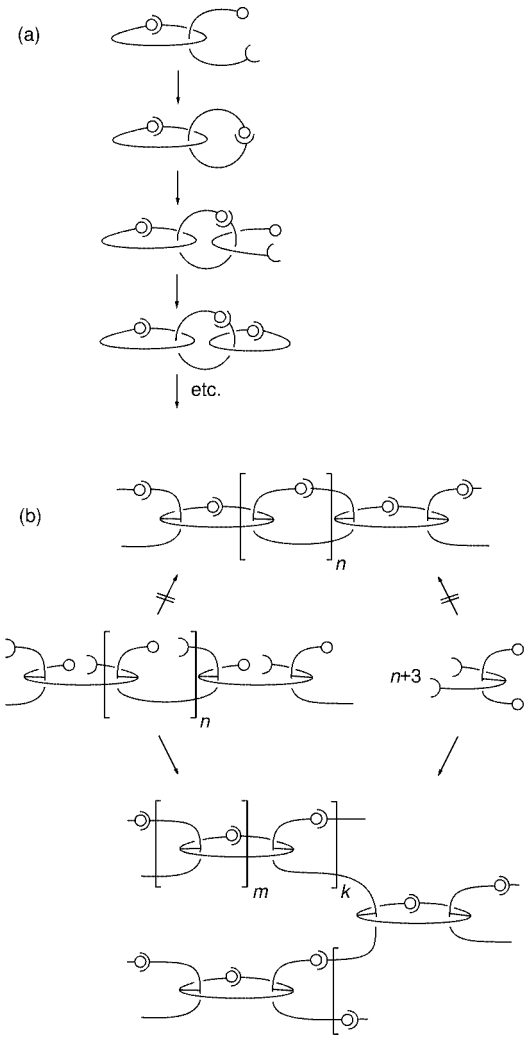


Scheme 11

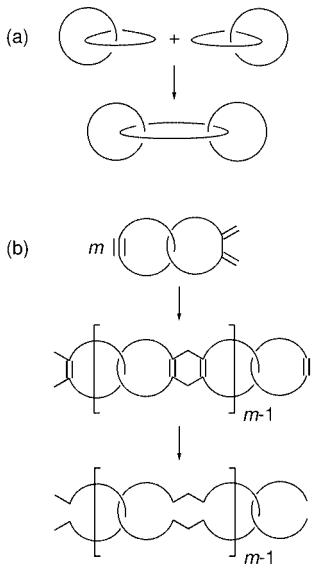
been isolated and higher [*n*]catenanes have been detected by mass spectrometry;[11] the Sauvage route has been used successfully to obtain [3]catenanes and necklace type [*n*]catenanes.[10] A proposal was recently made to extend the thermodynamically controlled catenane synthesis developed by Sanders to a recursive [*n*]catenane assembly.[39a]

Two closely related strategies have been suggested to circumvent recurring threading (Scheme 12, b).[78] Both start from supramolecular species in which the building blocks of the rings are preorganised so that after a well-defined cyclisation the rings are entwined and a jointed chain is obtained. Analogous polymer cyclisation, however, will result in structurally well-defined polymers only when a regioselectivity of 100% is achieved, i.e., when a strict programming exists regarding the functional groups that are to react with each other. Otherwise, as sketched in Scheme 12(b), loop formation and crosslinking will definitely occur. These side reactions correspond to the commonly found oligomerisation in simple cyclisation reactions.

Because cyclisation and threading are the bottlenecks of polycatenane syntheses, we have suggested[79] solving these two problems during a stage of the synthesis at which purification and structural proof are still easy. The most simple species exhibiting cyclic components and a topological bond is a [2]catenane. Now, if one of the rings of one [2]catenane is fused with one of the rings of another [2]catenane, a [3]catenane is formed having one larger ring instead of the two smaller ones, as depicted in Scheme 13(a). A poly-



Scheme 12



Scheme 13

catenane will be obtained if both rings of a [2]catenane undergo this ring fusion. This strategy not only circumvents threading and cyclisation of oligomeric or polymeric compounds, but it also enables the formation of topological isomers. Of course, the ring-fusion reaction must proceed without side reactions. A sequence of poly-Diels–Alder reaction and selective double-bond cleavage, e.g., by ozonolysis or cross-metathesis, seems to be a promising approach (Scheme 13, b). A first step into this direction was taken recently by Takata et al. who used a combination of a Diels–Alder reaction and ozonolysis to enlarge one ring of a [2]catenane.[80] Ideally, one could also find an electrocyclic reaction for the second step, which is the actual step of ring fusion. Although our catenanes are not yet suitably substituted, we are confident that our synthetic route to [2]catenanes is compatible with the introduction of the functionalities necessary for the ring-fusion chemistry.

Conclusion

With the synthesis of **18**, the spectrum of [2]catenanes has been broadened to compounds having huge rings that can rotate freely and have a considerable degree of freedom for lateral displacement. The lack of interaction between the two rings of the [2]catenanes challenged the typical methods used for structural analysis and stimulated us to apply EPR spectroscopy, which allows distance distributions to be determined and, thus, could be used to investigate the distribution of co-conformations in solution. The thermotropic liquid-crystalline phases of macrocycles **13** and catenanes **18** indicate that this field of research is still full of surprises. Major synthetic challenges remain for the preparation of poly[2]catenanes having higher degrees of polymerisation, and for the strategy proposed for the preparation of polycatenanes.

Acknowledgments

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