Synthesis of a [2]Catenane with Functionalities and 87-Membered Rings

Ömer Ünsal and Adelheid Godt*[a]

Abstract: This paper describes the efficient synthesis of a [2]catenane with 87-membered rings and with functionalities that should enable the preparation of a poly[2]catenane. For the ring formation, the oxidative dimerization of acetylenes was used. The entwinement of the rings was achieved with the help of diphenylcarbonate as a covalent template. The structure of [2]catenane **6** was unambiguously proven by NMR spectroscopy, mass spectrometry, and a comparison of the size exclusion chromatograms of starting materials, synthetic intermediates, and products.

Keywords: catenanes · macrocycles · mechanical bonds · supramolecular chemistry · template synthesis

Introduction

Catenanes[1] consist of chemically independent cyclic molecules, which penetrate each other and, therefore, are mechanically (topologically) linked. Being connected in this way, the rings should be allowed to rotate and translate to some extent independently of one another.[2] Our interest lies in gaining a deeper understanding of how this mobility in the catenane moiety will affect the material properties if, for example, [2]catenanes are units of a polymer chain.[3] To address this question, as a first step we developed a synthesis of a suitable [2]catenane. [2]Catenanes with huge rings and without interaction, which hinders the rotation of the rings, appear most suitable. The [2]catenane has to carry functionalities in order to be a building block for polymers. Furthermore, it is important that the [2]catenane is readily available. Here we report the efficient synthesis of a [2]catenane consisting of 87-membered rings with functional groups.[4]

Results and Discussion

The central challenge of catenane synthesis is the mechanical linkage of cyclic molecules. Numerous experiments have shown that suitable organization of the building blocks prior to ring formation increases the yield of mechanically linked rings at the expense of rings that are not entwined.[1, 5–10] Diphenylcarbonates with substituents like phenyl in the 2,6- and 2′,6′-positions adopt a conformation, in which the substituents point towards the corners of a distorted tetrahedron.[11] The carbonate group sits inside the distorted tetrahedron, and the planes of the two angular halves of the carbonate cross each other (Scheme 1). Such an arrangement appears ideal for the directed synthesis of catenanes by using a carbonate group as a covalent template as indicated by the work of Sauvage and Dietrich–Buchecker, who achieved a similar preorganization by Cu^{+}-phenanthroline complex formation.[1b, 6]

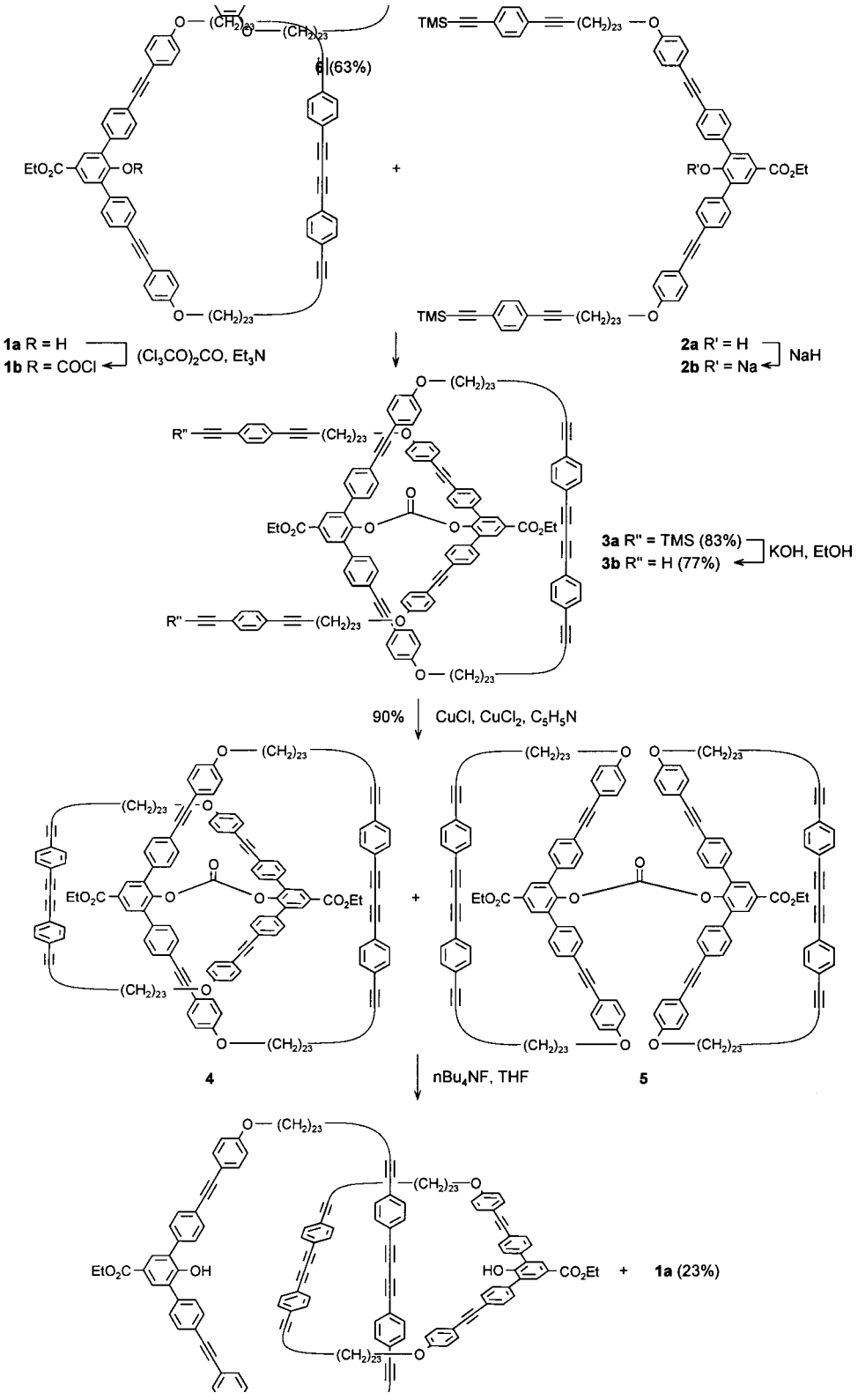
We chose the cyclic compound **1a** and the cycle precursor **2a** as our starting materials (Scheme 1).[12] They consist of an ethyl 4-hydroxybenzoate, which carries tolane units in the 3- and 5-positions. Long flexible chains are attached to the tolane units through ether bonds. The acetylene units at the chain ends of **2a** are to be used for ring formation by means of oxidative acetylene dimerization. The ester group should allow the formation of polymers, with the [2]catenane as a monomer.

Cyclic compound **1a** was transformed into the chloroformate **1b** by reaction with triphosgene in the presence of triethylamine.[13] Approximately 4% of the symmetric carbonate **5** was produced as a side product. For the preparation of the asymmetric carbonate **3a**, the cycle precursor **2a** was deprotonated with sodium hydride. The reaction of sodium salt **2b** with crude chloroformate **1b** gave **3a** in a nearly quantitative reaction (94%). The conversion can be conveniently determined by ^{1}H NMR spectroscopy, since the proton signals of the 4-hydroxybenzoate unit are shifted by $\delta = 0.12$ upfield upon transformation of phenols **1a** and **2a** into carbonate **3a**.

The asymmetric carbonate **3a** was isolated by column chromatography. According to thin-layer chromatography (TLC), the isolated fraction contained only one component. However, the ^{1}H NMR spectrum showed two sets of signals with a 1:1 ratio of intensity and a shift difference of approximately 0.01 ppm for some chemically comparable protons, for example, protons of the 4-hydroxybenzoate units,

[a] Dr. A. Godt, Ö. Ünsal
Max-Planck-Institut für Polymerforschung
Ackermannweg 10, D-55128 Mainz (Germany)
Fax: (+41) 6131-379100
E-mail: godt@mpip-mainz.mpg.de

  0947-6539/99/0506-1728 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 6



Scheme 1. Synthesis of [2]catenane **6**.

of the ArOCH_2 units, and of the ester groups. Also, for some chemically comparable carbon atoms, two signals show up in the ^{13}C NMR spectrum. The splitting as well as the ratio of intensity of the ^{1}H NMR signals do not change on varying the temperature [123 °C ([D_2]1,1,2,2-tetrachloroethane), −20 °C ([D_8]THF)]. Therefore, we exclude conformational isomerism, as further discussed below (compare with Scheme 2), as the reason for the appearance of the NMR spectra of **3a**. Rather we conclude that the cyclic and the open chain part of the carbonate have a slightly different influence on the ^{1}H and ^{13}C NMR resonances.

Carbonate **3a** was desilylated to give product **3b**. As in the case of carbonate **3a**, ^{1}H and ^{13}C NMR spectra of **3b** show two sets of signals for some chemically comparable protons or carbon atoms. The ratio of intensity of these two signal sets is 1:1 (^{1}H NMR in $CDCl_3$ or [D_5]pyridine). Compound **3b** was cyclized by oxidative acetylene dimerization under pseudo high dilution conditions.[14] The size exclusion chromatogram (SEC) of the crude cyclization product shows that almost exclusively compounds were formed which have a smaller hydrodynamic volume than the starting material **3b** (Figure 1). No signal of an alkyne proton was found in the ^{1}H NMR spectrum of the crude product. This is proof of a high degree of conversion. Two sets of signals in the aromatic region of the ^{1}H NMR spectrum (at room temperature and at 127 °C; [D_2]1,1,2,2-tetrachloroethane) indicate the presence of two compounds. Integration of the proton signals of the 4-hydroxybenzoate moiety gives a ratio of 2.8:1 of the two compounds in the crude material. Column chromatography gave again a mixture of the two compounds with a slightly different ratio of 2.6:1. Treatment of this product mixture with nBu$_4$NF resulted in carbonate cleavage,[15] and two products were formed. One of these is, according to TLC and NMR spectroscopy, identical with the cyclic compound **1a**. From this we concluded that on cyclization of **3b**, the dumbbell-shaped carbonate **5** was formed in addition to the intended precatenane **4**. This

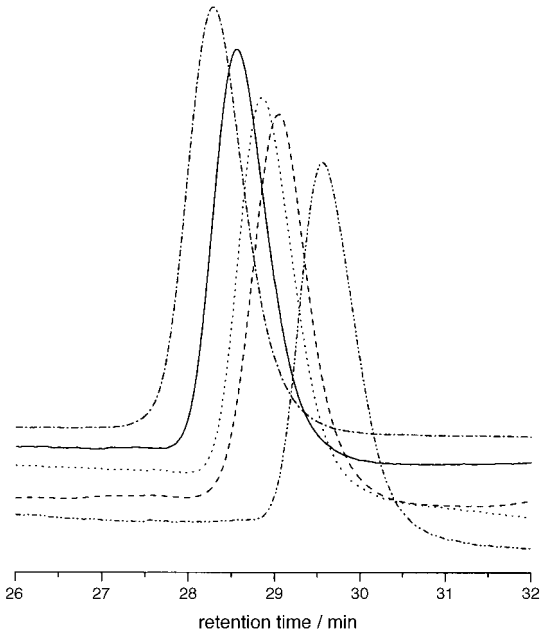


Figure 1. Size exclusion chromatograms (THF, room temperature, RI detection) of compounds **1a** (·····) and **3b** (·–·–·), of the crude product of cyclization of compound **3b** [(– – –); the ratio of **4**:**5** is approximately 2.8:1], and of the compounds **5** (···) and **6** (——).

hypothesis was confirmed by preparation of **5** starting from **1a** and triphosgene and by comparison of the ^{1}H NMR spectra of compound **5** with the crude product from the cyclization of **3b**. Furthermore, the relative intensities of the proton signals of the 4-hydroxybenzoate unit of **4** and **5** (2.6:1) in the mixture used for carbonate cleavage and of **6** and **1a** (2.8:1) in the crude product from the carbonate cleavage step are in accordance with the formation of cylic compound **1a** from **5** by means of carbonate cleavage. Compound **5** and the mixture of **4** and **5** have rather similar retention times on columns for SEC (Figure 1). Therefore it is conceivable that the SEC trace of the mixture of **4** and **5** in a ratio of 2.8:1 shows a monomodal distribution. The formation of **4** and **5** from **3b** can only be explained if compound **3b** is a mixture of conformers with entwined and non-entwined components (see Scheme 2). However, we were not able to detect the mixture or equilibrium of conformers by NMR spectroscopy. The splitting of signals into two signals of equal intensity in the case of compounds **3a** and **3b** as described above does not match with the ratio of 2.8:1 for **4** and **5** and clearly has another cause.

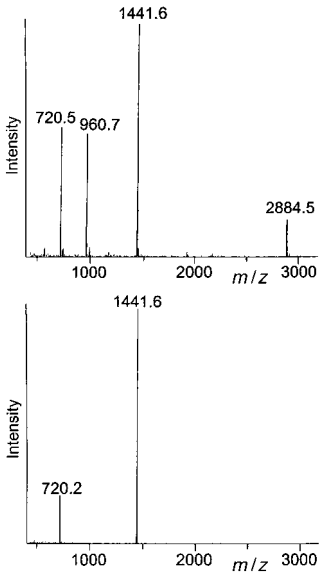


Figure 3. Field desorption mass spectra of cyclic compound **1a** (bottom) and catenane **6** (top). The sample of **6** contained traces of carbonates **4** and **5**.

A crucial point of this work was the structure elucidation of the main product, the [2]catenane **6**, which was formed upon carbonate cleavage. The ^{1}H NMR spectrum is identical with that of cyclic compound **1a** except for a signal shift up to 0.03 ppm (Figure 2). The ^{13}C NMR signals of **1a** and **6** have identical shifts. However, SEC (Figure 1) and TLC (**1a**: $R_f = 0.76$; **6**: $R_f = 0.52$; in petroleum ether/dichloromethane 1:2) give clear evidence that **1a** and **6** are different compounds. The high similarity of the NMR spectra of **1a** and **6** proves the structural integrity of the catenane. The field desorption mass spectrum of catenane **6** shows signals at *m*/*z* 2884.5, 1441.6, 960.7, and 720.5 (Figure 3). These data correspond well with the calculated data for a catenane with charges from one to four [M(**6**)$^+$: *m*/*z* 2884.2, M(**6**)$^{2+}$: *m*/*z* 1442.1, M(**6**)$^{3+}$: *m*/*z* 961.5, M(**6**)$^{4+}$: *m*/*z* 721.1].

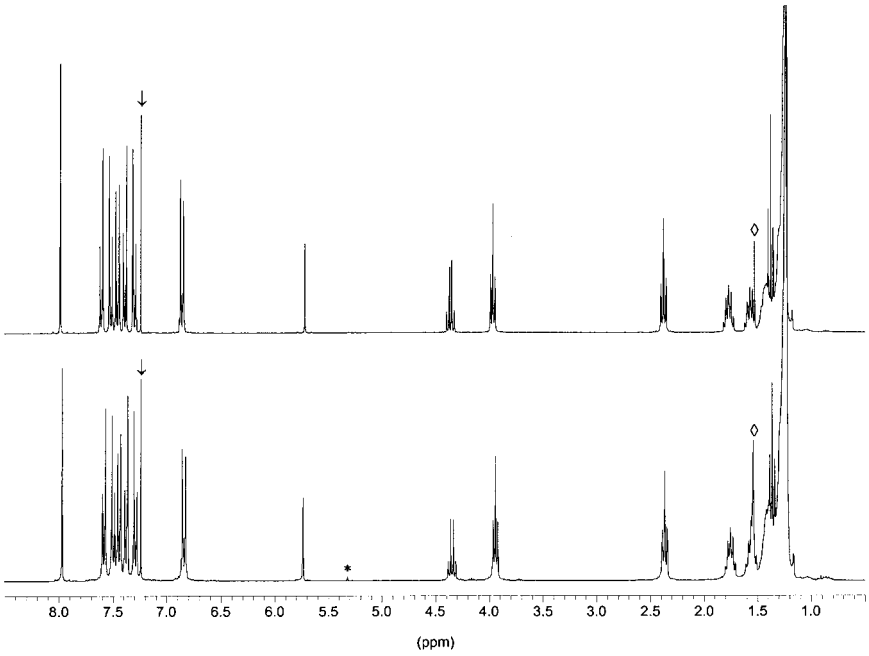


Figure 2. ^{1}H NMR spectra ($CDCl_3$, 300 MHz, room temperature) of cyclic compound **1a** (top) and catenane **6** (bottom). * CH_2Cl_2, ◇ H_2O, ↓ $CHCl_3$.

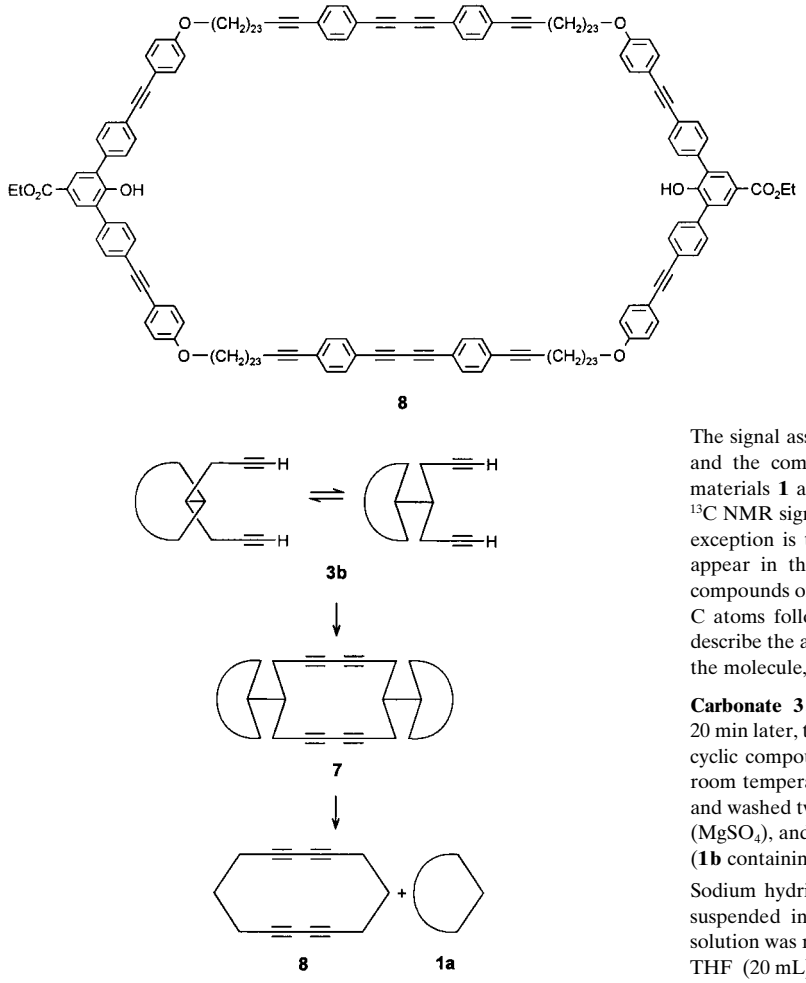
0947-6539/99/0506-1730 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 6

The signal of high intensity with m/z 960.7 is of particular interest. Such a signal is missing in the mass spectrum of **1a**. The only reasonable explanation is that it is a signal of a threefold charged catenane. This fact supports the assignment of the signal at m/z 2884.5 to M(**6**)$^+$. Also the signals at m/z 1441.6 and 720.5 could result from fragmentation of **6** into **1a** or corresponding open-chain compounds. However, high-resolution field desorption mass spectrometry shows half integral distances of the isotope signals for the signal of M^{2+}. The MALDI-TOF spectra of **1a** or **6** show signals at m/z 1441.8 and 2884.4, respectively.[16]

Mass spectra and NMR spectra of **6** are also consistent with the structure of isomeric monocyclic dimer **8**. The only way that **8** could have formed is via compound **7** (Scheme 2), which is a dimerization product of **3b** in the conformation with cyclic and acyclic components being not entwined. However, a high-yielding cyclization including a dimerization is of low probability. Furthermore, the reduced hydrodynamic volume of the product, formed upon acetylene dimerization, when compared to the hydrodynamic volume of the starting material **3b** unambiguously contradicts the formation of **7**. The formation of **7** is a dimerization, and it should result in an increase of the hydrodynamic volume. On the other hand, cleavage of the carbonate linkages of **7** should result in a volume reduction. Just the contrary is found; the hydrodynamic volume increases upon carbonate cleavage (Figure 1). Therefore, only the structure of [2]catenane **6** is consistent with all the accumulated data.

As mentioned in the introduction, our goal was to synthesize a functionalized [2]catenane with huge, noninteracting rings. The [2]catenane **6** carries four functionalities: two OH and two ester groups. After alkylation of the OH groups, the ester groups should be usable for polycondensation with, for example, diols. The [2]catenane **6** consists of two rings with 87 ring members. The rapid and quantitative formation of **5** from **1a** and triphosgene indicates a high flexibility of the cycle. The first hint that the rings do not interact is given by the NMR spectra; the shift and half width of the signals of **6** is nearly identical to that of the corresponding signals of cycle **1a**.

Using the described route, we were able to prepare 800 mg of [2]catenane **6** in one batch. The synthesis has a lot of steps, but these steps are very efficient, with yields of 70–90% of purified material. The same is true for the synthesis of the starting material **1a**.[12] The purification of the products is simple, and we do not envisage any trouble when running the synthesis on a larger scale.



Scheme 2. Route by which the monocyclic dimer **8** could have formed.

Experimental Section

General methods: All reactions were carried out under an inert atmosphere in dried Schlenk flasks. THF was dried over sodium/benzophenone, and triethylamine was dried over CaH_2. For flash chromatography, Merck silica gel (mesh 230–400) was used. If not stated otherwise, a mixture of petroleum ether (30–40 °C) and dichloromethane (1:1 v/v) was used as eluting solvent. Size exclusion chromatograms were obtained using an instrument from Waters (SDV gel, 10 m particle, pore sizes: 500, 10^5, and 10^6 Å) with THF (flow rate 10 mL min^{-1}) at 23 °C and RI detection. The melting points were determined using a melting table microscope (Reicher Thermovar). The NMR spectra were recorded on a Bruker instrument (AMX 300) at room temperature with $CDCl_3$. The signal assignment is based on increments taken from the literature[17] and the comparison of the spectra of **3**–**6** with those of the starting materials **1** and **2** and their synthetic precursors. The assignment of the ^{13}C NMR signals is in accordance with Dept-135 measurements. The only exception is the signal of C≡*C*H of compound **3b**. This signal does not appear in the DEPT spectrum, as we have observed in a variety of compounds of type ArC≡*C*H and AlkC≡*C*H. The description of the H and C atoms follows that given in Figure 4. The letters $\alpha,\beta,\gamma,\delta$ or $\alpha',\beta',\gamma',\delta'$ describe the atoms of the benzene rings of the acyclic and the cyclic part of the molecule, respectively.

Carbonate 3a: At room temperature, Et_3N (0.07 mL, 0.5 mmol) and, 20 min later, triphosgene (148 mg, 0.499 mmol) were added to a solution of cyclic compound **1a** (600 mg, 0.416 mmol) in THF (20 mL). After 4 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed twice with HCl (2 N). The combined organic phases were dried ($MgSO_4$), and the solvent was removed under vacuum. The off-white solid (**1b** containing about 4% of **5**) was used without further purification.

Sodium hydride (60% suspension in mineral oil, 19 mg, 0.47 mmol) was suspended in THF. After precipitation of NaH, the supernatant clear solution was removed by using a pipette, and the residue was suspended in THF (20 mL). Compound **2a** (660 mg, 0.415 mmol) was added to this suspension at room temperature. Fifteen minutes later, a solution of the chloroformate **1b** (obtained in the experiment described above) in THF

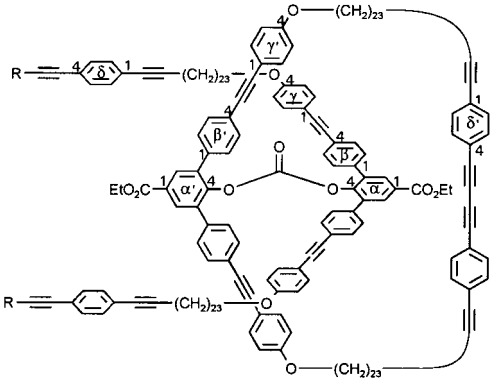


Figure 4. Lettering of the atoms for the assignment of the NMR data: The letters $\alpha,\beta,\gamma,\delta$ or $\alpha',\beta',\gamma',\delta'$ describe the atoms of the benzene rings of the acyclic and the cyclic part of the molecule, respectively.

(13 mL) was added. After 30 h, HCl (20 mL, 2 N) and CH_2Cl_2 (30 mL) were added to the reaction mixture. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were dried ($MgSO_4$), and the solvent was removed under acuum. Column chromatography gave **3a** (1.05 g, 83 %) as a beige colored wax. Another experiment starting from **1a** (230 mg) yielded **3a** (400 mg, 82 %).

M.p. 56.8 °C; ^{1}H NMR: $\delta = 7.87$, 7.86 (s, 4H, H_α-2, -6, $H_{\alpha'}$-2, -6), 7.58, 7.57 (half of an AA′XX′, 8H, H_γ-2, -6, $H_{\gamma'}$-2, -6), 7.40 – 7.27 (m, 32H, CH_β, $CH_{\beta'}$, CH_δ, $CH_{\delta'}$), 6.89 (half of an AA′XX′, 8H, H_γ-3, -5, $H_{\gamma'}$-3, -5), 4.32 (q, $J =$ 7 Hz, 4H, CO_2CH_2), 4.00, 3.98 (t, $J = 6$ Hz, 8H, $ArOCH_2$), 2.38, 2.37 (2t, $J = 7$ Hz, 8H, $CH_2C{\equiv}C$), 1.80 (m, 8H, OCH_2CH_2), 1.63 – 1.18 (m, 160H, $(CH_2)_{20}$), 1.32, 1.31 (2t, $J = 7$ Hz, 3H each, CH_3), 0.23 (s, 18H, $SiCH_3$); ^{13}C NMR: $\delta = 165.3$ (CO_2), 159.34, 159.31 (C_γ-4, $C_{\gamma'}$-4), 147.6 (CO_3), 147.19, 147.16 (C_α-4, $C_{\alpha'}$-4), 135.60, 135.56, 135.4 (C_α-3, -5, $C_{\alpha'}$-3, -5, C_β-1, $C_{\beta'}$-1), 133.2 (C_γ-2, -6, $C_{\gamma'}$-2, -6), 131.67 (C_β-3, -5, $C_{\beta'}$-3, -5), 132.2, 131.71, 131.5, 131.3 (C_α-2, -6, $C_{\alpha'}$-2, -6, C_δ-2, -6, $C_{\delta'}$-2, -6, C_δ-3, -5, $C_{\delta'}$-3, -5), 129.2 (C_α-1, $C_{\alpha'}$-1), 128.6 (C_β-2, -6, $C_{\beta'}$-2, -6), 125.2 ($C_{\delta'}$-1 or C_δ-4), 124.3 (C_δ-1 or C_δ-4), 123.3 (C_β-4, $C_{\beta'}$-4), 122.1 (C_δ-4 or C_δ-1), 120.6 ($C_{\delta'}$-4 or $C_{\delta'}$-1), 115.3 (C_γ-1, $C_{\gamma'}$-1), 114.72, 114.65 (C_γ-3, -5, $C_{\gamma'}$-3, -5), 104.8 (*C*≡CSi), 95.6 (C≡*C*Si), 93.6 ($CH_2C{\equiv}CAr_{\delta'}$), 92.6 ($CH_2C{\equiv}CAr_\delta$), 90.79, 90.76 ($Ar_\beta C{\equiv}CAr_\gamma$, $Ar_{\beta'}C{\equiv}CAr_{\gamma'}$), 88.29, 88.26 ($Ar_\beta C{\equiv}CAr_\gamma$, $Ar_{\beta'}C{\equiv}CAr_{\gamma'}$), 82.0 (*C*≡C–C≡*C*), 80.3 ($CH_2C{\equiv}CAr_\delta$), 80.2 ($CH_2C{\equiv}CAr_{\delta'}$), 75.2 (C≡*C*–*C*≡C), 68.2, 68.1 ($ArOCH_2$), 61.2 (CO_2CH_2), 29.7 – 28.7 (15 signals, $(CH_2)_{20}$), 26.1, 25.9 ($CH_2CH_2C{\equiv}C$), 19.52, 19.48 ($CH_2C{\equiv}C$), 14.3 (CH_3), – 0.1 ($SiCH_3$); $C_{213}H_{254}O_{11}Si_2$ (3046.54): calcd C 83.98, H 8.40; found C 83.71, H 8.52.

Carbonate 3b: A solution (1.32 mL) of KOH (285 mg, 5.1 mmol) in ethanol (51 mL) was added to a solution of **3a** (2.60 g, 0.853 mmol) in THF (30 mL). After 1.5 h at room temperature, the reaction was quenched with HCl (30 mL, 2 N). The aqueous phase was separated and extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), and the solvent was removed in vacuo. Column chromatography gave **3b** (1.9 g, 77 %) as a light yellow solid. Another experiment starting from **3a** (330 mg) yielded **3b** (254 mg, 81 %).

M.p. 89.9 °C; ^{1}H NMR: $\delta = 7.86$, 7.85 (s, 4H, H_α-2, -6, $H_{\alpha'}$-2, -6), 7.57, 7.56 (half of an AA′XX′ system, 8H, H_γ-2, -6, $H_{\gamma'}$-2, -6), 7.40 – 7.26 (m, 32H, CH_β, $CH_{\beta'}$, CH_δ, $CH_{\delta'}$), 6.88 (half of an AA′XX′ system, 8H, H_γ-3, -5, $H_{\gamma'}$-3, -5), 4.31, 4.30 (2q, $J = 7$ Hz, 4H, CO_2CH_2), 4.00, 3.97 (2t, $J = 6$ Hz, 8H, $ArOCH_2$), 3.11 (s, 2H, C≡CH), 2.38, 2.37 (2t, $J = 7$ Hz, 8H, $CH_2C{\equiv}C$), 1.80 (m, 8H, OCH_2CH_2), 1.31, 1.30 (2t, $J = 7$ Hz, 6H, CH_3), 1.63 – 1.17 (m, 160H, $(CH_2)_{20}$); ^{13}C NMR: $\delta = 165.3$ (CO_2), 159.4, 159.3 (C_γ-4, $C_{\gamma'}$-4), 147.6 (CO_3), 147.21, 147.18 (C_α-4, $C_{\alpha'}$-4), 135.62, 135.59, 135.4 (C_α-3, -5, $C_{\alpha'}$-3, -5, C_β-1, $C_{\beta'}$-1), 133.2 (C_γ-2, -6, $C_{\gamma'}$-2, -6), 131.7 (C_β-3, -5, $C_{\beta'}$-3, -5), 132.2, 131.9, 131.5, 131.4 (C_α-2, -6, $C_{\alpha'}$-2, -6, C_δ-2, -6, $C_{\delta'}$-2, -6, C_δ-3, -5, $C_{\delta'}$-3, -5), 129.2 (C_α-1, $C_{\alpha'}$-1), 128.6 (C_β-2, -6, $C_{\beta'}$-2, -6), 125.2 ($C_{\delta'}$-1), 124.8 (C_δ-1), 123.3 (C_β-4, $C_{\beta'}$-4), 121.1 (C_δ-4), 120.6 ($C_{\delta'}$-4), 115.3 (C_γ-1, $C_{\gamma'}$-1), 114.74, 114.67 (C_γ-3, -5, $C_{\gamma'}$-3, -5), 93.6 ($CH_2C{\equiv}CAr_{\delta'}$), 92.8 ($CH_2C{\equiv}CAr_\delta$), 90.80, 90.77 ($Ar_\beta C{\equiv}CAr_\gamma$, $Ar_{\beta'}C{\equiv}CAr_{\gamma'}$), 88.31, 88.28 ($Ar_\beta C{\equiv}CAr_\gamma$, $Ar_{\beta'}C{\equiv}CAr_{\gamma'}$), 83.4 (C≡CH), 82.0 (*C*≡C–C≡*C*), 80.23 ($CH_2C{\equiv}CAr_{\delta'}$), 80.18 ($CH_2C{\equiv}CAr_\delta$), 78.3 (C≡*C*H), 75.2 (C≡*C*–*C*≡C), 68.2, 68.1 ($ArOCH_2$), 61.3 (CO_2CH_2), 29.7 – 28.7 (13 signals,$(CH_2)_{20}$), 26.1, 25.9 ($CH_2CH_2C{\equiv}C$), 19.53, 19.48 ($CH_2C{\equiv}C$), 14.3 (CH_3); $C_{207}H_{248}O_{11}$ (2912.25): calcd C 85.37, H 8.58; found C 85.31, H 8.58.

Cyclization of 3b: Compound **3b** (1.50 g, 0.52 mmol) dissolved in pyridine (150 mL) was added to a suspension of CuCl (6.86 g, 69.2 mmol) and $CuCl_2$ (1.12 g, 8.30 mmol) in pyridine (1 L) at room temperature over a period of 120 h with the help of a syringe pump. After a further 24 h of reaction time, pyridine was distilled off (50 °C/10 mbar). The residue was dissolved in CH_2Cl_2 and HCl (2 N). The organic phase was separated and washed with HCl (2 N). The combined aqueous phases were extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), and the solvent was removed in vacuo. Column chromatography gave a mixture of **4** and **5** (1.35 g, 90 %; **4**:**5** ≅ 2.6:1) as a brownish solid.

^{1}H NMR: $\delta = 7.86$ (br s, 4H of **4**, H_α-2, -6 of **4**), 7.84 (s, 4H of **5**, H_α-2, -6 of **5**), 7.56, 7.55 (two halves of two AA′XX′ systems, 8H, H_γ-2, -6), 7.40 – 7.25 (m, 32H, $CH_{\beta'}$, $CH_{\delta'}$), 6.89 (half of an AA′XX′ system, 8H of **4**, H_γ-3, -5 of **4**), 6.87 (half of an AA′XX′ system, 8H of **5**, H_γ-3, -5 of **5**), 4.3 (q, $J = 7$ Hz, 4H, CO_2CH_2), 3.99 (t, $J = 6$ Hz, 8H, $ArOCH_2$), 2.37 (t, $J = 7$ Hz, 8H of **4**, $CH_2C{\equiv}C$ of **4**), 2.35 (t, $J = 7$ Hz, 8H of **5**, $CH_2C{\equiv}C$ of **5**), 1.79 (m, 8H, OCH_2CH_2), 1.30 (t, $J = 7$ Hz, 6H, CH_3), 1.60 – 1.17 (m, 160H, $(CH_2)_{20}$); ^{13}C NMR: $\delta = 165.3$ (CO_2), 159.4 (C_γ-4), 147.7 (CO_3), 147.2 (C_α-4), 135.6, 135.4 (br) (C_α-3, -5, C_β-1), 133.2 (C_γ-2, -6), 132.2 (C_α-2, -6, C_δ-2, -6), 131.7 (C_β-3, -5), 131.5 (C_δ-3, -5), 129.2 (C_α-1), 128.6 (br, C_β-2, -6), 125.2 (C_δ-1), 123.3 (C_β-4), 120.6 (C_δ-4), 115.3 (C_γ-1), 114.7 (C_γ-3, -5), 93.6 ($CH_2C{\equiv}C$), 90.8 ($Ar_\beta C{\equiv}CAr_\gamma$), 88.3 ($Ar_\beta C{\equiv}CAr_\gamma$), 82.0 (*C*≡C–C≡*C*), 80.2 ($CH_2C{\equiv}C$), 75.2 (C≡*C*–*C*≡C), 68.1 ($ArOCH_2$), 61.3 (CO_2CH_2), 29.6 – 28.7 (12 signals, $(CH_2)_{20}$), 25.9, 25.8 ($CH_2CH_2C{\equiv}C$), 19.5 ($CH_2C{\equiv}C$), 14.3 (CH_3).

Catenane 6: A solution of nBu$_4$NF (2.25 mL, 1 M) in THF was added to the mixture of **4** and **5** (1.30 g, 0.447 mmol; **4**:**5** ≅ 2.6:1) dissolved in THF (30 mL). After 24 h, the reaction mixture was diluted with CH_2Cl_2 and washed with water. The combined aqueous phases were extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$), and the solvent was removed in vacuo. Because of incomplete carbonate cleavage (approximately 65 % conversion), the product was treated once again, in exactly the same way as described above, resulting in complete cleavage. Column chromatography with petroleum ether – CH_2Cl_2 3:2 → 1:1 gave **6** (800 mg, 63 %) as an off-white solid and cycle **1a** (290 mg, 23 %). M.p. 79.5 °C; ^{1}H NMR: $\delta = 7.97$ (s, 4H, H_α-2, -6), 7.58, 7.50 (AA′XX′, 8H each, $CH_{\beta'}$), 7.46 (half of an AA′XX′ system , 8H, $H_{\gamma'}$-2, -6), 7.38, 7.29 (AA′XX′, 8H each, $CH_{\delta'}$), 6.84 (half of an AA′XX′ system, 8H, $H_{\gamma'}$-3, -5), 5.74 (s, 2H, OH), 4.35 (q, $J = 7$ Hz, 4H, CO_2CH_2), 3.94 (t, $J = 7$ Hz, 8H, $ArOCH_2$), 2.37 (t, $J = 7$ Hz, 8H, $CH_2C{\equiv}C$), 1.75 (m, 8H, OCH_2CH_2), 1.56 (m, 8H, $CH_2CH_2C{\equiv}C$), 1.36 (t, $J = 7$ Hz, 6H, CH_3), 1.29 (m, 152H, $(CH_2)_{19}$); ^{13}C NMR: $\delta = 166.1$ (CO_2), 159.4 ($C_{\gamma'}$-4), 153.3 ($C_{\alpha'}$-4), 135.9 ($C_{\beta'}$-1), 133.1 ($C_{\gamma'}$-2, -6), 132.2 ($C_{\delta'}$-2, -6 or $C_{\delta'}$-3, -5), 132.0 ($C_{\beta'}$-3, -5), 131.5 ($C_{\delta'}$-3, -5 or $C_{\delta'}$-2, -6), 131.4 ($C_{\alpha'}$-2, -6), 129.3 ($C_{\beta'}$-2, -6), 128.3 ($C_{\alpha'}$-3, -5), 125.2 ($C_{\delta'}$-1 or $C_{\delta'}$-4), 123.6, 123.3 ($C_{\alpha'}$-1, $C_{\beta'}$-4), 120.6 ($C_{\delta'}$-4 or $C_{\delta'}$-1), 115.0 ($C_{\gamma'}$-1), 114.6 ($C_{\gamma'}$-3, -5), 93.6 ($CH_2C{\equiv}C$), 90.6 ($Ar_{\beta'}C{\equiv}CAr_{\gamma'}$), 87.7 ($Ar_{\beta'}C{\equiv}CAr_{\gamma'}$), 82.0 (*C*≡C–C≡*C*), 80.3 ($CH_2C{\equiv}C$), 75.2 (C≡*C*–*C*≡C), 68.1 ($ArOCH_2$), 60.9 (CO_2CH_2), 29.7 – 28.67 (nine signals, $(CH_2)_{20}$), 25.9 ($CH_2CH_2C{\equiv}C$), 19.6 ($CH_2C{\equiv}C$), 14.4 (CH_3); $C_{206}H_{248}O_{10}$ (2884.24): calcd C 85.79, H 8.67; found C 85.66, H 8.75.

Intended formation of 5: Sodium hydride (60 % suspension in mineral oil; 3 mg, 0.08 mmol) was suspended in THF (2 mL). After precipitation of NaH, the supernatant clear solution was removed using a pipette, and the residue was again suspended in THF (5 mL). Compound **1a** (100 mg, 0.069 mmol) and, 10 min later, triphosgene (3.4 mg, 0.012 mmol) were added to this suspension. After 24 h of reaction at room temperature, the reaction mixture was worked up as described for **3a**. The conversion was determined by ^{1}H NMR spectroscopy to be 97 %. Column chromatography gave **5** (85 mg, 84 %) as a brownish solid.

^{1}H NMR: $\delta = 7.84$ (s, 4H, $H_{\alpha'}$-2, -6), 7.56 (half of an AA′XX′ system, 8H, $H_{\gamma'}$-2, -6), 7.40 – 7.25 (m, 32H, $CH_{\beta'}$, $CH_{\delta'}$), 6.88 (half of an AA′XX′ system, 8H, $H_{\gamma'}$-3, -5), 4.31 (q, $J = 7$ Hz, 4H, CO_2CH_2), 3.99 (t, $J = 6$ Hz, 8H, $ArOCH_2$), 2.35 (t, $J = 7$ Hz, 8H, $CH_2C{\equiv}C$), 1.79 (m, 8H, OCH_2CH_2), 1.31 (t, $J = 7$ Hz, 6H, CH_3), 1.60 – 1.17 (m, 160H, $(CH_2)_{20}$); ^{13}C NMR: $\delta = 165.3$ (CO_2), 159.3 ($C_{\gamma'}$-4), 147.7 (CO_3), 147.2 ($C_{\alpha'}$-4), 135.6, 135.4 ($C_{\alpha'}$-3, -5, $C_{\beta'}$-1), 133.2 ($C_{\gamma'}$-2, -6), 131.7 ($C_{\beta'}$-3, -5), 132.2, 131.5 ($C_{\alpha'}$-2, -6, $C_{\delta'}$-3, -5, $C_{\delta'}$-2, -6), 129.2 ($C_{\alpha'}$-1), 128.6 ($C_{\beta'}$-2, -6), 125.2 ($C_{\delta'}$-1 or $C_{\delta'}$-4), 123.3 ($C_{\beta'}$-4), 120.6 ($C_{\delta'}$-4 or $C_{\delta'}$-1), 115.4 ($C_{\gamma'}$-1), 114.7 ($C_{\gamma'}$-3, -5), 93.6 ($CH_2C{\equiv}C$), 90.8

0947-6539/99/0506-1732 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 6

($Ar_{\beta}C{\equiv}CAr_{\gamma}$), 88.3 ($Ar_{\beta}C{\equiv}CAr_{\gamma}$), 82.0 ($C{\equiv}C{-}C{\equiv}C$), 80.2 ($CH_2C{\equiv}C$), 75.2 ($C{\equiv}C{-}C{\equiv}C$), 68.0 ($ArOCH_2$), 61.2 ($CO_2CH_2$), 29.6–28.7 (12 signals, $(CH_2)_{20}$), 25.8 ($CH_2CH_2C{\equiv}C$), 19.6 ($CH_2C{\equiv}C$), 14.3 (CH_3); $C_{207}H_{246}O_{11}$ (2910.23): no correct elemental analysis was obtained; MALDI-TOF MS (dithranol as matrix): *m*/*z*: 2911.3 (most probable calculated mass: 2909.9).

Acknowledgments

We thank L. Goix for recording the MALDI-TOF mass spectra, Dr. J. Räder for his help with the recording of the FD-MS spectra, the German Science Foundation for financial support, and Dr. B. Ederer for carefully checking the manuscript.

[1] a) G. Schill, *Catenanes, Rotaxanes, and Knots*, Academic, New York, **1971**; b) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Chem. Rev.* **1987**, *87*, 795; c) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725.

[2] a) J.-P. Sauvage, *Acc. Chem. Res.* **1998**, *31*, 611; b) M. Asakawa, P. R. Ashton, S. E. Boyd, C. L. Brown, S. Menzer, D. Pasini, J. F. Stoddart, M. S. Tolley, A. J. P. White, D. J. Williams, P. G. Wyatt, *Chem. Eur. J.* **1997**, *3*, 463; c) M. Asakawa, P. R. Ashton, V. Balzani, A. Credi, C. Hamers, G. Mattersteig, M. Montalti, A. N. Shipway, N. Spencer, J. F. Stoddart, M. S. Tolley, M. Venturi, A. J. P. White, D. J. Williams, *Angew. Chem.* **1998**, *110*, 357; *Angew. Chem. Int. Ed.* **1998**, *37*, 333; d) A. Livoreil, J.-P. Sauvage, N. Armaroli, V. Balzani, L. Flamigni, B. Ventura, *J. Am. Chem. Soc.* **1997**, *119*, 12114; e) D. A. Leigh, K. Moody, J. P. Smart, K. J. Watson, A. M. Z. Slawin, *Angew. Chem.* **1996**, *108*, 326; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 306; f) D. A. Leigh, A. Murphy, J. P. Smart, M. S. Deleuze, F. Zerbetto, *J. Am. Chem. Soc.* **1998**, *120*, 6458.

[3] a) Y. Geerts, D. Muscat, K. Müllen, *Macromol. Chem. Phys.* **1995**, *196*, 3425; b) D. Muscat, A. Witte, W. Köhler, K. Müllen, Y. Geerts, *Macromol. Rapid Commun.* **1997**, *18*, 233; c) J.-L. Weidmann, J.-M. Kern, J.-P. Sauvage, Y. Geerts, D. Muscat, K. Müllen, *Chem. Commun.* **1996**, 1243; d) S. Shimada, K. Ishikawa, N. Tamaoki, *Acta Chem. Scand.* **1998**, *52*, 374; e) S. Menzer, A. J. P. White, D. J. Williams, M. Belohradský, C. Hamers, F. M. Raymo, A. N. Shipway, J. F. Stoddart, *Macromolecules*, **1998**, *31*, 295; f) C. Hamers, O. Kocian, F. M. Raymo, J. F. Stoddart, *Adv. Mater.* **1998**, *10*, 1366; g) C. Hamers, F. M. Raymo, J. F. Stoddart, *Eur. J. Org. Chem.* **1998**, 2101.

[4] The only published example of a [2]catenane with even larger rings [polystyrene and poly(2-vinylpyridine) macrocycles]: Y. Gan, D. Dong, T. E. Hogen-Esch, *Polym. Prepr. Am. Chem. Soc.* **1995**, *36(1)*, 408. This catenane has no functional groups and was isolated only in a very small amount.

[5] a) G. Schill, C. Zürcher, *Naturwissenschaften* **1971**, *58*, 40; b) K. Rißler, G. Schill, H. Fritz, W. Vetter, *Chem. Ber.* **1986**, *119*, 1347.

[6] a) C. O. Dietrich-Buchecker, J.-P. Sauvage, *Tetrahedron* **1990**, *46*, 503; b) J.-P. Sauvage, *Acc. Chem. Res.* **1990**, *23*, 319; C. O. Dietrich-Buchecker, C. Hemmert, A.-K. Khémiss, J.-P. Sauvage, *J. Am. Chem. Soc.* **1990**, *112*, 8002; c) J.-M. Kern, J.-P. Sauvage, J.-L. Weidmann, *Tetrahedron*, **1996**, *52*, 10921; B. Mohr, M. Weck, J.-P. Sauvage, R. H. Grubbs, *Angew. Chem.* **1997**, *109*, 1365; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1310.

[7] D. B. Amabilino, P. R. Ashton, C. L. Brown, E. Córdova, L. A. Godínez, T. T. Goodnow, A. E. Kaifer, S. P. Newton, M. Pietraszkiewicz, D. Philp, F. M. Raymo, A. S. Reder, M. T. Rutland, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, D. J. Williams, *J. Am. Chem. Soc.* **1995**, *117*, 1271.

[8] C. A. Hunter, *J. Am. Chem. Soc.* **1992**, *114*, 5303.

[9] a) R. Jäger, F. Vögtle, *Angew. Chem.* **1997**, *109*, 966; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 930; b) F. Vögtle, T. Dünnwald, T. Schmidt, *Acc. Chem. Res.* **1996**, *29*, 451; c) S. Baumann, R. Jäger, F. Ahuis, B. Kray, F. Vögtle, *Liebigs Ann./Recueil* **1997**, 761.

[10] a) A. G. Johnston, D. A. Leigh, R. J. Pritchard, M. D. Deegan, *Angew. Chem.* **1995**, *107*, 1324; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1209; b) A. G. Johnston, D. A. Leigh, L. Nezhat, J. P. Smart, M. D. Deegan, *Angew. Chem.* **1995**, *107*, 1327; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1212.

[11] Results from X-ray structure analysis on single crystals of model compounds; A. Godt, Ö. Ünsal, V. Enkelmann, unpublished results.

[12] Ö. Ünsal, A. Godt, unpublished results on the synthesis of the starting material.

[13] H. Eckert, B. Forster, *Angew. Chem.* **1987**, *99*, 922; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 894.

[14] D. O'Krongly, S. R. Denmeade, M. Y. Chiang, R. Breslow, *J. Am. Chem. Soc.* **1985**, *107*, 5544.

[15] No indication of competing ester cleavage was found. Contrary to that, in the presence of hydroxide in THF, the carbonate group was inert, while the ester group was cleaved.

[16] Dithranol was used as a matrix. Additional signals with much lower intensity were found for $[M{+}Na]^+$, $[M{+}K]^+$, $[M{+}$dithranol$]$, and for the clusters $[2M(\mathbf{6})]^+$ (5771.4), $[2M(\mathbf{1a})]^+$ (2885.3), and $[3M(\mathbf{1a})]^+$ (4328.1).

[17] a) M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der organischen Chemie*, Thieme, Stuttgart, **1979**; b) H.-O. Kalinowski, S. Berger, S. Braun, *^{13}C-NMR-Spektroskopie*, Thieme, Stuttgart, **1984**.

Received: December 16, 1998 [F1498]