Macrobicyclic Hexalactones – Synthesis, Host-Guest Properties and Electrochemistry

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Abstract. The synthesis of a family of new host type molecules (1-4) bearing six lactone structural units is described. One of the lactones (1) forms crystals which contain benzene in a 1:2 (host:guest) ratio. The complexation behaviour towards potential guest molecules and the electrochemical properties of the molecules are studied. Compared to an analogous open chained ester (18) the electrochemical potentials of the bicyclic lactones 1, 2 are higher due to the different steric environment.

Key words. Benzene inclusion, cyclovoltammetry, electrochemistry, ester, host/guest chemistry, lactone, macro-bicyclic compounds, macrocyclic molecules, triphenylamine units.

1. Introduction

There has been much progress with respect to the inclusion chemistry of cyclodextrins [1] and, in particular, of synthetic macrocyclic cavities [2]. One aim of such work is to enclose a nonpolar guest inside a water soluble host cavity by taking advantage of the hydrophobic and other effects.

Here we report on the synthesis of some new host molecules (1-4) bearing triphenylamine units as trifunctional spacers, which are bridged by ester units with different kinds of divalent spacer groups (B in 1-4).

The triphenylamine units incorporated in all of these potential host molecules possessing a large spacious cavity is of interest because it should allow electrochemical reactions (oxidations) [3] in the neighbourhood of the molecular cavity [4].

If the bridging units B consist of a hydrocarbon chain, a water insoluble macrobicyclic compound 1 is obtained. When quaternary amino groups are introduced into the bridge B, the solubility in polar solvents should increase. Yet the design of an optimal host structure is complicated by the fact that, on the one hand, for electrochemical investigations of this type of triphenylamine derivative water is not a suitable solvent, and, on the other hand, water insoluble host compounds cannot take advantage of the hydrophobic effect as a driving force for host/guest complexation.

The following substances were chosen as diol components: 1,4-butanediol (5; for 1); 2,6-Bis(hydroxymethyl)pyridine (6; for 2); 3,5-Bis(hydroxymethyl)-N,N-dimethylaniline (7; for 3) and N-methyldiethanolamine (8; for 4).

The lactones 1 and 2, formed by the first two diols, should be especially suited to electrochemical investigations because of the electrochemical stability of their functional groups. In analogy to the open chained water soluble diesters 9 and 10 of benzoic acid, the lactones 3 and 4 should be sufficiently hydrophilic after quaternization of the nitrogen atoms in the bridges.

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2. Experimental

4,4',4"-Tris(p-bromophenyl)amine (11) [5]: A solution of 23.97 g (150 mmol) of bromine in 150 mL of trichloromethane was slowly added to a solution of 12.27 g (50.0 mmol) of triphenylamine in 100 mL of trichloromethane. After work-up 21.4 g (89%) of the desired product was obtained, m.p. 144–145°C. ¹HNMR (90 MHz, CDCl₃/TMS_{int.}): δ = 6.96, 7.40 (AA'BB', J = 9 Hz, 12H, ar-H) ppm. MS: m/z = 481, 483 (M[⊕], 100%). C₁₈H₁₂Br₃N (482.01); Calcd. C 44.85, H 2.51, N 2.91; Found C 44.99, H 2.58, N 3.06.

4,4'4"-Nitrilotris-benzoic acid (12): To a solution of 4.82 g (10.0 mmol) of 11 in ca. 50 mL of dry diethylether 21 mL (33.6 mmol) of a 1.6M n-butyllithium solution was added at 0°C in an ultrasonic bath. A strong CO₂ stream was bubbled through the precipitated lithiated compound for 30 min and subsequently for 30 min at room temperature. Work-up of the mixture with NaHCO₃ solution/ether yielded 3.4 g (90%) of the crude acid 12 after precipitation with HCl. A further purification could be achieved by chromatographic work-up on reversed phase column material (LiChroprep RP-8, 25–40 μ m) with methanol/water (2.7 : 1) and yielded 1.1 g (29%) of the pure acid. $R_F = 0.46$; m.p. 271–272°C. ¹H-NMR (90 MHz, CD₃OD = 3.35 ppm): $\delta = 7.21$, 8.03 (AA'BB', J = 9 Hz, 12H, ar-H) ppm. MS: m/z = 337 (100%). C₂₁H₁₅NO₆ (377.35); Calcd. C 66.84, H 4.01, N 3.71; Found C 66.84, H 4.17, N 3.95.

4,4',4"-Nitrilotris-benzoic acid chloride (13): 3.77 g (19.0 mmol) of 12 were refluxed with 20 mL of thionylchloride for 3 h. After evaporation of the excess of SOCl₂ the residue was recrystallized from toluene/n-hexane and yielded 3.8 g (88%) of the desired yellow product, m.p. 235-237°C. ¹H-NMR (90 MHz, $CD_2Cl_2 = 5.25$ ppm): $\delta = 7.29$, 8.16 (AA'BB', 12H, ar-H, J = 9 Hz) ppm. MS: m/z = 431, 433 (M $^{\oplus}$), 396, 398 (M $^{\oplus}$ -Cl, 100%). $C_{21}H_{12}Cl_3NO_3$ (432.69); Calcd. C 58.29, H 2.80, N 3.24; Found C 58.73, H 2.73, N 3.27.

4,4',4''-Nitrilotris(1,4-phenylene-carbonyloxy)tributanol (14); [Nitrilotris(1,4-phenylene-carbonyloxymethylene-2,6-pyridinediyl)]trimethanol (15); Nitrilotris[1,4-phenylene-carbonyloxymethylene(5-dimethylamino)-1,3-phenylene]trimethanol (16); 2,2',2''-Nitrilotris-[1,4-phenylene-carbonyloxyethylene-(N-methylimino)]triethanol (17): 4.30 g (10.0 mmol) of the crude acid chloride 13 (obtained from the crude acid 12) dissolved in 100 mL of dry THF were added to a boiling mixture of 100 mmol of the corresponding diol (5–8), 10 mL of pyridine, a little amount of DMAP and 150 mL of dry THF during a 4 h period. After complete addition the mixture was refluxed for an additional 2 h and the solvent was evaporated in vacuo. The excess of diol was solvated by water and the oily residue was purified by chromatography on silica gel (63–100 μ m) with trichloromethane/ethanol (6:1).

14: Yield: 1.6 g (27%), $R_F = 0.49$ (CHCl₃/EtOH 6 : 1), m.p. 82–83°C. ¹H-NMR (90 MHz, CD₃OD/TMS_{int.}): $\delta = 1.76$ (m, 12H, CH₂), 3.62 (t, 6H, CH₂OH, J = 6 Hz), 4.29 (t, 6H, CH₂OCOR, J = 6 Hz), 7.13, 7.99 (AA'BB', 12H, ar-H, J = 9 Hz) ppm. ¹³C-NMR (22.36 MHz, CD₂Cl₂/TMS_{int.}): $\delta = 26.41$, 30.13 (CH₂), 62.43, 65.96 (OCO—CH₂, —CH₂OH), 125.04, 126.88, 132.28, 151.87 (ar-C), 167.37 (ester-C) ppm. MS: m/z = 593 (M[®]); C₃₃H₃₉NO₉ (593.65); Calcd. C 66.77, H 6.62, N 2.36; Found C 66.29 [6], H 6.45, N 2.28.

15: Yield: 1.96 g (26.5%), $R_F = 0.45$ (CHCl₃/EtOH 6: 1), m.p. 57–59°C. ¹H-NMR (200 MHz, DMSO = 2.5 ppm): $\delta = 4.56$ (d, 6H, CH₂OH, J = 6 Hz), 5.36 (s, 6H, CH₂—OCO), 5.46 (t, 3H, OH, J = 6 Hz), 7.22, 8.01 (AA'BB', 12H, J = 9 Hz, ar-H), 7.34 (d, 3H, J = 8 Hz), 7.44 (d, 3H, J = 8 Hz, 7.83 (t, 4H, J = 8 Hz). ¹³C-NMR (50.3 MHz, CDCl₃/TMS_{int.}): $\delta = 64.13$, 66.94 ((CH₂OH, OCO–CH₂), 119.82, 120.22, 124.01, 125.28, 131.57, 137.62, 150.63, 155.07, 159.20 (ar-C), 165.57 (ester-C) ppm. C₄₂H₃₆N₄O₉ (740.77); Calcd. C 68.10, H 4.90, N 7.56; Found C 67.92; H 4.89, N 7.83.

16: Yield: 2.0 g (23%), $R_F = 0.61$ (CHCl₃/EtOH 6:1), m.p. 100–102°C. ¹H-NMR (200 MHz, CDCl₃/TMS_{int.}): $\delta = 2.97$ (s, 18H, N—CH₃), 4.65 (s, 6H, CH₂OH), 5.28 (s, 6H, CH₂OCOR), 6.70 (s, 6H, ar-H), 6.77 (s, 3H, ar-H), 7.09, 7.97 (AA/BB', 12H, ar-H, J = 9 Hz) ppm. ¹³C-NMR (50.3 MHz, CDCl₃/TMS_{int.}): $\delta = 40.65$ (N—CH₃), 65.74, 67.23 (CH₂OH, CH₂OCOR), 110.89, 111.60, 114.94, 123.87, 125.62, 131.45, 137.27, 142.39, 150.48, 151.09 (ar-C), 165.92 (ester-C) ppm. C₅₁H₅₄N₄O₉ (867.01); Calcd. C 70.65, H 6.28, N 6.46; Found C 69.91 [6], H 6.06, N 6.34.

17: Yield: 315 mg (46.3%), oil (from 1 mmol of pure acid chloride; the product was not purified by chromatography). 1 H-NMR (200 MHz, CD₃OD = 3.35 ppm): δ = 2.37 (s, 9H, NCH₃), 2.64 (t, 6H, N—CH₂—CH₂—OH, J = 6 Hz), 2.84 (t, 6H, N—CH₂—CH₂—OCOR, J = 6 Hz), 3.66 (t, 6H, CH₂OH, J = 6 Hz), 4.39 (t, 6H, CH₂OCO, J = 6 Hz), 7.09, 7.94 (AA'BB', 12H, ar-H, J = 9 Hz) ppm. 13 C-NMR (50.3 MHz, CDCl₃ = 77.1 ppm): δ = 42.01 (N—CH₃), 55.80, 58.23, 58.91, 62.37 (chain-C), 123.77, 125.26, 131.19, 150.32 (ar-C), 165.79 (ester-C) ppm.

Cyclization of the esters: 1.00 mmol of the 'elongated triester' (14-17) and 1.00 mmol of the pure acid chloride 13 were dissolved separately in 50 mL of a mixture of dry THF and dry benzene and during a 6 h period in an argon atmosphere simultaneously dropped into a boiling mixture of 200 mL of THF/benzene (1:1), 10 mL of pyridine and a small amount of cesium carbonate. After complete addition the mixture was refluxed for an additional 8 h and after that the solvent was removed in vacuo. The dried residue was taken up in a dichloromethane/water mixture, the aqueous layer again twice extracted and the organic layer dried. After evaporation of the solvent the crude product was purified on silica gel with dichloromethane/acetone (4:1) as solvent. The resulting esters which were often oily, were dissolved in a small amount of dichloromethane and precipitated as colourless powders by adding a large excess of n-hexane.

6,13,23,39,46-Hexaoxo-7,12,24,39,40,45-hexaoxa-1,18-diazaoctacyclo[16.16.16.2^{2,5}.2^{14,17}. $2^{19,22}.2^{31.34}.2^{35.38}.2^{47,50}$]dohexaconta-2,4,14,16,19,21,31,33,35,37,47,49,51,53,55,57,59,61-octadecane (1): Yield: 88 mg (9.6%), $R_F = 0.82$ (CH₂Cl₂/acetone 4:1), m.p. 170–172°C. ¹H-NMR (200 MHz, CDCl₃): $\delta = 1.98$ (m, 12H, CH₂), 4.39 (m, 12H, CH₂OCO), 6.86, 7.87 (AA′BB′, 24H, ar-H, J = 9 Hz) ppm. ¹³C-NMR (50.3 MHz, CDCl₃): $\delta = 26.12$ (CH₂), 64.03 (CH₂OCO), 123.79, 125.96, 131.39, 150.30 (ar-C), 165.75 (ester C) ppm. MS: m/z = 916 (M $^{\oplus}$). C₅₄H₄₈N₂O₁₂ (916.98); Calcd. C 70.73, H 5.28, N 3.05; Found C 70.61, H 5.51, N 2.76.

6,16,26,36,45,55-Hexaoxo - 7,15,27,35,46,54-hexaoxa - 1,21,72,73,74-pentaazaundecacyclo- $[19.19.19.2^{2,5}.2^{17,20}.2^{22,25}.2^{37,40}.2^{41,44}.2^{56,59}.1^{9,13}.1^{29,33}.1^{48,52}]$ tetraheptaconta - 2,4,9,11,13-(72),17,19,22,24,29,31,33(73),37,39,41,43,48,50,52(74),56,58,60,62,64,66,68,70-hepta-

cosaene (2): Yield: 78 mg (7.3%), $R_F = 0.59$ (CH₂Cl₂/acetone 4: 1), m.p. > 300°C (dec.). ¹H-NMR (200 MHz, CDCl₃): $\delta = 5.39$ (s, 12H, CH₂), 6.88, 7.84 (AA′BB′, 24H, ar-H, J = 9 Hz), 7.30(d, 3H, ar-H, J = 8 Hz), 7.70 (t, 6H, ar-H, J = 8 Hz) ppm. ¹³C-NMR (50.3 MHz, CD₂Cl₂): $\delta = 66.63$ (CH₂), 121.85, 123.97, 125.87, 131.52, 137.39, 150.25, 156.08 (ar–C, 165.73 (ester–C) ppm. MS: m/z = 1063 (M[⊕]). C₆₃H₄₅N₅O₁₂ (1064.08); Calcd. C 71.11, H 4.26, N 6.58; Found C 70.61, H 4.45, N 6.58.

 $11,31,50\text{-}Tris(dimethylamino)-6,16,26,36,45,55\text{-}hexaoxo-7,15,27,35,46,54\text{-}hexaoxa-1,21-diazaundecacyclo}[19.19.19.2^{2,5}.2^{17,20}.2^{22,25}.2^{37,40}.2^{41,44}.2^{56,59}.1^{9,13}.1^{29,33}.1^{48,52}]tetrahepta-conta-2,4,9,11,13(72),17,19,22,24,29,31,33(73),37,39,41,43,48,50,52(74),56,58,60,62,64,66,68,70-heptacosaene (3): Yield: 98 mg (8.2%), <math>R_F = 0.78$ (CH₂Cl₂/acetone 4:1), m.p. > 300°C (dec.). ¹H-NMR (200 MHz, CDCl₃): $\delta = 2.98$ (s, 18H, NCH₃), 5.36 (s, 12H, CH₂OCO), 6.56 (s, 6H, ar-H), 7.01 (s, 3H, ar-H), 6.94, 7.92 (AA′BB′, 24H, ar-H, J = 9 Hz) ppm. ¹³C-NMR (22.36 MHz, CDCl₃): $\delta = 40.65$ (NCH₃), 66.39 (CH₂(OCO), 109.65, 111.83, 123.87, 125.87, 131.48, 138.08, 150.28, 150.64 (ar-C), 165.56 (ester-C) ppm. MS (FAB, glycerine matrix): m/z = 1190 (M + H); C₇₂H₆₄N₅O₁₂ (1190.32); Calcd. C 72.65, H 5.34, N 5.88; Found C 72.72, H 5.86, N 5.97.

 $10,28,45\text{-}Trimethyl-6,14,24,32,41,49\text{-}hexaoxo-7,13,24,31,42,48\text{-}hexaoxa-1,10,19,28,45-pentaazaoctacyclo}[17.17.17.2^{2,5}.2^{15,18}.2^{20,23}.2^{33,36}.2^{37,40}.2^{50,53}]pentahexaconta-2,4,15,17,20,22,33,35,37,39,50,52,54,56,58,60,62,64\text{-}octadecaene} (4): Yield: 85 mg (8.5%), <math>R_F = 0.7$ (CH₂Cl₂/EtOH 6:1), m.p. 143–145°C (dec.). ¹H-NMR (200 MHz, CDCl₃): $\delta = 2.37$ ($s, 9H, NCH_3$), 2.77–2.96 (m, 12H, NCH₂), 4.34–4.54 (m, 12H, CH₂OCO), 6.85, 7.83 (AA'BB', 24H, ar-H, J = 9 Hz) ppm. ¹³C-NMR (50.3 MHz, CDCl₃): $\delta = 42.39$ (NCH₃), 56.20 (NCH₂), 61.98 (CH₂OCO), 123.63, 125.76, 131.40, 150.00 (ar-C), 165.83 (ester-C) ppm FAB-MS $C_{57}H_{57}N_5O_{12}$ (1004.11).

Electrochemical Experiments: A 2×10^{-3} M solution of the lactone (1–3, 18) in CH₃CN/CH₂Cl₂ (1:1) (0.1M LiClO₄) was prepared and analyzed by cyclovoltammetry. A Methrom EA-876-5 cell served as the electrolysis vessel. It was equipped with a platinum working electrode (0.18 cm²) and a platinum counter electrode as well as a Ag/AgNO₃ reference electrode. For recording the cyclovoltammograms an Amel potentiostate, model 553, combined with a Kontron, model PG 8200, function generator and a Hewlett-Packard 7045A xy recorder was used. The potential scan rate was varied from 10–360 mV/s.

3. Syntheses

The preparation of all cyclic esters was achieved by the following sequence (Scheme 1): triphenylamine was easily brominated to give the product 11 [5] in high yield. Reaction of 11 with *n*-butyllithium in ether, followed by reaction with CO₂ yielded the triacid 12, which was purified by chromatography on reversed phase column material (RP 8). The acid chloride 13, which was easily obtained, could be reacted with a large excess of the corresponding diol (5–8) to yield the pure intermediate products 14–17 after chromatographic purification. Cyclization of these triols with the equivalent quantity of the acid chloride 13 led to the bicyclic lactones 1–4 after chromatographic purification with yields ranging between 7–10%.

4. Host/Guest Interactions

4.1. CRYSTALLINE BENZENE ADDUCT

CPK space filling models suggest that the shape of the molecular cavity of the lactones 1-4 should allow the inclusion of flat guest molecules of the size of benzene. Indeed, by slow crystallization of the bicyclic lactone 1 from benzene/n-heptane, large, strong refracting crystals were obtained, which contain *two* equivalents of benzene (host/guest stoichiometry determined by ¹H-NMR spectroscopy).

The quality of the crystals rendered them suitable for an X-ray crystal structure analysis. However, because of the large size and complexity of the unit cell a relation between the measured reflexions and the structure has not been achieved so far by an orientating study. The question whether a (crystal lattice) clathrate or an inclusion inside the molecular cavity is present, can therefore not definitely be decided.

4.2. 1H-NMR INVESTIGATIONS

The bicyclic esters 3 and 4 can easily be converted into the corresponding ammonium salts. Yet, the iodides obtained with iodomethane are insoluble in water in contrast to the open chained esters 9 and 10. Thus, 1 H-NMR investigations could be carried out only in DMSO- d_6 as solvent. The shifts of the proton signals found with potential guest substances (e.g. 2,3-dihydroxynaphthalene, triphenylene, naphthalene) were only small (<0.1 ppm). In this solvent no strong indication for a complexation of guests in the cavity of 3 and 4 is found.

5. Electrochemical Studies

Due to their triphenylamine unit all esters are accessible for electrochemical investigations by cyclovoltammetry. The stable radical cations of the triphenylamine units may be

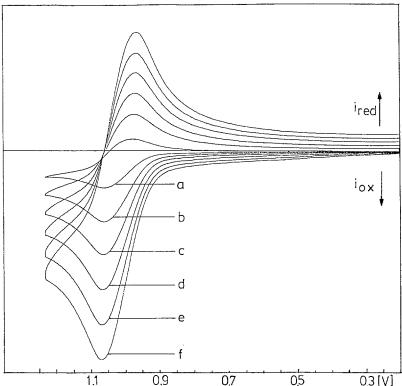


Fig. 1. Cyclovoltammograms of the lactone 2. Potential range 200–1230 mV [Ag/AgNO₃ (0.1M in CH₃CN)], potential scan rate (a–f): 10, 40, 90, 160, 250, 360 mV/s, concentration of 2: 2×10^{-3} M in CH₃CN/CH₂Cl₂ (1:1) (0.1M LiClO₄). The Ag/AgNO₃ reference electrode has a potential of 590 mV vs. NHE.

generated and regenerated electrochemically and serve as oxidizing agents in numerous indirect electrochemical oxidations [7]. As is known, the oxidation potentials of triphenylamine units are very sensitive to steric effects of substituents or bridges in the 4,4',4"-position, which result in specific conformational arrangements of the aromatic groups [4, 8].

Accordingly, the redox potential of the bicyclic compounds 1 and 2, in comparison to that of the open chained compound 18, may be used as a probe for steric effects [4].

The cyclovoltammograms of the new ring compounds 1 and 2 (Figure 1) and that of 18 are quite similar. They all show one redox pair which can be attributed to the formation of the triarylamine radical cation. It exhibits electrochemical and chemical reversibility for all compounds, and the oxidative peak current is diffusion controlled. The potential of the first oxidation step of the more strained (compared to 1) lactone 2 is about 85 mV and that of the less strained lactone 1 about 35 mV shifted to more positive values in comparison to the open chained compound 18 (see Table I). This reflects the different steric environment due to the different conformations of the phenylene groups in the bicyclic compound.

A different electrochemical behaviour is shown by the lactone 3. During the first potential scan (40 mV/s) (Figure 2) an irreversible weak anodic peak is observed at 1015 mV (vs. NHE) as well as a reversible redox pair at 1655/1580 mV (vs. NHE). The redox potential and the peak current of the second redox pair during the first scan are comparable to those of the other bicyclic lactones. The potential of the irreversible anodic peak has a value

Table I. Potentials of compounds 1, 2 and 18^a

Cpd.	$E_{\text{ox}1}$	$E_{\rm red1}$
1	1595	1545
2	1645	1575
18	1560	1500

^a Potentials in mV vs. NHE.

comparable to the oxidation potential of N,N-dimethylaniline [9], whereas the second reversible redox pair corresponds to the triphenylamine unit in the lactones. During the following potential scans without stirring in between, the first oxidation peak is moved to more positive potentials and overlaps with the oxidation peak of the triphenylamine units. At the same time the peak current of the triphenylamine redox pair is rising continuously, until it reaches its maximum value after the 8th scan. The maximum peak current is larger than that of the first scan by a factor of about three. Simultaneously, the corresponding oxidative peak potential moves to less positive potentials, whereas the reduction potential remains at nearly constant values. Thereby the peak potential difference decreases from

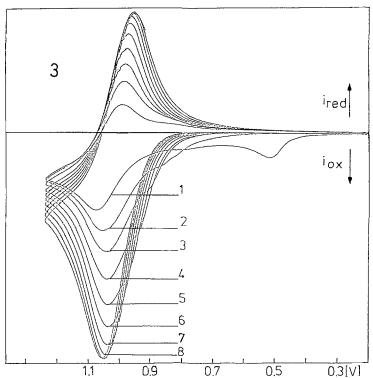


Fig. 2. Cyclovoltammograms of the lactone 3. Potential range 200–1230 mV [Ag/AgNO₃ (0.1M in CH₃CN)], potential scan rate: 40 mV/s, the numbering corresponds to the sequence of the scans; concentration of 3: 2×10^{-3} M in CH₃CN/CH₂Cl₂ (1:1) (0.1M LiClO₄). The Ag/AgNO₃ reference electrode has a potential of 590 mV vs. NHE.

75 mV to 55 mV. This behaviour may be due to an increase of the surface concentration of 3 either by adsorption or polymerization. However, more detailed electroanalytical studies are necessary to explain this unusual behaviour.

As a consequence of this study the synthesis of host molecules, which can be switched electrochemically and are capable of incorporating guest molecules inside their cavity and reacting them by a redox function, remains an interesting goal in the field of host/guest chemistry, concave chemistry and organic catalysts.

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