

by NMR. The rotaxane was concentrated mainly in the benzene fraction, with an additional amount in the chloroform fraction. From the former fraction the rotaxane (0.74 g, 11.2%) was isolated: uv (ethanol λ_{max} 252 m μ (ϵ 1010), 256 (1150), 262 (1200), 275 (3520); ir (Nujol) 1595, 1500, 1255, 1105, 765, 745 cm $^{-1}$. No OH absorption was found at 3300–3500; NMR (CDCl $_3$) δ 3.17 (m, 4 H, CH $_2$ OCH $_2$), 3.58 (s, 112 H, -CH $_2$ -O-), 3.78 (m, 8 H, -CH $_2$ CH $_2$ OAr), 4.10 (m, 8 H, -CH $_2$ OAr), 6.81 (s, 8 H, catechol protons), 7.19 (m, 30 H, Ph $_3$ C-).

Anal. Calcd for C $_{115.2}$ H $_{160.4}$ O $_{33.6}$: C, 65.66; H, 7.89. Found: C, 65.61; H, 7.70.

The CCl $_4$ fraction contained ω,ω' -di(*O*-trityl)poly(ethylene glycol): NMR (CCl $_4$) δ 3.17 (m, 4 H, -CH $_2$ OCH $_2$), 3.58 (s, 58 H, -CH $_2$ O-), 7.21 (m, 30 H, Ph $_3$ C-); $\overline{\text{DP}}$ of PEG chain from NMR 15.5 (mol wt 700).

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Synthesis of a Catenane by a Statistical Double-Stage Method

Giora Agam and Albert Zilkha*

Contribution from the Department of Organic Chemistry,

The Hebrew University of Jerusalem, Jerusalem, Israel. Received August 11, 1975

Abstract: A novel two-stage statistical synthesis of catenanes was developed based on converting a rotaxane to a catenane. In the first stage, [2]- ω,ω' -bis-*O*-[*p*-(α -bromotolyl)diphenylmethyl]poly(ethylene glycol) 400-[dibenzo-58.2-crown-19.4]rotaxane was synthesized by the statistical method by mixing the "crown" polyether with poly(ethylene glycol) 400 to produce a threading equilibrium mixture at maximum concentration and blocking the hydroxyl end groups with bromomethyltrityl groups. In the second stage the rotaxane was cyclized through the α -bromotolyl end groups in very dilute solution in DMF with zinc/copper couple to yield the catenane [2]-{*cyclo*-[1,2-diphenylethane-*p,p'*-di(α -benzhydryl)poly(ethylene glycol) 400]}-[dibenzo-58.2-crown-19.4] in 14% yield. Besides the catenane, a fraction of oligorotaxane having a $\overline{\text{DP}}$ of 3 was formed by linear condensation polymerization.

The statistical method for preparing topological isomers gives very low yields of catenane.^{1,2} It presents two contradictory requirements: very high concentration of chain and ring molecules to permit maximum threading and, at the same time, very low concentrations for the cyclization of the chain to produce a macrocyclic ring.

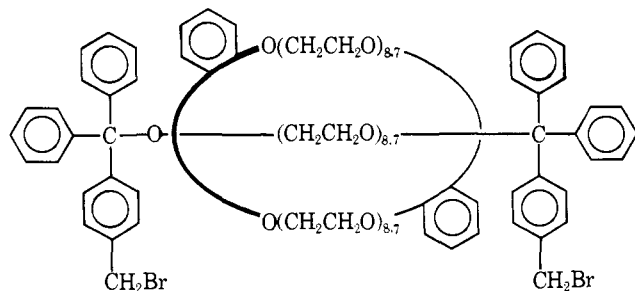
Previously³ we reported the statistical synthesis in relatively high yield (15%) of [2]-[ω,ω' -di(*O*-trityl)poly(ethylene glycol) 400]-[dibenzo-58.2-crown-19.4]rotaxane, where the ring is a macrocyclic crown polyether based on poly(ethylene glycol) 400. In the present work we made use of the relative stability of a similar rotaxane to cyclize its linear chain through its two

blocking groups, under conditions of high dilution to yield a catenane.

Results and Discussion

A rotaxane III, having terminal functional groups for cyclization, was prepared by mixing poly(ethylene glycol) 400 with the macrocyclic "crown" polyether,³ dibenzo-58.2-crown-19.4 (I), in equimolar amounts. The mixture was heated at 120 °C for 30 min to affect threading equilibration, followed by reacting the glycol chain ends with the blocking group, *p*-(α -bromotolyl)diphenylbromomethane (II), which has been synthesized for this purpose.

Several means of attaching the blocking group in this reaction were investigated. The principle of minimum dilution of the reaction mixture to ensure high yields of rotaxane was utilized. Direct combination of the reactants under vacuum to remove generated hydrogen bromide gave rather low yields (25–30%). Addition of amines resulted in the formation of polymers as was previously noted with similar compounds.⁴ Similar results were obtained in the presence of solid calcium carbonate. However, solid potassium carbonate gave 45–50% yield in the tritylation reaction. The rotaxane (III) desired,



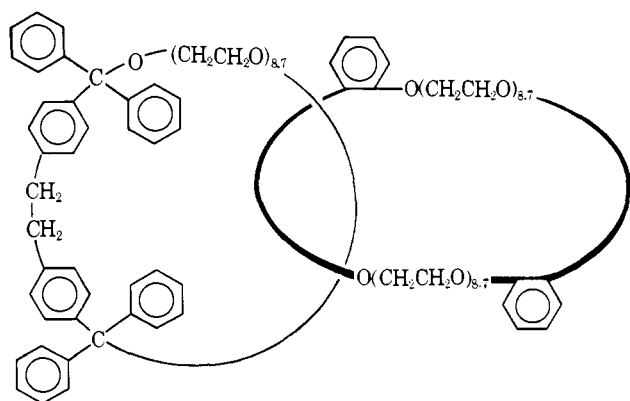
III

[2- ω,ω' -bis-*O*-[*p*-(α -bromotolyl)diphenylmethyl]poly(ethylene glycol) 400-[dibenzo-58.2-crown-19.4]rotaxane, was isolated by partition chromatography on a silica gel-water system in relatively high yield (18.5%).

Elementary analysis and spectra δ , (ir, uv, and NMR) of the rotaxane indicated the presence of an equimolar mixture of the ring and chain components. TLC showed that the rotaxane has R_f between, and distinct from, its two components. Partition chromatography also indicated the structure of the rotaxane.

Hydrolysis of the bromomethyltrityl blocking groups by boiling 80% acetic acid gave, in about 60% yield, the three expected products: poly(ethylene glycol) 400, *p*-(α -bromotolyl)diphenylmethanol, and dibenzo-58.2-crown-19.4 (I). The identity of I with the starting material is regarded as evidence for the absence of a chemical bond between the two components. Molecular weight determination by the Rast method⁵ gave, as did the previously prepared rotaxane,³ the mean average weight of its components, apparently due to the relative freedom of movement in the molecule.

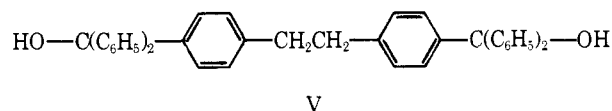
The cyclization of the rotaxane to the catenane (IV) had to be carried out at high dilution to ensure maximum yield. Several reagents were tried for the cyclization using the *O*-tritylated poly(ethylene glycol) as substrate. Zinc/copper couple⁶ in DMF was found to be an effective reagent for the dehalogenation-coupling reaction of the bromomethyltrityl blocking groups. The catenane (IV) was obtained in 14% yield



IV

after separation by adsorption chromatography. Ir, uv, and NMR spectra of the catenane corresponded to spectra of equimolar mixtures of its components. The mass spectrum did

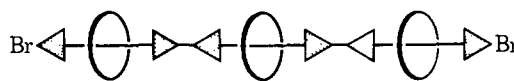
not show any molecular ion, probably due to the thermal instability of the trityl bonds and to the relatively high molecular weight of the product.^{7–9} Cryoscopically measured molecular weight showed again the mean average weight of the components, probably due to the large rings which permit freedom of movement to a great extent. The catenane was clearly distinguished from its components (and their mixtures) by TLC on silica gel GF 254, developed by a mixture of methanol-butanol (5:4). Hydrolysis of the trityl groups in the catenane molecule by boiling in 80% acetic acid for 1.5 h and TLC analysis of the hydrolysate confirmed the presence of poly(ethylene glycol) 400, the crown ring (I), as well as 1,2-bis[4-(α -hydroxybenzhydryl)phenyl]ethane¹⁰ (V) which shows that



V

coupling of the blocking groups did occur. We thus conclude that the isolated product is a catenane.

Another topological isomer produced in the cyclization reaction as a result of linear polymerization was apparently an oligorotaxane having the schematic structure shown below.



It was isolated in 23% yield, and evidence for its structure was obtained from spectral and elementary analyses and TLC. Its molecular weight, as measured by the Rast method, was again found to be the mean weight of its four components (three rings and one chain).

In conclusion, the synthesis of the catenane reported is the first case of converting one topological isomer (rotaxane) to another (catenane) in which the topological isomers are obtained in few stages and in relatively high yield.

Experimental Section

Materials and Apparatus. Uv spectra (in ethanol) were taken on a Unicam SP800 spectrometer, ir spectra (in KBr) on a Perkin-Elmer Model 457 instrument, NMR spectra on a Varian HA-100 instrument, and mass spectra on an Atlas MAT CH4 instrument. TLC was carried out on silica gel GF 254 (Merck) visualized by uv lamp and iodine vapors adsorption. Molecular weights were determined by the Rast method⁵ using camphor and carbon tetrabromide. Chloroform and carbon tetrachloride for column chromatography were distilled under reduced pressure. Dimethylformamide was distilled over P_2O_5 . Poly(ethylene glycol) 400 (Fluka) was dried by azeotropic distillation with benzene.

Dibenzo-58.2-crown-19.4 (I)³ was prepared according to Pederson's method¹¹ starting with poly(ethylene glycol) 400.

***p*-(α -Bromotolyl)diphenylmethanol.** *N*-Bromosuccinimide (18.7 g, 0.105 mol) and α,α' -azobis(isobutyronitrile) (0.95 g) were added to a solution of crude diphenyl-*p*-tolylmethanol¹² (27.4 g, 0.1 mol) in carbon tetrachloride (150 ml), and the mixture was heated under reflux for 2.5 h. It was cooled and filtered, and the solvent was evaporated. The residue was separated by column chromatography on alumina (activity II–III), using the eluent mixtures hexane/ CCl_4 and $CCl_4/CHCl_3$. *p*-(α -Bromotolyl)diphenylmethanol (10.5 g, 30%) was isolated as an orange viscous liquid, which could not be crystallized from many solvents, even on prolonged standing: NMR (CCl_4) δ 2.45 (s, 1, OH), 4.25 (s, 2, $ArCH_2Br$), 7.01 (s, 14, aromatic). No peak of $ArCH_3$ at δ 2.35 was found.

Anal. Calcd for $C_{20}H_{17}OBr$: C, 67.99; H, 4.82; Br, 22.66. Found: C, 68.43; H, 4.75; Br, 22.81.

***p*-(α -Bromotolyl)diphenylbromomethane.** To a solution of *p*-(α -bromotolyl)diphenylmethanol (10.6 g, 0.03 mol) in ether (100 ml), anhydrous calcium chloride (4 g) was added, and dry HBr was passed through the mixture for 2 h. The mixture was filtered and evaporated to yield a brown viscous liquid, which was crystallized from heptane to give *p*-(α -bromotolyl)diphenylbromomethane (9.9 g, 79%): mp 93

°C uncor; NMR (CCl₄) δ 4.25, (s, 2, ArCH₂Br), 7.02 (s, 14, aromatic hydrogens); ir, no OH absorption at 3445 cm⁻¹.

Anal. Calcd for C₂₀H₁₆Br₂: C, 57.69; H, 3.85; Br, 38.46. Found: C, 57.49; H, 4.16; Br, 38.63.

ω,ω'-Bis-O-[p-(α-bromotolyl)diphenylmethyl]poly(ethylene glycol) 400, *p*-(α-Bromotolyl)diphenylbromomethane (5.0 g, 0.012 mol) was heated under nitrogen at 120 °C with poly(ethylene glycol) 400 (2.0 g, 0.005 mol), and anhydrous potassium carbonate (1.8 g, 0.013 mol) was added portionwise during 1 h with stirring. The mixture was stirred for an additional 5 h, cooled, diluted with CCl₄ (30 ml), and filtered. The product, a brown viscous liquid (2.1 g, 47%), was isolated by column chromatography on alumina (activity I) containing 25% water, using mixtures of hexane/CCl₄ as eluents. NMR (CDCl₃) δ 3.10 (m, 4, CH₂OAr₃), 3.56 (s, 31, -CH₂O-), 4.32 (s, 4, ArCH₂Br), 7.20 (m, 28, aromatic hydrogens); ir, no OH absorption at 3300–3500⁻¹.

Anal. Calcd for C_{57.4}H_{66.8}O_{9.7}Br₂: C, 64.33; H, 6.24; Br, 14.94. Found: C, 64.06; H, 6.35; Br, 15.01.

[2]-{ω,ω'-Bis-O-[p-(α-bromotolyl)diphenylmethyl]poly(ethylene glycol) 400}-[dibenzo-58.2-crown-19.4]rotaxane (III), Dibenzo-58.2-crown-19.4 (1.9 g, 0.002 mol) was mixed with poly(ethyleneglycol) 400 (0.8 g, 0.002 mol) and heated under nitrogen at 120 °C for 1 h. *p*-(α-Bromotolyl)diphenylbromomethane (2.5 g, 0.006 mol) was added, followed by anhydrous potassium carbonate (1 g). The mixture was stirred at 120 °C for 5 h, diluted with CCl₄, and filtered. The filtrate was separated by gradient partition chromatography using silica gel (Hopkin and Williams MFC) (50 g) containing 25% water, with the eluent mixtures cyclohexane/CCl₄ and CCl₄/CHCl₃. The course of the elution was followed by TLC on silica gel, developed with the mixture methanol (5)–1-butanol (4). (*R_f* of rotaxane, 0.15–0.53; of I, 0.0–0.1, and of ω,ω'-bis-O-[p-(α-bromotolyl)diphenylmethyl]poly(ethylene glycol) 400, 0.77–0.95.) The rotaxane was obtained as a brown viscous liquid (0.65 g, 18.5%). The ir and NMR spectra were identical with those of an equimolar mixture of the rotaxane components.

Anal. Calcd for C_{104.2}H_{144.4}O_{29.1}Br₂: C, 61.89; H, 7.15; Br, 7.92; Mn 2020. Found: C, 61.80; H, 7.26; Br, 8.08; Mn (Rast), 964 ± 83.

The rotaxane was hydrolyzed by boiling in acetic acid (80%). The hydrolysate was evaporated, and the residue was separated by extraction with chloroform and water. The aqueous phase yielded poly(ethylene glycol) 400, while the chloroformic phase gave *p*-(α-bromotolyl)diphenylmethanol and dibenzo-58.2-crown-19.4 in 55–60% yield on separation on preparative TLC using silica gel PF254. All compounds were identified by chromatographic and spectroscopic methods as well as elemental analysis.

cyclo-[1,2-Diphenylethane-*p,p'*-di(α-benzhydryl)poly(ethylene glycol) 400]. To a solution of ω,ω'-bis-O-[p-(α-bromotolyl)diphenylmethyl]poly(ethylene glycol) 400 (0.25 g, 2.3 × 10⁻⁴ mol) in DMF (400 ml), freshly prepared Zn/Cu powder (200 mg), prepared according to Corbin et al.,⁶ was added. The mixture was stirred for 96 h at room temperature, filtered, centrifuged, and evaporated to dryness in vacuo until the NMR spectrum showed no more DMF. The residue was separated by gradient chromatography on Kieselgel 60 (Merck, activity 2–3) with CCl₄/CHCl₃ and CHCl₃/methanol mixtures, and then by preparative TLC on silica gel, developed by toluene (100)–dioxane (40)–methanol (23). The product (*R_f* = 0.4–0.6) (0.034 g,

16%) was obtained as a brown viscous liquid: NMR (CDCl₃) δ 2.91 (s, 4, ArCH₂CH₂Ar) (new peak); peak at 4.32 (ArCH₂Br) disappeared.

Anal. Calcd for C_{57.4}H_{66.8}O_{9.7}: C, 75.63; H, 7.33; Mn, 911. Found: C, 76.10; H, 7.36; Br, 0.42; Mn (Rast), 902 ± 110.

Another product that was separated in the chromatography was that of oligo-ω,ω'-bis[α-(4-benzyl)benzhydryl]poly(ethylene glycol) 400 (0.049 g, 23%) having Br end groups.

Anal. Calcd for C_{172.2}H_{200.4}O_{29.1}Br₂ (DP_n = 3): C, 71.44; H, 6.93; Br, 5.53; Mn, 2892. Found: C, 71.28; H, 7.05; Br, 5.80; Mn (in CBr₄) 3210 ± 440.

The ir spectrum showed the characteristic absorptions of ω,ω'-bis-O-[p-(α-bromotolyl)diphenylmethyl]poly(ethylene glycol) 400, and the NMR spectrum showed peaks for ArCH₂Br (δ 4.32,s) and for ArCH₂CH₂Ar (δ 2.91,s), and the integration ratio was 1:2, respectively,

[2]-{cyclo-[1,2-Diphenylethane-*p,p'*-di(α-benzhydryl)poly(ethylene glycol) 400]-[dibenzo-58.2-crown-19.4]catenane (IV). The rotaxane III (0.43 g) was dissolved in DMF (700 ml) and cyclized by reaction with Zn/Cu couple (6 g), as described before. The mixture was separated by chromatography on Kieselgel 60, elution being carried out with a gradient of chloroform–methanol mixture (0–20% methanol). The separation was followed by TLC on silica gel, developed with toluene–dioxane–methanol (100:40:23). The catenane (0.055 g, 14%), having *R_f* 0.3–0.4, was isolated as brown viscous liquid.

Anal. Calcd for C_{104.2}H_{144.4}O_{29.1}: C, 64.79; H, 7.76; Mn 1860. Found: C, 64.89; H, 7.59; Mn 1978 ± 150.

The ir and NMR spectra were identical with those of an equimolar mixture of the catenane components.

Another fraction that was separated in the chromatograph of the cyclization reaction mixture was that of [4]-[oligo-ω,ω'-bis-α-(4-benzyl)benzhydryl]poly(ethylene glycol) 400]-tris(dibenzo-58.2-crown-19.4)]rotaxane (0.032 g, 8%) having Br end groups and DP_n = 3.

Anal. Calcd for C_{312.6}H_{433.2}O_{87.3}Br₂ (DP = 3): C, 65.51; H, 7.54; Br, 2.78. Found: C, 65.42; H, 7.60; Br, 2.81.

The principal absorptions in the ir spectrum were the same as those for the starting rotaxane. The NMR spectrum showed absorptions at δ [2.9 (ArCH₂CH₂Ar) and 4.32 (ArCH₂Br)] in the integration ratio 1.95:1.

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