

Supporting Information

An Hermaphrodite [2]Rotaxane: Preparation and Analysis of Structure

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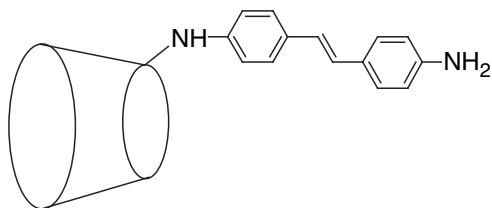
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General Information:

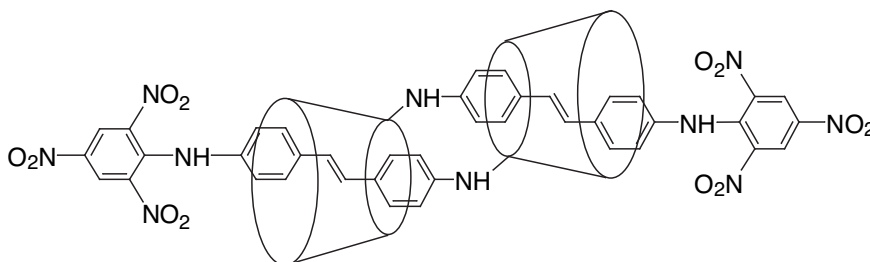
TLC was performed on Keiselgel 60 F₂₅₄ coated plates (Merck), developed with butanol/ethanol/water (5:4:3), and visualised using ultraviolet light and/or by dipping into a solution of 0.1% 1,3-dihydroxynaphthalene in ethanol/water/sulfuric acid (200:157:43), followed by heating. R_f values are quoted relative to those of 6^A-*O*-tosyl- α -cyclodextrin **1** (i.e., R_f 1.0). Under these conditions α -cyclodextrin had R_f 0.65. Preparative HPLC was performed using a SymmetryPrep C18 column (7 μ m, 19 \times 300 mm, Waters), eluted with acetonitrile/water (75:25). Analytical HPLC was performed using a Symmetry C18 column (5 μ m, 4.6 \times 250 mm, Waters), eluted with acetonitrile/water (75:25) at a flow rate of 1 mL min⁻¹. Under the analytical conditions 6^A-*O*-tosyl- α -cyclodextrin **1** and α -cyclodextrin had retention times (t_R) of 3.4 and 6.8 min, respectively.

6^A-[(*E*)-4'-Aminostilben-4-ylamino]-6^A-deoxy- α -cyclodextrin (3**):**



A mixture of 6^A-*O*-tosyl- α -cyclodextrin **1** (0.5 g, 0.45 mmol), (*E*)-4,4'-diaminostilbene (284 mg, 1.35 mmol) and potassium iodide (70 mg) in *N*-methylpyrrolidinone (10 mL) was stirred at 80 °C for 40 h, then it was added dropwise into acetone (75 mL). The resulting precipitate was collected by filtration and mixed with water (100 mL), to give a suspension which was filtered. The filtrate was concentrated in vacuo and the residue was subjected to preparative HPLC to give the title compound **3** as an off-white powder (100 mg, 19%); TLC R_f : 1.05; Analytical HPLC t_R : 3.6 min; ESI m/z : 1165 (M+H)⁺; ¹H NMR (D₂O, δ): 7.63 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 6.99 (d, J = 8.3 Hz, 2H), 6.84 (d, J = 16.6 Hz, 2H), 6.70 (d, J = 16.6 Hz, 2H), 6.47 (d, J = 8.3 Hz, 2H), 5.12–4.97 (m, 6H), 4.17–2.96 (m, 36H).

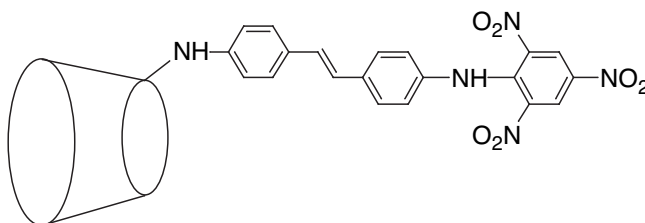
6^A-[(*E*)-4'-(2,4,6-Trinitrophenylamino)stilben-4-ylamino]-6^A-deoxy- α -cyclodextrin-[2]-rotaxane (7**):**



The stilbene **3** (20 mg, 17 μ mol) was dissolved in 0.2 M pH 10 aqueous carbonate buffer (0.5 mL) at 25 °C, then sodium 2,4,6-trinitrobenzenesulfonate dihydrate (7.3 mg, 21 μ mol) was added and the mixture was stirred at 25 °C for 10 h before it was added dropwise into acetone (10 mL). The resulting suspension was centrifuged and the supernatant was decanted. The remaining solid was washed with acetone (10 mL) and analysed by HPLC to show the presence of the rotaxane dimer **7** and the corresponding monomer **6** in the ratio ca. 50:1. Preparative HPLC of this material gave the title compound **7** as a dark red powder (15.3 mg, 65%); TLC R_f : 0.9; Analytical HPLC t_R : 2.8 min; MALDI-TOF m/z : 2753 ($M+H$)⁺; ¹H NMR (D₂O, δ) 9.20 (s, 4H), 7.82 (d, J = 7.8 Hz, 4H), 7.36 (d, J = 7.8 Hz, 4H), 7.17 (d, J = 7.8 Hz, 4H), 6.93 (d, J = 16.1 Hz, 4H), 6.88 (d, J = 16.1 Hz, 4H), 6.51 (d, J = 7.8 Hz, 4H), 5.13–4.99 (m, 12H), 4.16–3.00 (m, 72H).

6^A-[(*E*)-4'-(2,4,6-Trinitrophenylamino)stilben-4-ylamino]-6^A-deoxy- α -cyclodextrin

(6):



A mixture of the stilbene **3** (20 mg, 17 μ mol) and sodium 2,4,6-trinitrobenzenesulfonate dihydrate (144 mg, 0.41 mmol) in *N,N*-dimethylformamide (5 mL) was stirred at 25 °C for 24 h before it was added dropwise into acetone (10 mL). The resulting suspension was centrifuged and the supernatant was decanted. The remaining solid was washed with acetone (10 mL) and analysed by HPLC to show the presence of the rotaxane dimer **7** and the corresponding monomer **6** in the ratio ca. 1:25. Preparative HPLC of this material gave the title compound **6** as a dark red powder (15.0 mg, 64%); TLC R_f : 1.2; Analytical HPLC t_R : 5.8 min; MALDI-TOF m/z : 1377 ($M+H$)⁺; ¹H NMR (d_4 -methanol, δ) 9.06 (s, 2H), 7.47 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 16.6 Hz, 2H), 6.90 (d, J = 16.6 Hz, 2H), 6.74 (d, J = 8.8 Hz, 2H), 5.00–4.90 (m, 6H), 4.04–3.46 (m, 36H).