Supporting Information

Rotational isomerism of the amide units in rotaxanes based on a cyclic tetraamide and secondary ammonium ions

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Experimental
Synthesis of the ammonium salts 6a and 6b.

Synthesis of the bulky aniline derivative 7a.

Synthesis of the bulky aniline derivative 7b.

1,4-Benzodioxan-2-one (4)
1,4-Benzodioxan-2-one was prepared according to a literature procedure.¹ Chloroacetyl chloride (8.73 mL, 110 mmol) was added to a solution of catechol (11.0 g, 100 mmol) and Et₃N (27.7 mL, 200 mmol) in CH₂Cl₂ (100 mL) at 0 °C and then the
mixture was heated under reflux for 1 day. The reaction mixture was diluted with AcOEt (300 mL). The organic phase was washed sequentially with H₂O, 10% NaHCO₃, and sat. NaCl, dried (MgSO₄), and concentrated. The residue was purified through gel column chromatography (SiO₂; hexane/AcOEt, 10:1) to give colorless crystals (9.04 g, 60%). ¹H NMR (500 MHz, CDCl₃) δ: 4.67 (s, 2H), 7.01–7.12 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ: 64.8, 117.3, 117.5, 123.4, 125.4, 141.0, 142.4, 163.2.

The ¹H and ¹³C NMR spectra of 6a were identical to those reported previously.¹

**Mono-ammonium salt (6a)**²

Et₃N (3 drops) was added to a solution of 4-(dimethoxymethyl)benzylamine (1.20 g, 6.62 mmol) and terephthalaldehyde mono(diethyl acetal) (2.07 g, 9.93 mmol) in CH₂Cl₂ (23 mL) at room temperature and then the mixture was stirred for 18 h at the same temperature. After addition of Na₂SO₄ and filtration of the reaction mixture, the filtrate was concentrated. The residue was dissolved in EtOH (43 mL). NaBH₄ (0.345 g, 17.1 mmol) was added to the solution at room temperature. After stirring overnight, 1 N NaOH was added to the mixture and then the EtOH was evaporated. The residue was diluted with water. The aqueous phase was extracted with CH₂Cl₂. The combined extracts were dried (Na₂SO₄) and concentrated. The residue was purified chromatographically (SiO₂; AcOEt) to give a crude product (2.14 g), which was used without further purification.

A solution of the crude amine in THF (40 mL) and 10% HCl (10 mL) was stirred for 22 h. The acidic solution was neutralized with sat. Na₂CO₃ and then the THF was evaporated. CH₂Cl₂ was added. The organic phase was separated, washed with sat. NaCl, dried (Na₂SO₄), and concentrated. The residue was dissolved in Et₂O (40 mL). A solution of HCl in dioxane (4.2 M, 2.03 mL, 8.59 mmol) was added and then the precipitate was collected through filtration and washed with iPr₂O. The solid was suspended in acetone (35 mL) and H₂O (35 mL). NH₄PF₆ (4.67 g, 28.6 mmol) was added and then the mixture was stirred for 3.5 h. After evaporation of the acetone, the precipitate was filtered off and washed with water to give a white powder (1.83 g, 47%). ¹H NMR (500 MHz, DMSO-d₆, 30 °C) δ: 4.33 (s, 4H), 7.69–7.74 (m, 2H), 7.69–8.01 (m, 4H), 9.38 (br s, 2H), 10.04 (s, 2H). ¹³C NMR (125 MHz, DMSO-d₆, 30 °C) δ: 50.0, 129.7, 130.6, 136.4, 138.1, 192.8.

The ¹H and ¹³C NMR spectra of 6a were identical to those reported previously.²

**Bis-ammonium salt (6b)**

![Diagram of bis-ammonium salt (6b)](image_url)
Compound 6b (white powder, 4.79 g, 40%) was synthesized from ethylenediamine (0.860 mL, 12.8 mol) and 4-(dimethoxymethyl)benzylamine (5.60 g, 26.9 mmol), using the procedure described above. IR (KBr, $\nu_{\text{max}}$, cm$^{-1}$): 3617, 3549, 3381, 2918, 2763, 1694, 1612, 1445, 1216, 1179, 1021, 836, 562. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 3.25 (br s, 4H), 4.34 (br s, 4H), 7.69 (d, $J = 7.0$ Hz, 4H), 8.01 (d, $J = 7.0$ Hz, 4H), 8.96 (br s, 4H), 10.05 (s, 2H). $^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta$: 42.5, 49.9, 129.9, 130.4, 192.8. HRMS (FAB) calcd. for C$_{18}$H$_{21}$N$_2$O$_2$+ [M – HCl – Cl]$^+$ m/z 297.1598, found 297.1623.

3,5-Diphenylnitrobenzene (S3)

Tetrakis(triphenylphosphine) palladium (46.2 mg, 0.040 mmol) was added to a two-phase solution of 3,5-dibromonitrobenzene (S2, 1.12 g, 4.00 mmol), phenylboronic acid (1.22 g, 10.0 mmol), and triphenylphosphine (0.105 g, 0.40 mmol) in toluene (15 mL), EtOH (7.5 mL), and 2 M aqueous Na$_2$CO$_3$ (10 mL, 20.0 mmol) and then the mixture was heated under reflux for 40 h. After evaporation of the organic solvent, water was added to the residue. The aqueous phase was extracted with AcOEt. The combined organic phases were washed with sat. Na$_2$CO$_3$ and sat. NaCl, dried (MgSO$_4$), filtered, and concentrated. The residue was washed with MeOH to afford a white solid (0.562 g, 55%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.43–7.49 (m, 2H), 7.50–7.55 (m, 4H), 7.67–7.71 (m, 4H), 8.12 (t, $J = 1.5$ Hz, 1H), 8.43 (t, $J = 1.5$ Hz, 4H). The $^1$H NMR spectrum of S3 was identical to that reported previously.

3,5-Diphenylaniline (7a)

Raney Ni (W-2, catalytic amount) was added to a solution of the nitrobenzene S3 (0.652 g, 11.2 mmol) and hydrazine monohydrate (0.95 mL, 19.5 mmol) in THF (10 mL) and EtOH (10 mL) and then the mixture was heated under reflux overnight. The reaction mixture was filtered through Celite and the filtrate was concentrated. The residue was washed with AcOEt and hexane to afford a white solid (0.480 g, 83%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.83 (br s, 2H), 6.90 (d, $J = 1.5$ Hz, 2H), 7.21 (t, $J = 1.5$ Hz, 2H), 7.32–7.38 (m, 2H), 7.41–7.47 (m, 4H), 7.59–7.64 (m, 4H). The $^1$H NMR spectrum of S3 was identical to that reported previously.
References
Figure S1. VT $^1$H NMR spectra (600 MHz, DMSO-d$_6$) of the cyclic tetraamide 1, recorded at (a) 25, (b) 50, (c) 75, (d) 100, and (e) 125 °C.
Figure S2. VT $^1$H NMR spectra [600 MHz, CDCl$_3$/CD$_3$CN (1:1)] of a mixture of the cyclic tetraamide 1 (2.0 mM) and the mono-ammonium salt 6a (1.4 eq), recorded at (a) 20, (b) 10, (c) 0, and (d) –10 °C.
Figure S3a. COSY spectrum (600 MHz, CDCl₃, 25 °C) of the [2]rotaxane 8a.
**Figure S3b.** ROESY spectrum (600 MHz, CDCl$_3$, 25 °C) of the [2]rotaxane 8a.
Figure S4a. COSY spectrum (600 MHz, CDCl₃, 25 °C) of the [2]rotaxane 8b.
Figure S4b. ROESY spectrum (600 MHz, CDCl₃, 25 °C) of the [2]rotaxane 8b.
Figure S5. VT $^1$H NMR spectra (600 MHz, DMSO-$d_6$) of the [2]rotaxane 8a, recorded at (a) 25, (b) 50, (c) 75, (d) 100, and (e) 125 °C.
Figure S6. $^1$H NMR spectra (600 MHz) of the [2]rotaxane 8b in (a) CDCl$_3$ and (b) DMSO-$d_6$. 
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Figure S7b. ROESY spectrum (600 MHz, DMSO-$d_6$, 25 °C) of the [2]rotaxane 8a.
Figure S8a. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 50 °C) of 2a.

Figure S8b. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 2a.
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**Figure S9b.** $^{13}$C NMR spectrum (125 MHz, D$_2$O/DMSO-$d_6$, 5:1, 30 °C) of 2b.
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Figure S10b. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, 55 °C) of 3.
Figure S11a. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of 4.

Figure S11b. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 4.
Figure S12a. $^1$H NMR spectrum (500 MHz, DMSO-$d_6$, 110 °C) of 5.

Figure S12b. $^{13}$C NMR spectrum (150 MHz, CDCl$_3$) of 5.
**Figure S13a.** $^1$H NMR spectrum (500 MHz, DMSO-$d_6$, 110 °C) of 1.

**Figure S13b.** $^1$H NMR spectrum (500 MHz, CDCl$_3$) of 1.
Figure S14a. $^1$H NMR spectrum (500 MHz, DMSO-$d_6$, 30 °C) of 6a.

Figure S14b. $^{13}$C NMR spectrum (125 MHz, DMSO-$d_6$, 30 °C) of 6a.
Figure S15a. $^1$H NMR spectrum (500 MHz, DMSO-$d_6$) of 6b.

Figure S15b. $^{13}$C NMR spectrum (125 MHz, DMSO-$d_6$) of 6b.
Figure S16. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of S3.

Figure S17. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of 7a.
Figure S18. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of 7b.
Figure S19a. $^1$H NMR spectrum (600 MHz, CDCl$_3$) of the [2]rotaxane 8a.

Figure S19b. $^{13}$C NMR spectrum (150 MHz, CDCl$_3$, 40 °C) of the [2]rotaxane 8a.
Figure S20a. $^1$H NMR spectrum (600 MHz, CDCl$_3$) of the [2]rotaxane 8b.

Figure S20b. $^{13}$C NMR spectrum (150 MHz, CDCl$_3$) of the [2]rotaxane 8b.