Novel template effect for the preparation of [2]rotaxanes with functionalised centre pieces

Pradyut Ghosh, Oliver Mermagen, and Christoph A. Schalley*

Supplementary Information

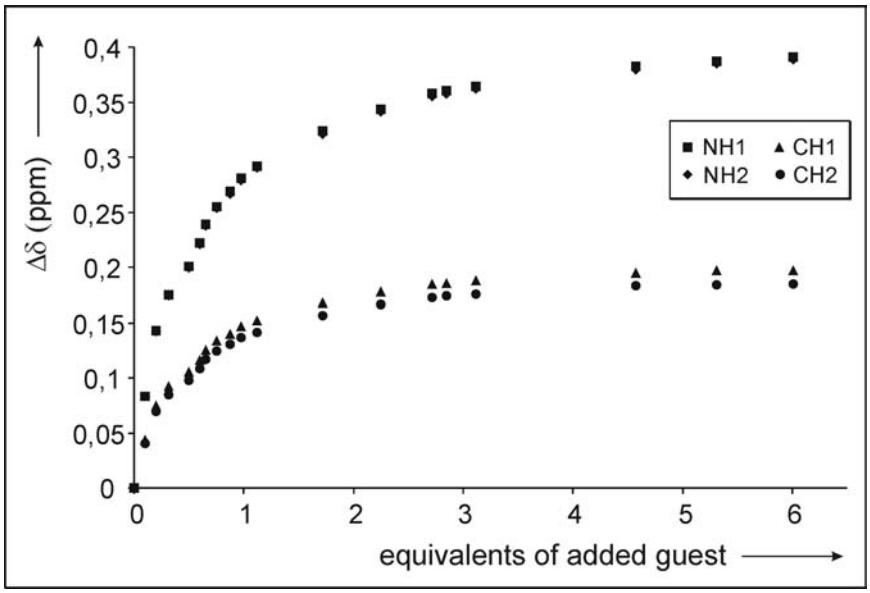
a) Synthesis and selected analytical data

Synthesis of the axle centre piece **8** consists of three steps. In brief, acid chloride **6** is prepared from the corresponding acid, followed by reaction with mono-Boc protected ethylene diamine yielding diamide **7** which is purified as a colourless wax-like solid by column chromatography on silica gel with 8:1 CH_2Cl_2/MeOH as the eluent. Finally, the methyl and Boc groups can be cleaved in one step with BBr_3. Centre piece **11** can be synthesised analogously.

To a solution of 0.1 mmol of the axle centre piece in 20 ml CH_2Cl_2, 1.05 eq. of P_1 base are added and the mixture is stirred for ca. 15 min at r.t. Then, the wheel is added and the mixture stirred for another 15 min, followed by slow, simultaneous addition of 2 eq. of triphenyl acetic acid chloride and 2 eq. of triethyl amine. After complete addition, the mixture is stirred over night. The work-up includes acidification by 1 M HCl and threefold extraction of the acidic aqueous phase with CH_2Cl_2. After evaporation of the solvents, rotaxane **10** is separated by column chromatography on silica gel with 4:1 CH_2Cl_2/EE. Yield: 20 – 30%. Selected analytical data for **10**: ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 15.70 (s, 1H, OH), 8.71 (s, 2H, NH), 8.55 (s, 2H, NH), 8.52 (s, 2H, NH), 8.45 (s, 2H, NH), 8.05 (d, ^{4}J=1.2 Hz, 1H, ArH_{wh}), 8.03 (d, ^{4}J=1.2 Hz, 2H, ArH_{wh}), 8.02 (s, 1H, ArH_{wh}), 7.99 (d, ^{3}J=7.8 Hz, 2H, ArH_{wh}), 7.70 (t, ^{3}J=7.8 Hz, 1H, ArH_{wh}), 7.13-7.02 (m, 24H, *o*-,*m*-PhH_{ax}), 6.97-6.92 (s, 8H, ArH_{wh}), 6.90-6.81 (m, 9H, *p*-PhH_{ax}, ArH_{ax}), 2.86-2.71 (m, 8H, CH_{2ax}), 2.32-2.18 (m, 8H, CH_{2wh}), 1.92 (s, 12H, CH_3), 1.91 (s, 12H, CH_3), 1.63-1.53 (m, 8H, CH_{2wh}), 1.52-1.44 (m, 4H, CH_{2wh}), 1.40 (s, 9H, *t*-BuCH_3). ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 165.3, 165.1, 161.0, 152.9, 148.1, 143.2, 143.2, 135.3, 135.2, 135.2, 134.9, 134.8, 132.1, 132.0, 131.4, 130.4, 128.0, 127.9, 127.1, 126.1, 67.6, 45.1, 35.4, 35.3, 31.4, 26.3, 23.2, 19.0, 18.8, 18.7. MALDI-MS ($C_{116}H_{118}N_8O_9$): 1808 [MK^+] (3%), 1791 [MNa^+] (37%), 1769 [MH^+] (100%), 983 [wheelNa^+] (3%), 961 [wheelH^+] (5%), 807 [axleH^+] (< 2%).

b) Determination of the binding constant

In the literature (ref. 10), values for the binding of *p*-substituted phenolates in wheel **3** are given as $K > 10^5\ M^{-1}$ in dichloromethane solution. In our case, the phenolate is substituted in both positions ortho to the phenolate oxygen, which might well reduce the binding constant. Consequently, we attempted to perform NMR titration experiments in order to obtain binding constant data for **8•3**. However, due to solubility problems (a precipitate is formed in CH_2Cl_2 during the titration), we were only able to obtain a binding constant in DMSO:CH_2Cl_2 = 1:1 solution. The binding constant was determined by a non-linear fit of the titration curve shown in the figure below with the global analysis software package Specfit (Spectrum Software Associates, Chapel Hill, NC, USA; H. Gampp, M. Maeder, C. J. Meyer, A. D. Zuberbühler, *Talanta* **1986**, *33*, 943 and literature cited therein). A value of $K = 2200 \pm 700\ M^{-1}$ was obtained. In pure, non-competitive solvents like CH_2Cl_2, a much higher value can be expected, since DMSO strongly competes as a hydrogen-bond acceptor for H bond formation.



^{1}H-NMR titration curves derived from the shift differences Δδ (ppm) of the amide NH and isophthalic acid CH protons of the wheel.