

Stabilization of fulleropyrrolidine *N*-oxides through intrarotaxane hydrogen bonding.

Aurelio Mateo-Alonso,^{ab*} Peter Brough^b and Maurizio Prato^{ab*}

^a*Italian Interuniversity Consortium on Materials Science and Technology (INSTM), Unit of Trieste.*

^b*Dipartimento di Scienze Farmaceutiche, Università degli Studi di Trieste, Piazzale Europa 1, 34127 Trieste, Italy.*

Experimental

NMR spectra were recorded on a Jeol (400 MHz) at room temperature. Chemical shifts reported in ppm are referred to TMS. Singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (c). The assignments corresponds to the lettering shown in Scheme 1. Mass Spectroscopy: Electrospray (ES-MS) experiments were recorded at Università degli Studi di Trieste on a Perkin-Elmer API1 at 5600 eV by Dr. Fabio Hollan. UV-Vis measurements were recorded on a Varian 5000 UV-Vis-NIR spectrometer. Commercially available products were used without further purification. Thread **1** and rotaxane **2** were prepared as described somewhere else.¹

General Procedure – Synthesis of *N*-oxides **2 and **4**.** To a solution of compounds **1** or **2** (25 mg in 100 mL CHCl₃) was added, dropwise, *m*CPBA (1 equiv, in 25 mL CHCl₃) over a period of 1 h. Progress was monitored by TLC. The solution was stirred for an additional 30 min and then filtered through a short column of SiO₂, first washing with toluene to remove organic compounds and then with eluent solution to take the product mixture. A concentration on a rotavap to a small amount of liquid (approximately 3 mL) and flash chromatography on SiO₂ and reprecipitation from CHCl₃/Et₂O gave the *N*-oxide as a brown powder.

Thread *N*-oxide **2** C₉₃H₄₈N₄O₄ (MW, 1284.40), 31 % yield (8 mg). The eluent used was Toluene/EtOH (8:2). UV (CH₂Cl₂. λ max, nm): 255, 322, 430, 703. ¹H NMR (400 MHz, CDCl₃, r.t.): δ = 8.27 (bs, 1H, A); 7.35-7.10 (m, 10H, 2xPh); 6.05 (bs, 1H, B); 5.37 (bs, 1H, C); 5.33 (c, 4H, *J* = 10.6 and 46.7 Hz, D); 4.45-4.15 (m, 5H, E+J+G); 3.88 (dd, 2H, *J* = 5.8 and 7.5 Hz, F); 3.19 (c, 2H, *J* = 6.8 and 13.4 Hz, I); 2.70-2.50 (m, 4H, K); 2.05 (t,

2H, $J = 6.98$ Hz, L); 1.60-0.70 (m, alkyl). $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$, r.t.): $\delta = 8.71$ (bs, 1H, A); 7.90-7.80 (m, 2H, B+C); 7.40-7.10 (m, 10H, 2xPh); 5.54 (d, 2H, $J = 10.4$ Hz, D); 5.15 (d, 2H, $J = 10.4$, D); 4.18 (t, 1H, $J = 7.9$ Hz, E); 4.05-3.95 (m, 4H, G+J); 3.67 (dd, 2H, $J = 5.9$ and 8.0 Hz, F); 2.97 (c, 2H, $J = 6.6$ and 12.8 Hz, I); 2.40 (t, 2H, $J = 5.23$ Hz, L); 1.40-0.90 (m, alkyl).

Rotaxane *N*-oxide 4 $\text{C}_{125}\text{H}_{76}\text{N}_8\text{O}_8$ (MW, 1817.99), 24 % yield (6 mg). The eluent used was $\text{CHCl}_3/\text{EtOH}$ (97:3). UV (THF, λ_{max} , nm): 209, 310, 430, 703. MS ($\text{CHCl}_3/\text{CH}_3\text{OH}$ 1:1, m/z): 1819 ($\text{M}+\text{H}^+$). $^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3:\text{CD}_3\text{OD}$ 99:1, r.t.): $\delta = 8.37$ (s, 2H, a); 8.25-8.15 (m, 8H, b+c); 7.58 (t, 2H, $J = 7.8$ Hz, d); 7.40 (s, 8H, e); 7.33-7.17 (m, 10H, 2xPh); 5.75 (bs, 1H, B); 5.54 (bs, 1H, C); 5.11 (bs, 1H, A); 5.06 (c, 4H, $J = 10.8$ and 27.9, D); 4.80-4.70 (m, 4H, f); 4.55-4.45 (m, 4H, f); 4.18 (t, 1H, $J = 7.6$ Hz, E); 3.87 (dd, 2H, $J = 5.7$ and 7.8 Hz, F); 3.20 (bs, 2H, J); 3.15-3.00 (m, 4H, G+I); 2.05-1.90 (m, 6H, K+L); 1.65-0.90 (m, alkyl). $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$, r.t.): $\delta = 8.98$ (bs, 4H, c); 8.51 (s, 2H, a); 7.98 (d, 4H, $J = 7.6$ Hz, b); 7.55 (t, 2H, $J = 8.2$ Hz, d); 7.38 (s, 8H, e); 7.35-7.10 (m, 10H, 2xPh); 4.95 (d, 2H, $J = 9.2$ Hz, D); 4.68-4.57 (m, 4H, f); 4.40-4.25 (m, 6H, f+D); 4.18 (t, 1H, $J = 8.3$ Hz, E); 3.66 (t, 2H, $J = 6.3$ Hz, F); 3.15 (bs, 2H, J); 3.09 (bs, 2H, G); 2.91 (c, 2H, $J = 7.2$ Hz, I); 2.27-2.11 (m, 4H, K); 1.90 (t, 2H, $J = 6.9$ Hz, L); 1.35-0.7 (m, alkyl).

Deoxygenation of thread *N*-oxide 2 to thread 1. A solution of *N*-oxide 2 (8 mg) in Toluene-MeOH (4:1, 10 ml) was refluxed for 12 hours. Evaporation of the solvent yielded the corresponding thread 1.

References

- ¹ A. Mateo-Alonso, G. Fioravanti, M. Marcaccio, F. Paolucci, D. C. Jagesar, A. M. Brouwer, and M. Prato, *Org. Lett.*, 2006, **8**, 5173.