Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information for

Contrasting anion recognition behaviour exhibited by halogen and hydrogen bonding rotaxane hosts

Stuart P. Cornes, Charles H. Davies, David Blyghton, Mark R. Sambrook and Paul D. Beer*

Synthesis – General Remarks

All commercial solvents and reagents were used as purchased, unless otherwise stated. Anhydrous solvents were degassed with N_2 and dried by passing them through an MBraun-800 column. Triethylamine was distilled and stored over KOH pellets. Tetrabutylammonium (TBA) salts, Grubbs' second generation catalyst and $Cu(MeCN)_4 \cdot PF_6$ were stored in a desiccator with P_2O_5. TBTA was prepared following a literature procedure[S1]. Water was distilled and microfiltered using a Milli-Q Millipore machine. Chromatography was undertaken using silica gel (particle size: 40-63 μm) or preparative TLC plates (20 x 20 cm, 1 cm silica thickness).

^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded using Varian Mercury 300, Bruker AVIII400 and Bruker AVIII500 spectrometers. Mass spectra were recorded on a Waters LCT Premier instrument (low resolution) or a Bruker μTOF instrument (high resolution).

Characterisation of rotaxanes 8.PF_6 and 9.PF_6

XB Rotaxane 8.PF_6

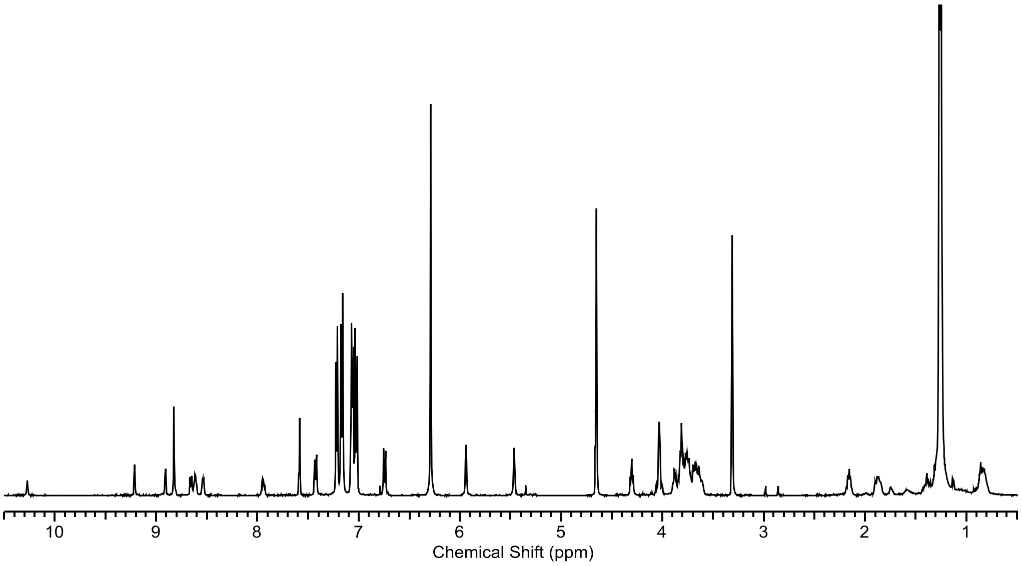


Figure S1: ^{1}H NMR spectrum of rotaxane **8.PF_6** (1:1 $CDCl_3$/CD_3OD, 298 K, 500 MHz)

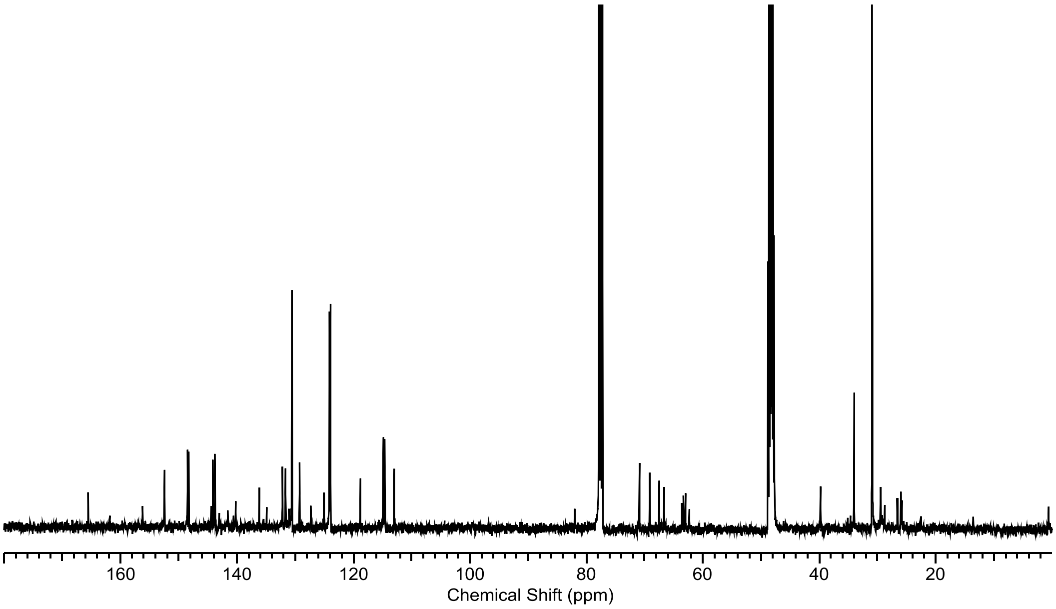


Figure S2: ^{13}C NMR spectrum of rotaxane **8.PF_6** (1:1 $CDCl_3$/CD_3OD, 298 K, 126 MHz)

HB Rotaxane 9.PF_6

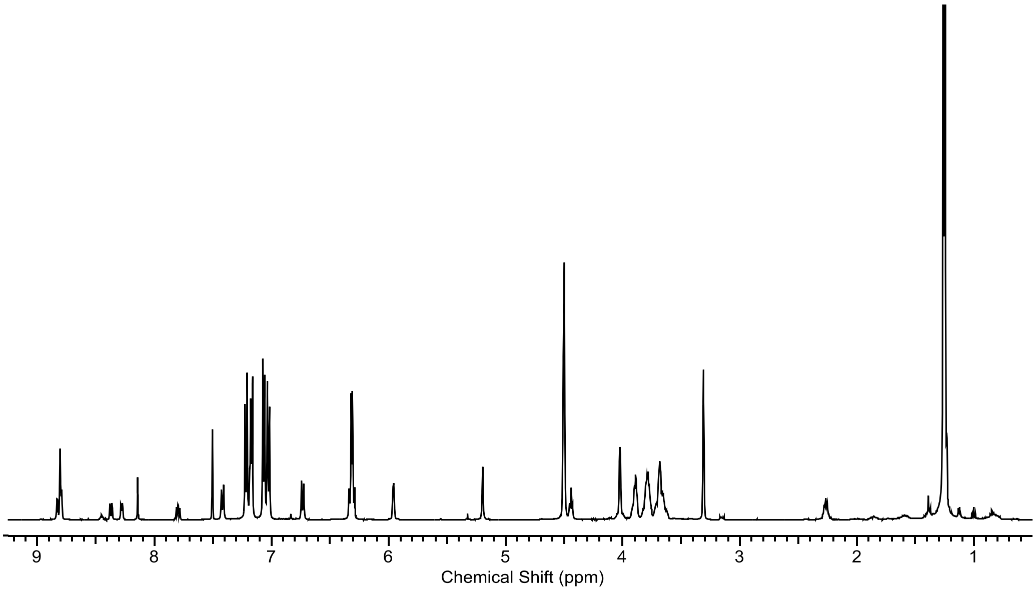


Figure S3: ^{1}H NMR spectrum of rotaxane **9.PF_6** (1:1 $CDCl_3$/CD_3OD, 298 K, 500 MHz)

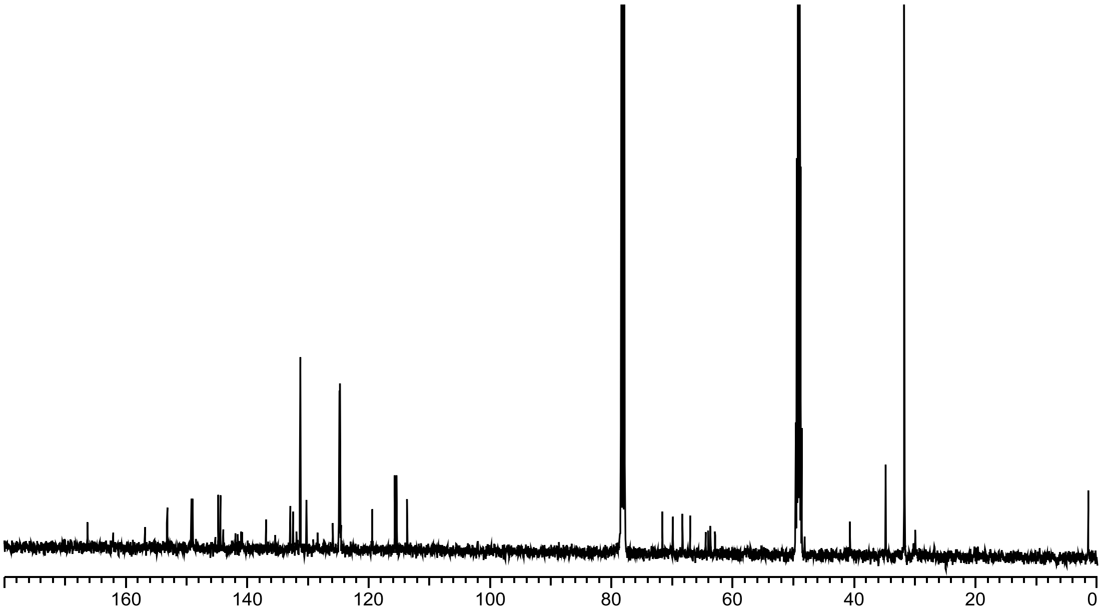


Figure S4: ^{13}C NMR spectrum of rotaxane **9.PF_6** (1:1 $CDCl_3$/CD_3OD, 298 K, 126 MHz)

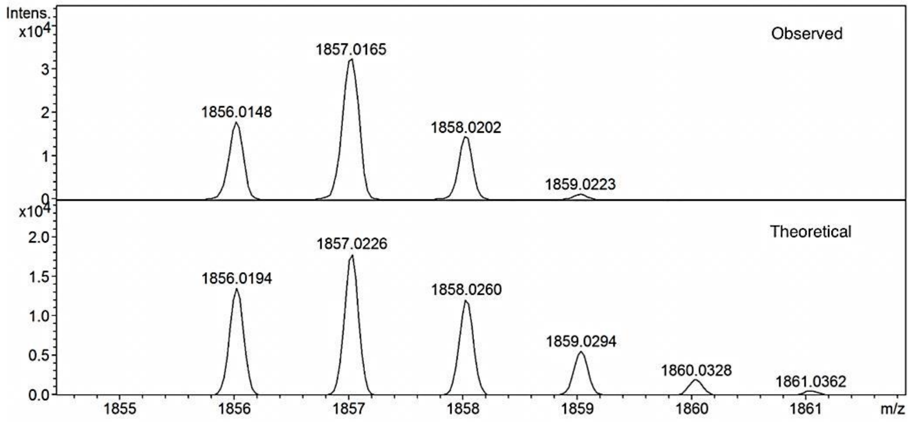
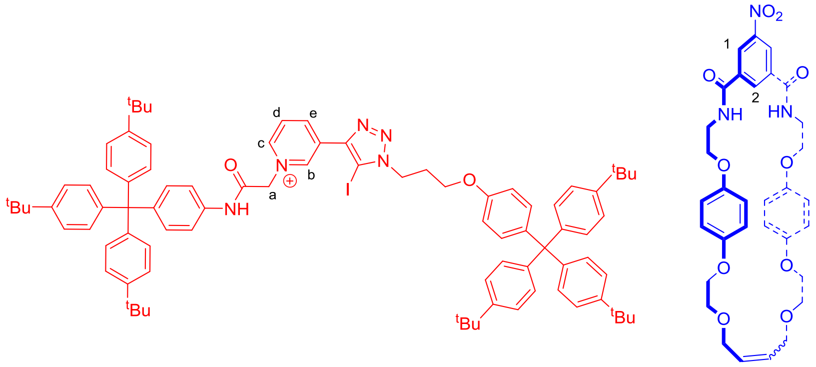


Figure S5: High resolution mass spectrum of rotaxane **9.PF$_6$**

ROESY NMR Spectra

XB Rotaxane 8.PF$_6$



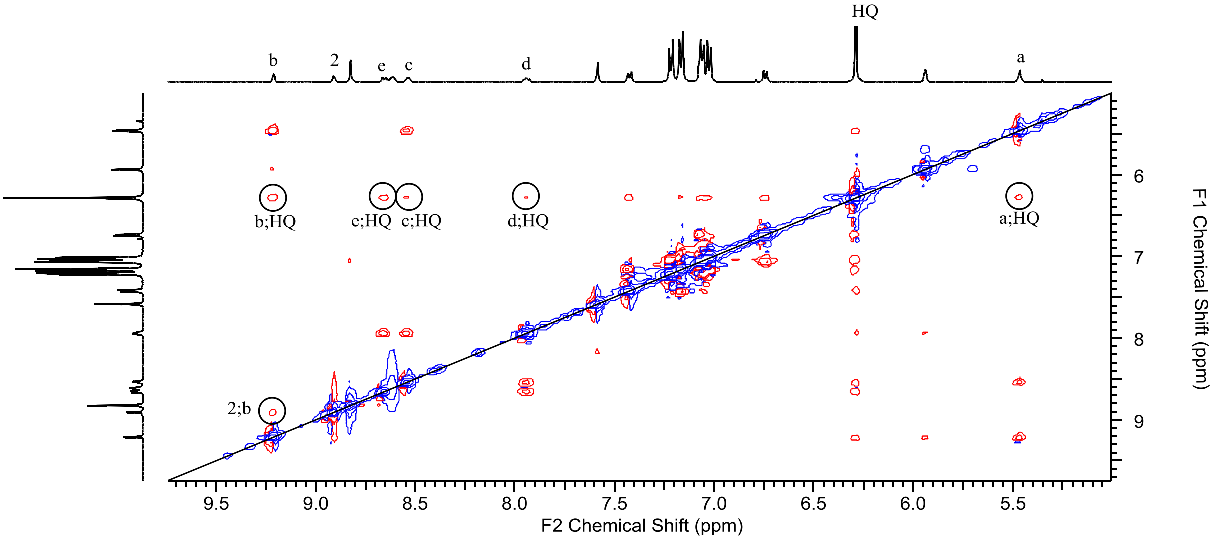
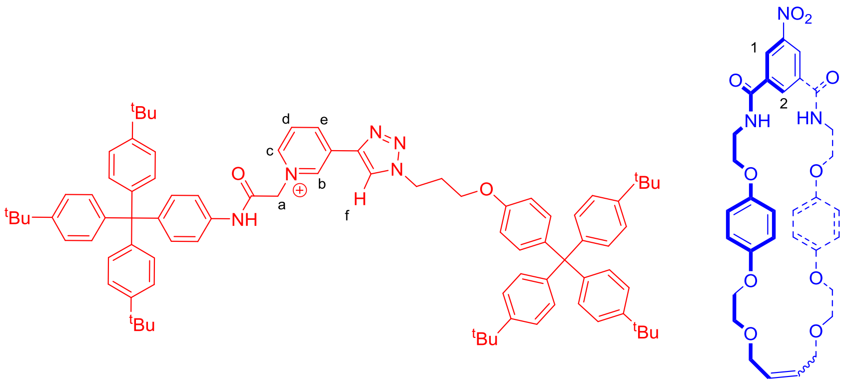


Figure S6: Truncated ^{1}H-^{1}H ROESY NMR spectrum of rotaxane **8.PF$_6$** with coupling interactions highlighted (1:1 CDCl$_3$/CD$_3$OD, 298 K, 500 MHz).

HB Rotaxane 9.PF$_6$



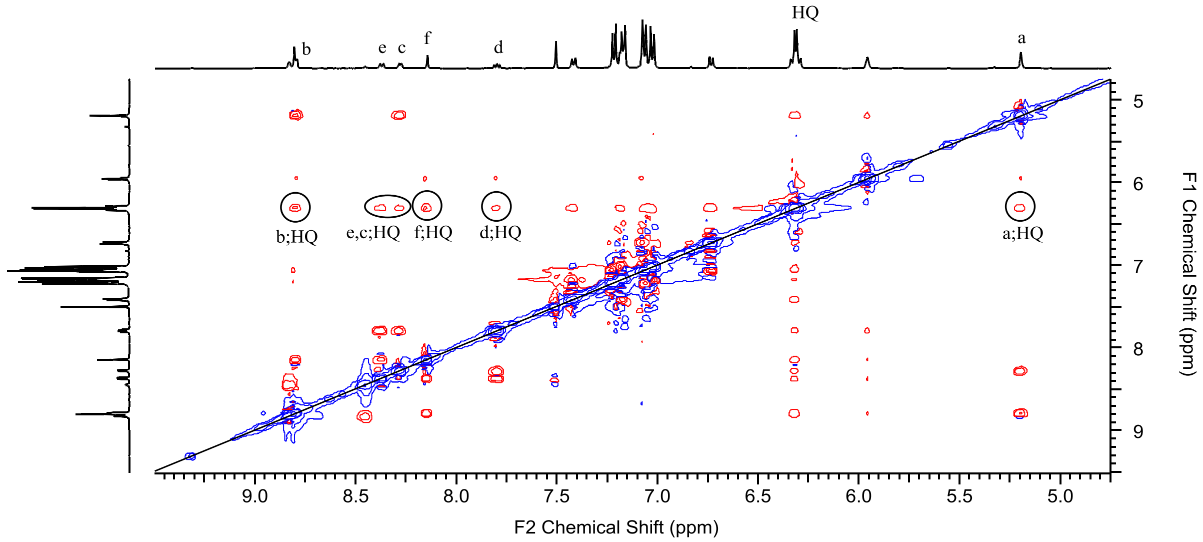


Figure S7: Truncated ^{1}H-^{1}H ROESY NMR spectrum of rotaxane **9.PF$_6$** with coupling interactions highlighted (1:1 CDCl$_3$/CD$_3$OD, 298 K, 500 MHz).

^{1}H NMR Titration Protocol

Titration experiments were performed on a Bruker AVIII500 spectrometer operating at 500 MHz for ^{1}H NMR and at a temperature of 298 K. An initial volume of host rotaxane of 0.5 mL was used at a concentration of 2 mM. Solutions of the respective anions (50 mM) as their TBA salts were added in aliquots, with spectra recorded at 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, 10.0 equivalents. Association constants were calculated form the data obtained using the software package WinEQNMR2[S2], following the macrocycle proton 2. An estimate of the association constant and the observed chemical shifts of proton 2 from each of the spectra recorded were added to the programs input file. Refinement of the data using a non-linear least-squares regression analysis gave an optimised fit between the observed and calculated data. Comparison of the experimental and calculated binding isotherms confirmed that a 1:1 binding model was appropriate.

References

S1 B-Y. Lee, S. R. Park, H. B. Jeon and K. S. Kim, *Tetrahedron Lett.*, 2006, **47**, 5105.

S2 M. J. Hynes, *J. Chem. Soc. Dalton Trans.*, 1993, 311.