ORGANIC LETTERS

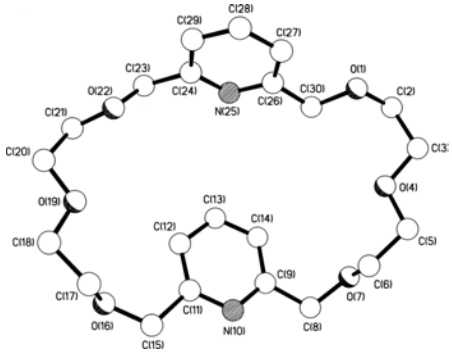
Ammonium Ion Binding with Pyridine-Containing Crown Ethers

Theresa Chang, Aaron M. Heiss, Stuart J. Cantrill, Matthew C. T. Fyfe, Anthony R. Pease, Stuart J. Rowan, J. Fraser Stoddart, Andrew J. P. White, David J. Williams

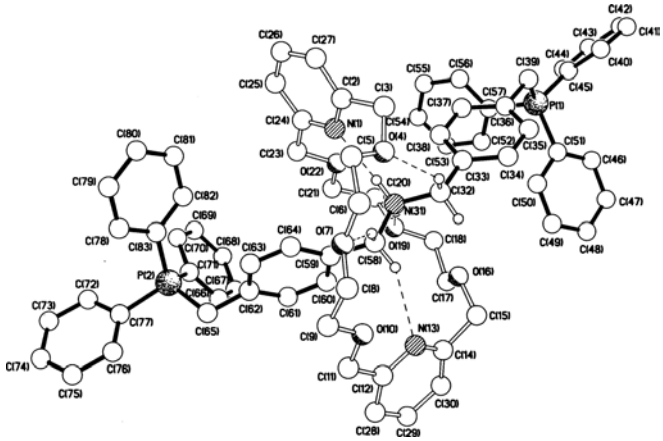
SUPPORTING INFORMATION
(3 PAGES)

EXPERIMENTAL PROCEDURES FOR **DP24C8** AND **4**-H·3PF_6

CRYSTAL DATA FOR [**DP24C8**]
CAN BE FOUND IN THE ACCOMPANYING FILE CALLED "FS9818.CIF"



CRYSTAL DATA FOR [**DP24C8**·**4**-H][3PF_6]
CAN BE FOUND IN THE ACCOMPANYING FILE CALLED "FS0004.CIF"



Experimental Section

General

All reagents and solvents were used as received unless otherwise stated. Reactions were carried out under an atmosphere of anhydrous argon. Reactions were monitored by TLC on silica plates (Merck, 0.25 mm) and visualized with UV light (254 nm). Melting points given are uncorrected. NMR Spectra were recorded on either a Bruker ARX 400 MHz or ARX 500 spectrometer. Chemical shifts reported are referenced to the residual solvent peak.

Synthesis

Dipyridyl[24]crown-8 (DP24C8)

THF (250 mL) was added to a 1 L round-bottomed flask and NaH (2.15 g, 0.090 mol) was added portionwise and heated under reflux. Diethyleneglycol (2.38 g, 0.022 mol) and 2,6-bis(*p*-toluenesulfonyloxymethyl)pyridine (10.04 g, 0.022 mol) were dissolved in THF (200 mL) and then added dropwise to the reaction mixture over 12 h. The mixture was refluxed for a further 3 d before being quenched with *i*–PrOH/MeOH/H_2O. The solvent was evaporated under *in vacuo* and the residue partitioned between CH_2Cl_2 (200 mL) and brine (100 mL). The organic layer was dried ($MgSO_4$) and evaporated to afford a red brown residue that was passed through a short pad of SiO_2 (200 g: gradient elution with CH_2Cl_2/Me_2CO, 2:1 to 1:1) to give the title compound as a colorless oil that solidified upon standing (1.10 g, 12 %); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67 (m, 8H), 3.73 (m, 8H), 4.65 (s, 8H), 7.35 (d, *J* = 7.8 Hz, 4H), 7.49 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ = 70.2, 70.8, 73.9, 120.0, 137.3, 157.8; FABMS: *m/z* (%): 441 (26) $[M + Na]^+$, 419.0 (100) $[M + H]^+$.

4-H·3PF_6.

Triphenylphosphine (264 mg, 1.0 mmol) was added to a solution of **3**-H·PF_6 (253 mg, 4.8 mmol) and DP24C8 (200 mg, 4.8 mmol) in CH_3NO_2 (1 mL). The reaction was left to stir for 16 h. at

room temperature. The resulting white precipitate, **5**-H·3PF_6, (0.215 g, 45 %) was filtered and washed with CH_2Cl_2 (This compound has been characterized previously: see ref. 1). Et_2O was added to the solution and the resulting precipitate filtered and washed with Et_2O. The precipitate was dissolved in MeCN and a saturated solution of NH_4PF_6 was added untill no further precipitation was observed. The resulting solid was filtered, washed with water and dried. The crude compound was purified by flash chromatography with 5% MeOH in CH_2Cl_2 to yield 0.250 g (39 %) of **4**-H·3PF_6. ^{1}H NMR (400 MHz, CD_3CN) δ = 3.32-3.34 (m, 8H), 3.42-3.44 (m, 8H), 4.19 (s, 8H), 4.39-4.43 (m, 4H), 4.58 (d, *J* = 15.1 Hz, 4H), 6.80-6.86 (m, 4H), 7.14 (d, *J* = 8.1 Hz, 4H), 7.21 (d, *J* = 7.7 Hz, 4H), 7.49-7.55 (m, 12H), 7.62-7.66 (m, 12H), 7.69 (t, *J* = 7.6 Hz, 2H), 7.84-7.86 (m, 6H); ^{13}C NMR (CD_3CN, 100 MHz) δ = 29.4 (J_{PC} = 48.6 Hz), 51.3, 70.1, 70.4, 73.5, 122.6, 128.0 (J_{PC} = 8.3 Hz), 129.1, 130.2 (J_{PC} = 12.6 Hz), 130.4 (J_{PC} = 3.0 Hz), 131.1 (J_{PC} = 5.4 Hz), 132.9 (J_{PC} = 3.9 Hz), 134.1 (J_{PC} = 9.7 Hz), 135.4 (J_{PC} = 2.9 Hz), 138.1, 156.6; ^{31}P NMR (162 MHz, CD_3CN): δ = 21.8 (Ph_3P^+), –144.6 (septet, *J* = 706 Hz, PF_6^-). FABMS *m*/*z* (%): 1456 (38) $[M\text{-}PF_6]^+$, 1310 (100) $[M\text{-}2PF_6]^+$, 1164 (84) $[M\text{-}3PF_6]^+$.

(1) Rowan, S. J.; Cantrill, S. J.; Stoddart, J. F. *Org. Lett.* **1999**, *1*, 129-132.