A Demonstration of Anion Templation and Selectivity in Pseudorotaxane Formation**

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In recent years progress in the synthesis of rotaxane and catenane architectures has reached the stage at which their design is both a function of whether the components of these systems can be interlocked and what function the assembled products possess.[1] Control over the relative disposition of the constituents in the final structure, their co-conformations,[2] is usually a derivative of the residual noncovalent interactions initially employed to construct them. Examples of the interactions applied for these purposes to date include hydrogen bonding, π stacking, metal–ligand dative bonding, and hydrophobic binding between species which are neutral or cationic in nature.[3] With few exceptions, the participation of anions in the formation of interpenetrated and interlocked molecular entities has largely been unexplored and they are rarely incorporated as an operative feature in the resulting ensembles.[2, 4] The ubiquitous nature of anions in both natural and synthetic systems should make their application in the synthesis of mechanically bonded assemblies highly valuable. Here we report the formation of a [2]pseudorotaxane that is templated selectively by chloride and, to a lesser extent, bromide anions.

We have approached the integration of anionic species into a pseudorotaxane superstructure by employing the chloride ion itself as a central core, about which two coordinating ligands are orthogonally disposed (Figure 1). Crabtree and co-workers have shown that simple isophthalamide molecules such as **1a** (Scheme 1) are receptors for anions in chloroform.[5] In particular, fluoride and chloride ions bind more strongly to these receptors than bromide and iodide ions as a result of their size complementarity with the hydrogen-bond donor

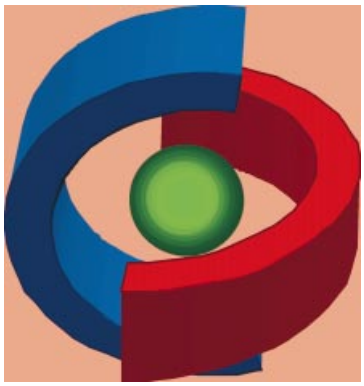
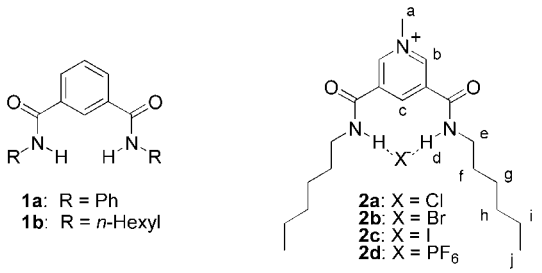


Figure 1. Proposed anion template. Hydrogen bond donating ligands are represented in red and blue, the chloride anion in green.



Scheme 1. Structure of hydrogen bond donating ligands **1a** and **b**, as well as the ion pair threads **2a**–**d**.

cleft created by the amide groups and their mutually *ortho* aryl proton. Unfortunately for our purposes, these receptors bind the halides with a 1:1 stoichiometry that is unsuitable for the formation of the desired template. The utilization of a cationic receptor as one of the ligands in the system could potentially solve this problem. Thus, $\mathbf{2}^+$ should include a chloride anion much more tightly in its cleft as a consequence of the increased acidity of the protons involved in substrate binding and the favorable electrostatics provided by the cationic nature of the pyridinium ring. This enhancement can be demonstrated by the large downfield ^{1}H NMR shifts observed in acetone for only protons c and d of $\mathbf{2}^+$ in the series **2d**–**2a** ($\Delta\delta = 1.59$ and 1.67, respectively). The resulting tight ion pair leaves the chloride anion with an empty meridian that could bind another neutral hydrogen bond donor ligand in the absence of a competitive solvent. In fact, a ^{1}H NMR titration of **1b** with **2a** in acetone produced a 1:1 association constant of $100\,\text{M}^{-1}$, while the same treatment of **1b** with **2d** produced no detectable change in the system.[6]

The second component of the system, macrocycle **5**, was designed to act as the wheel through which **2a** would thread to form the [2]pseudorotaxane. It was anticipated that the isophthalamide fragment incorporated within the macrocyclic cavity would satisfy the coordinatively unsaturated chloride ion. In addition, the hydroquinone and polyether functionality should stabilize the pyridinium cation in the interpenetrated structure. Compound **5** was synthesized in three steps (Scheme 2) beginning with the facile condensation of known 2-(4-benzyloxy)phenoxyethylamine[7] and commercially available isophthaloyl dichloride to yield **3**. The benzyl protecting groups were removed catalytically and the resulting diol **4** was treated with tetraethylene glycol di-*p*-tosylate and Cs_2CO_3 in DMF to give the final product.

The first indication that **2a** threads through macrocycle **5** in acetone came from the observation of a charge-transfer absorption at approximately 370 nm in the UV/Vis spectrum upon the admixture of one equivalent of each of these two colorless components (Figure 2). The resulting pale yellow color, which can be attributed to π stacking between the pyridinium and hydroquinone rings, is not produced when **2b**–**d** are mixed with **5**.

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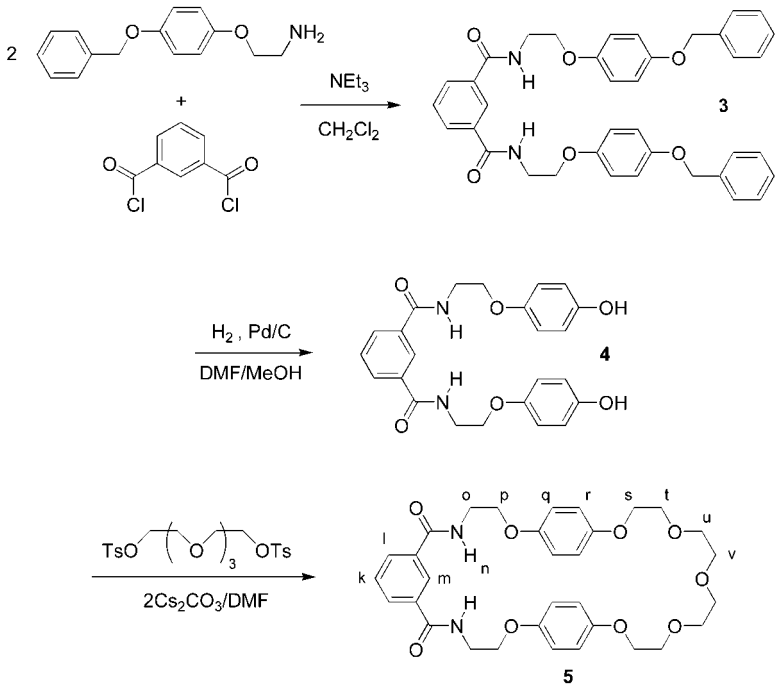

Scheme 2. Synthesis of macrocycle **5**. Ts = tosyl = toluene-4-sulfonyl.

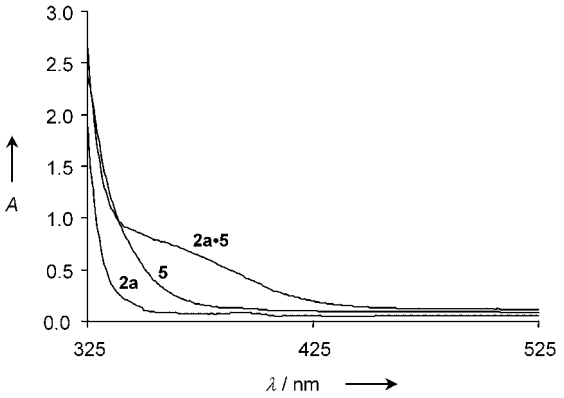

Figure 2. UV/Vis spectra of **2a**, **5**, and **2a**·**5** in acetone.

Examination of the ^{1}H NMR spectra of 1:1 mixtures of **5** with each of **2a**–**d** in acetone revealed complexation-induced shifts in all cases. Table 1 summarizes some of the larger shifts that occur in the aryl and amide protons of the components. The most apparent trend is the marked increase in the size of the shifts of both species in the series **2d** < **2c** < **2b** < **2a**. The effects of π stacking on the aryl protons of both the pyridinium (protons b and c) and hydroquinone (protons q and r) rings is evident in the upfield shifts they display. The increase in these shift values as the anion decreases in size indicates a concomitant increase in the ability of the cation to reside within the macrocyclic ring. The upfield shifts of protons c and d, relative to the free ion pairs, are most likely also a result of the polarization of the anion towards the hydrogen-bond donors of the macrocyclic ring which reduces the strength of the hydrogen bonds to the cationic donors. Indeed, protons m and n do display downfield shifts indicative of hydrogen bonding to the anion. Once again, these values increase as the anion becomes smaller, more polarizing, and a better fit for the anion "pocket" created in the pseudorotaxane superstructure.

In order to determine the overall strength of these interactions macrocycle **5** was titrated with threads **2a**–**d** in acetone and association constants were determined by monitoring the shift of the hydroquinone protons r.[6] Table 1 shows that the association constants measured display the same trend as the magnitudes of the shifts, with pseudorotaxane formation being templated preferentially by a chloride anion. These results give a chloride selectivity of approximately 37:1 over iodide, although there is a difference of just 0.39 Å between the ionic radii of the two anions.

Further proof of the [2]pseudorotaxane structure of the complex **2a**·**5** is found in the solid state. Pale yellow crystals of the [2]pseudorotaxane were grown by slow diffusion of diisopropyl ether into a 1:1 solution of the two components in chloroform. The ^{1}H NMR spectrum of the crystals dissolved in acetone is identical to that of a solution of a 1:1 mixture of the separate compounds. Single-crystal X-ray analysis[8] reveals the ion pair **2a** threaded through the cavity of the macrocycle in the manner intended (Figure 3 and 4). The chloride ion engages in six hydrogen bonds with the two hydrogen bond donor clefts of the thread and macrocycle (N–Cl: 3.33–3.47 Å, C–Cl: 3.42 and 3.54 Å), and sits within 0.07 Å of the planes of both clefts described by these atoms which intersect at 90°. The C_2 axis of the pyridinium ring forms an angle of 145° with the C_2 axis of the isophthaloyl ring. This arrangement results in the amide protons forming a coordination sphere around the chloride ion similar to that of a trigonal bipyramid with an unoccupied axial position. The pyridinium ring is π stacked between the hydroquinone rings of the macrocycle (mean plane separation: 3.35 and 3.43 Å, centroid–centroid separation: 3.70 and 3.54 Å, angles formed by the ring planes: 1.2 and 3.1°, respectively) and the

Table 1. Association constants (K_a), free energies of complexation (ΔG), and selected ^{1}H NMR shifts of **2a**–**d** with **5** in [D$_6$]acetone at 298 K.

Complex	K_a [M^{-1}]	$-\Delta G$ [kJ mol^{-1}]	Chemical shift ($\Delta\delta$)[a]						
			H_b	H_c	H_d	H_m	H_n	H_q	H_r
5·**2a**	2400	19.3	−0.35	−0.98	−1.02	0.65	0.51	−0.24	−0.41
5·**2b**	700	16.2	−0.17	−0.53	−0.51	0.44	0.27	−0.15	−0.31
5·**2c**	65	10.3	−0.05	−0.13	−0.11	0.09	0.05	−0.01	−0.09
5·**2d**	35	8.81	−0.01	0.00	−0.04	0.02	0.01	0.00	−0.05

[a] Shifts determined from 1:1 mixtures at a concentration of 2.5×10^{-3} M.

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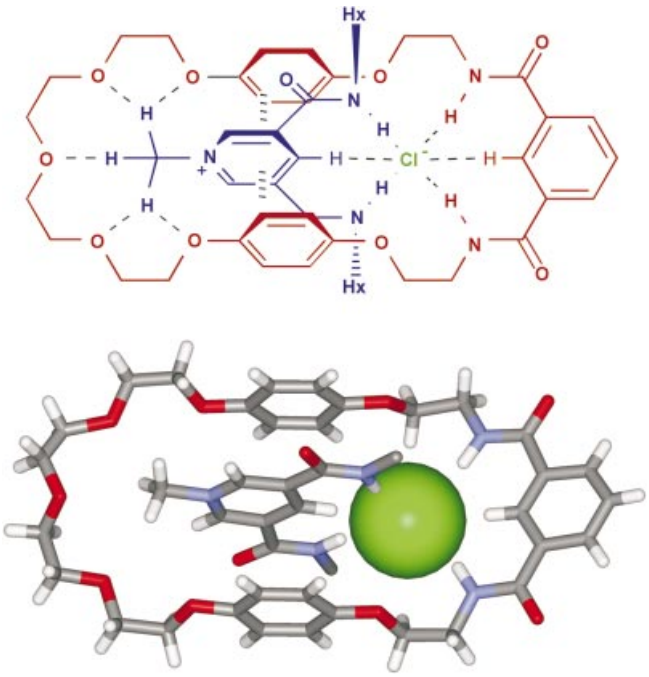

Figure 3. Solid-state structure of **2a**·**5**. Top: Schematic representation of the [2]pseudorotaxane highlighting the interactions between the components. Bottom: Stick representation of the crystal structure. The outermost five carbon atoms and hydrogen atoms of the hexyl chains have been removed and the chloride anion shown as a CPK sphere for clarity.

N-methyl group of the pyridinium cation is stabilized by C–H···O hydrogen bonds with the polyether oxygen atoms (C–O 3.20–3.46 Å).

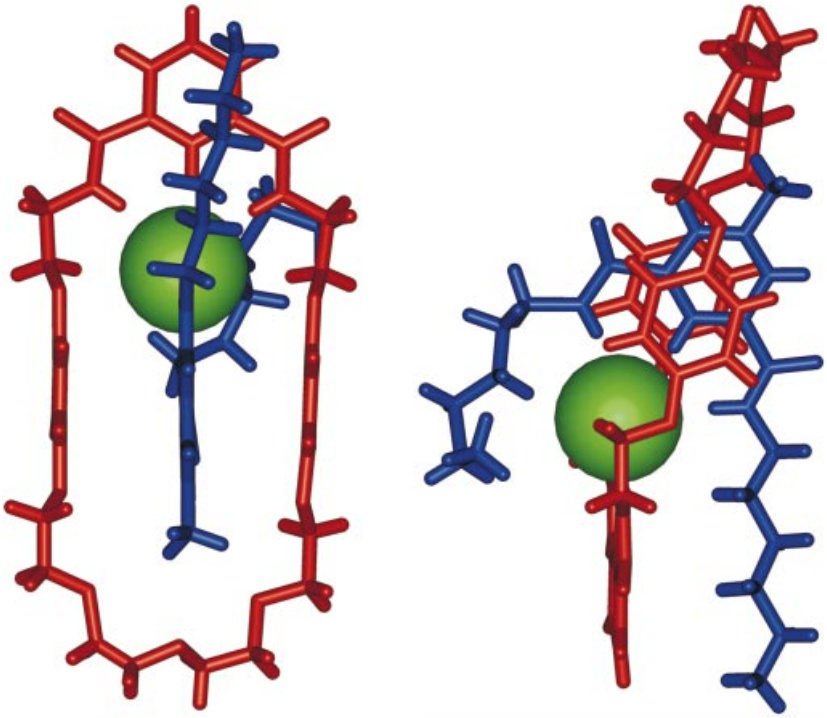

Figure 4. Stick representations of the solid-state structure of **2a**·**5** (blue: $\mathbf{2}^{+}$, red: **5**, green: Cl^{-}). Left: view through the annulus of the macrocyclic ring; right: view in the plane of the macrocyclic ring. The chloride anion is represented as a CPK sphere for clarity.

These results produce a picture of pseudorotaxane formation in which the macrocycle binds **2a** through both first- and second-sphere coordination of the chloride ion. Replacement of chloride by a larger anion destabilizes the entire recognition motif. This process leads to mismatch with both the anion binding pocket created by the four amide groups and, as a result, the ability of the cation to reside within the macrocyclic ring. Thus, the entire structure of the [2]pseudorotaxane hinges on the nature of the anion involved in the binding event. We are currently involved in the application of this template to the construction of rotaxanes and catenanes and anticipate that interlocked compounds based on this protocol will display unique properties in the realms of anion recognition and anion-controlled movement of their constituent parts.

Experimental Section

3,5-Pyridinedicarbonyl chloride was synthesized by a literature procedure[9] from commercially available 3,5-pyridinedicarboxylic acid.

N,*N*′-Bis(*n*-hexyl)-3,5-pyridinedicarboxamide: A solution of 3,5-pyridinedicarbonyl chloride (1 g, 4.90 mmol) in dichloromethane (25 mL) was added over 30 min to a stirred solution of hexylamine (0.677 g, 5.88 mmol), triethylamine (0.607 g, 6.00 mmol), and dichloromethane (50 mL) cooled to 0 °C. The reaction was allowed to proceed for a further 2 h and then warmed to room temperature. The solution was washed with aqueous citric acid (2 M, 4 × 50 mL). The organic layer was dried with $MgSO_4$ and evaporated to give the desired product as a white solid (1.47 g, 87 %). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 9.02$ (s, 2H, *o*-ArH), 8.48 (s, 1H, *p*-ArH), 7.77 (br m, 2H, NH), 3.41 (m, 4H, α-CH_2), 1.59 (m, 4H, β-CH_2), 1.28 (m, 12H, γ, δ, ε-CH_2), 0.84 (m, 6H, CH_3).

2c: *N*,*N*′-Bis(*n*-hexyl)-3,5-pyridinedicarboxamide (1.00 g, 3.00 mmol) and methyl iodide (4.26 g, 30.0 mmol) were added to chloroform (50 mL) and refluxed for 24 h. Addition of the resulting solution to diethyl ether (250 mL) gave **2c** as a bright yellow solid (1.18 g, 83 %). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): $\delta = 9.99$ (s, 1H, H_c), 9.62 (s, 2H, H_b), 9.06 (br s, 2H, H_d), 4.78 (s, 3H, H_a), 3.44 (m, 4H, H_e), 1.70 (m, 4H, H_f), 1.34 (m, 12H, $H_{g\text{-}i}$), 0.89 (m, 6H, H_j); elemental analysis calcd for $C_{20}H_{34}IN_3O_2$: C 50.53, H 7.21, N 8.84; found: C 50.30, H 7.31, N 8.95.

2a: A solution of **2c** (1.00 g, 2.10 mmol) in acetone/water (10 mL) was passed through an Amberlite IRA-400(Cl) ion-exchange column that was pretreated with aqueous 1 N HCl. Evaporation of the eluent gave **2a** as a white solid (0.670 g, 87 %). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): $\delta = 10.90$ (s, 1H, c), 10.06 (br s, 2H, H_d), 9.51 (s, 2H, H_b), 4.78 (s, 3H, H_a), 3.40 (m, 4H, H_e), 1.68 (m, 4H, H_f), 1.34 (m, 12H, $H_{g\text{-}i}$), 0.89 (m, 6H, H_j); elemental analysis calcd for $C_{20}H_{34}ClN_3O_2$: C 62.56, H 8.93, N 10.94; found: C 62.57, H 8.95, N 11.02.

2b: A solution of **2c** (1.00 g, 2.10 mmol) in chloroform (50 mL) was washed with an aqueous 1 M NH_4Br solution (8 × 50 mL) until the organic phase was completely colorless. The organic layer was dried with $MgSO_4$ and evaporated to give **2b** as a white solid (0.720 g, 80 %). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): $\delta = 10.55$ (s, 1H, H_c), 9.65 (br s, 2H, H_d), 9.56 (s, 2H, H_b), 4.79 (s, 3H, H_a), 3.42 (m, 4H, H_e), 1.70 (m, 4H, H_f), 1.34 (m, 12H, $H_{g\text{-}i}$), 0.89 (m, 6H, H_j); elemental analysis calcd for $C_{20}H_{34}BrN_3O_2$: C 56.07, H 8.00, N 9.81; found: C 56.10, H 8.39, N 9.80.

2d: A solution of **2c** (1.00 g, 2.10 mmol) in methanol (4 mL) was added to a saturated aqueous solution of NH_4PF_6 (10 mL). The resulting mixture was heated to its boiling point and reduced to approximately 2/3

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volume. Cooling the solution gave **2d** as a white crystalline precipitate (0.881 g, 85%). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): $\delta = 9.58$ (s, 2H, H$_b$), 9.31 (s, 1H, H$_c$), 8.39 (br s, 2H, H$_d$), 4.78 (s, 3H, H$_a$), 3.48 (m, 4H, H$_e$), 1.64 (m, 4H, H$_f$), 1.33 (m, 12H, H$_{g\text{-}i}$), 0.88 (m, 6H, H$_j$); elemental analysis calcd for $C_{20}H_{34}F_6N_3O_2P$: C 48.68, H 6.94, N 8.52; found: C 48.59, H 6.98, N 8.58.

3: 2-(4-Benzyloxy)phenoxyethylamine (4 g, 16.4 mmol) and triethylamine (2.02 g, 20.0 mmol) were dissolved in dichloromethane (100 mL) and cooled to 0 °C. A solution of isophthaloyl dichloride (1.66 g, 8.20 mmol) in dichloromethane (50 mL) was added over 30 min, which resulted in the formation of a white precipitate. The mixture was stirred for a further 2 h and then filtered and washed with dichloromethane (2×25 mL) and methanol (2×25 mL) to yield **3 as** a white solid (5.06 g, 92%). ^{1}H NMR (300 MHz, [D$_6$]DMSO, TMS): $\delta = 8.78$ (br s, 2H, NH), 8.34 (s, 1H, isophth.-CH), 7.98 (d, $J = 7.6$ Hz, 2H, isophth.-CH), 7.55 (t, $J = 7.6$ Hz, 1H, isophth.-CH), 7.37 (m, 10H, benzyl-CH), 6.90 (m, 8H, phenyl-CH), 5.02 (s, 4H, benzyl-CH$_2$), 4.06 (t, $J = 5.9$ Hz, 4H, OCH$_2$), 3.61 (m, 4H, NCH$_2$).

4: A mixture of **3** (2 g, 3.24 mmol) and Pd/C (0.2 g) in DMF/methanol (100 mL, 4:1) was stirred under an H_2 atmosphere for 24 h. Celite (10 g) was added and the mixture filtered through a pad of celite to give a light yellow solution. The solution was evaporated under vacuum to give **4** as an off-white solid (1.36 g, 96%). ^{1}H NMR (300 MHz, [D$_6$]DMSO, TMS): $\delta =$ 8.91 (s, 2H, OH), 8.77 (br s, 2H, NH), 8.35 (s, 1H, isophth.-CH), 7.98 (d, $J =$ 8.2 Hz, 2H, isophth.-CH), 7.56 (t, $J = 8.2$ Hz, 1H, isophth.-CH), 6.79 (d, $J =$ 8.8 Hz, 4H, phenyl-CH), 6.66 (d, $J = 8.2$ Hz, 4H, phenyl-CH), 4.10 (t, $J =$ 5.9 Hz, 4H, OCH$_2$), 3.60 (m, 4H, NCH$_2$).

5: A solution of **4** (1 g, 2.29 mmol) and tetraethylene glycol di-*p*-tosylate (1.15 g, 2.29 mmol) in DMF (100 mL) was added to a stirred mixture of Cs_2CO_3 (1.57 g, 4.81 mmol) in DMF at 60 °C over a period of 24 h. The resulting mixture was stirred and heated for a further 24 h and cooled to room temperature. Filtration and evaporation of the solvent under vacuum gave a brown oil which was extracted with hot chloroform (2×100 mL). The chloroform was reduce to a light brown oil, which was purified by chromatography on silica gel (ethyl acetate) to give **5** as a white solid (0.368 g, 27%). ^{1}H NMR (300 MHz, [D$_6$]acetone, TMS): $\delta = 8.31$ (s, 1H, H$_m$), 8.03 (m, 4H, H$_l$, H$_n$), 7.56 (t, $J = 7.7$ Hz, 1H, H$_k$), 6.83 (m, 8H, H$_q$, H$_r$), 4.12 (t, $J = 5.0$ Hz, 4H, H$_p$), 4.02 (m, 4H, H$_s$), 3.78 (m, 8H, H$_o$, H$_t$), 3.63 (m, 8H, H$_u$, H$_v$); elemental analysis calcd for **5**$\cdot$H$_2$O $C_{32}H_{40}N_2O_{10}$: C 62.73, H 6.58, N 4.57; found: C 62.69, H 6.56, N 4.51.

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[6] All titrations were performed with the concentration of receptor or host (**1b** or **5**) held at 2.5×10^{-3} M and following the movement of the appropriate protons upon addition of **2a** – **2d**. In the case of **1b** data was obtained by observation of both the amide and mutually *ortho* aryl protons; both methods gave the same K_a values within experimental error. Association constants were determined from the data using the program EQNMR (M. J. Hynes, *J. Chem. Soc. Dalton Trans.* **1993**, 311 – 312) and fit 1:1 binding models. The estimated errors in all cases were less than 10%.

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[8] Crystal structure data for **2a**$\cdot$**5**: $M_r = 972.60$, triclinic, space group $P\bar{1}$, $a = 9.547(12)$, $b = 17.56(2)$, $c = 17.90(3)$ Å, $\alpha = 64.12(1)$, $\beta = 87.09(1)$, $\gamma = 85.00(1)°$, $U = 2688$ Å^3, $Z = 2$, $\rho_{calcd} = 1.202$ g cm^{-3}, $T = 293$ K. 7882 independent reflections were measured on a MarResearch Image Plate system using $Mo_{K\alpha}$ radiation. The crystal was positioned at 70 mm from the Image Plate. 100 frames were measured at 2° intervals with a counting time of 10 mins to give 7882 independent reflections. Data analysis was carried out with the XDS program (W. Kabsch, *J. Appl. Crystallogr.* **1988**, *21*, 916). The structure was solved using direct methods with the Shelx86 program (G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467). The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structure was refined on F^2 using Shelxl (G. M.Sheldrick, **1993**, program for crystal structure refinement, University of Gottingen). The final R values were $R_1 = 0.1060$ and $wR_2 = 0.2880$ for 1870 data with $I > 2\sigma(I)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-164881. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] F. Rob, H. J. Van Ramesdonk, W. Van Gerresheim, P. Bosma, J. J. Scheele, J. W. Voerhoeven, *J. Am. Chem. Soc.* **1984**, *106*, 3826 – 3832.

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