Pyridinium CH · · · anion and π-stacking interactions in modular tripodal anion binding hosts: ATP binding and solid-state chiral induction

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The preparation of two new tripodal 'pinwheel' type anion hosts based on a triethylbenzene core and bipyridinium or ethylnicotinium arms is reported. The new materials bind anions *via* CH · · · anion interactions. Complexes with Br^- and PF_6^- have been characterised by X-ray crystallography as both solvates in a pure form. In the bipyridinium host CH · · · F interactions to PF_6^- induce a chiral C_3 symmetric conformation that is disrupted in the hydrate. The compound is also selective for ATP^{2-} in aqueous acetonitrile.

Introduction

The design of molecular hosts capable of selectively binding anionic guests is a notoriously challenging area and consequently has given rise to a plethora of imaginative and ingenious systems designed to tackle the problem.[1–16] Successful strategies include both positively charged[14,15,17–31] and neutral[1,10,13,32–35] receptors. Binding is enhanced by host preorganisation in both two[36,37] and three dimensions[38,39] and by hydrogen bonding interactions, particularly to amide[8,40–42] or ammonium NH functionalities.[15] Previously we have adopted a simple electrostatic strategy involving a preorganised host cavity with high positive charge density. Guest anions that are complementary to the cavity dimensions are bound preferentially.[3,23,43–49] Greater selectivity may be achieved, however, by modulating electrostatic interactions with more directional hydrogen bonding. While amine[29] and urea NH donors[50] have proved particularly effective, there is now clear evidence that aryl CH · · · anion interactions may also be of considerable importance.[28,29,51–56] Thus we have reported a series of flexible, cationic pyridinium hosts based on di-substituted aromatic rings,[28,52] triethylbenzene[28–30,52] and calixarene cores.[57] the triethylbenzene derivatives in particular form part of an extensive family of cationic and neutral 'pinwheel' type hosts, pioneered by the wide ranging work of Anslyn[58–68] and of Kim and Duan.[53–56] We now report the synthesis and anion binding properties of simple, conformationally flexible cationic pinwheel hosts that bind to guest species *via* CH · · · X^- interactions.

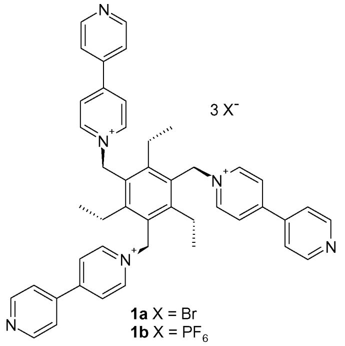
Experimental

Instrumental

NMR spectra were measured with a Bruker Avance NMR spectrometer and the chemical shifts are reported in ppm relative to tetramethylsilane. Fast atom bombardment (low resolution) mass spectra were obtained with a Kratos MS 890 Mass Spectrometer. Elemental Analysis for carbon, hydrogen and nitrogen was carried out by the Elemental Analysis Service at the London Metropolitan University.

X-Ray crystallography

Crystals were mounted using silicone grease on a thin glass fibre. All crystallographic measurements were carried out with a Nonius KappaCCD diffractometer equipped with graphite monochromated Mo-Kα radiation using wide ϕ and ω-scans. Data collection temperature was 120 K, maintained by using an Oxford Cryosystem low temperature device. Integration was carried out by the Denzo-SMN package.[69] Data sets were corrected for Lorentz and polarization effects and for the effects of absorption (Scalepack[69]) and crystal decay where appropriate. Structures were solved using the direct methods option of SHELXS-97[70] and developed using conventional alternating cycles of least-squares refinement (SHELXL-97)[71] and difference Fourier synthesis with the aid of the program XSeed.[72] In all cases non-hydrogen atoms were refined anisotropically except for some disordered, while C–H hydrogen atoms were fixed in idealised positions and allowed to ride on the atom to which they were attached. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. Where possible, non C–H hydrogen atoms were located experimentally and their positional and isotropic displacement parameters refined. Otherwise a riding model was adopted. All calculations were carried out on an IBM-PC compatible personal computer.



1a X = Br
1b X = PF_6

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Crystal data for 1a. $C_{48}H_{60}Br_3N_6O_{4.5}$, M 1032.75 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 10.6106(4) Å, b = 12.4052(5) Å, c = 20.5253(5) Å. U = 2527.15(15) Å^3, D_c = 1.357 Mg m^{-3}, Z = 2, μ = 24.42 cm^{-1}, T = 100(2) K, Reflections measured: 16485, unique data: 8867 (R_{int} = 0.089), parameters: 592, $R1$ [$F^2 > 2\sigma(F^2)$] 0.0740, $wR2$ (all data) 0.1982.†

Crystal data for 1b. $C_{47}H_{42}F_{18}N_7P_3$, M 1139.79 g mol^{-1}, hexagonal, space group $P6_3$, a = 11.9328(2) Å, c = 20.0477(5) Å. U = 2472.18(9) Å^3, D_c = 1.531 Mg m^{-3}, Z = 2, μ = 2.31 cm^{-1}, T = 120(2) K, Reflections measured: 6895, unique data: 3524 (R_{int} = 0.036), parameters: 229, $R1$ [$F^2 > 2\sigma(F^2)$] 0.0396, $wR2$ (all data) 0.0993.

Crystal data for 1b·3H$_2$O. $C_{45}H_{53}F_{18}N_6O_4P_3$, M = 1176.84, yellow plate, 0.20 × 0.20 × 0.10 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 11.1149(15), b = 30.678(3), c = 15.2165(19) Å, β = 90.413(5)°, V = 5188.4(11) Å^3, Z = 4, D_c = 1.507 g cm^{-3}, F_{000} = 2416, T = 120(2) K, $2\theta_{max}$ = 52.0°, 17021 reflections collected, 8705 unique (R_{int} = 0.1699). Final $GooF$ = 1.015, $R1$ = 0.1203, $wR2$ = 0.3550, $R1$ based on 3577 reflections with $I > 2\sigma(I)$, $wR2$ based on all data (refinement on F^2), 669 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.228 mm^{-1}.

Crystal data for 1c. $C_{60}H_{64}F_{12}N_6O_7P_2$, M = 1271.11, yellow block, 0.40 × 0.30 × 0.20 mm^3, monoclinic, space group Cc (No. 9), a = 9.8279(2), b = 30.0349(10), c = 20.0581(6) Å, β = 99.280(2)°, V = 5843.3(3) Å^3, Z = 4, D_c = 1.445 g cm^{-3}, F_{000} = 2640, T = 120(2) K, $2\theta_{max}$ = 52.0°, 18382 reflections collected, 10607 unique (R_{int} = 0.0389). Final $GooF$ = 1.006, $R1$ = 0.0515, $wR2$ = 0.1210, $R1$ based on 8767 reflections with $I > 2\sigma(I)$, $wR2$ based on all data (refinement on F^2), 843 parameters, 74 restraints. Lp and absorption corrections applied, μ = 0.172 mm^{-1}. Absolute structure parameter = 0.09(9).[73]

Crystal data for 2a. $C_{41}H_{50}Br_3Cl_6N_3O_6$, M = 1133.27, 0.30 × 0.20 × 0.10 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 10.8286(8), b = 18.3316(12), c = 24.2103(14) Å, β = 100.766(3)°, V = 4721.3(5) Å^3, Z = 4, D_c = 1.594 g cm^{-3}, F_{000} = 2288, T = 120(2) K, $2\theta_{max}$ = 52.0°, 29345 reflections collected, 9276 unique (R_{int} = 0.1495). Final $GooF$ = 1.036, $R1$ = 0.0785, $wR2$ = 0.1764, $R1$ based on 5961 reflections with $I > 2\sigma(I)$ (refinement on F^2), $wR2$ based on all data, 595 parameters, 30 loose ISOR restraints on disordered ethyl groups. Lp and absorption corrections applied, μ = 2.950 mm^{-1}.

Syntheses

Materials were obtained from standard commercial sources.

Synthesis of 1a. 1,3,5-Tri(bromomethyl)-2,4,6-triethylbenzene[74] (0.50 g, 1.13 mmol) in CH_2Cl_2 (300 cm^3) was added dropwise to a stirred solution containing a tenfold excess of 4,4′-bipyridine in CH_2Cl_2 (500 cm^3) over a period of 20 h. The desired product was isolated as a yellow solid by filtration of the resulting mixture. Yield 0.82 g, 0.90 mmol, 80%. Anal. Calc. for $C_{45}H_{45}Br_3N_6 \cdot 4.5H_2O$: C, 54.56; H, 5.49; N, 8.48. Found: C, 54.72; H, 4.83; N, 8.33%. The presence of water of solvation was revealed by X-ray crystallography and IR spectroscopy, ν(OH) 3300 cm^{-1}. FAB-MS m/z 829 [M·Br$_2$]$^+$. ^{1}H NMR (D_2O, 400 MHz, δ/ppm): 8.83 (m, 6H, bipy), 8.66 (m, 6H, bipy), 8.37 (m, 6H, bipy), 7.83 (m, 6H, bipy), 6.07 (s, 6H, CH_2N^+), 2.67 (m, 6H, CH_2Me), 0.88 (m, 9H, Me).

Synthesis of 1b. A tenfold excess of ammonium hexafluorophosphate (0.90 g, 5.5 mmol) dissolved in water (200 cm^3) was added dropwise to a stirred solution of **1a** in water (200 cm^3) over 6 h. The product was isolated as a white powder by filtration. Yield: 0.47 g, 0.42 mmol, 77%. Anal. Calc. for $C_{45}H_{45}F_{18}N_6P_3$: C, 48.92; H, 4.11; N, 7.61. Found: C, 48.88; H, 4.15; N, 7.61%. FAB-MS m/z 961 [M·(PF$_6$)$_2$]$^+$. ^{1}H NMR: (CD_3CN, 400 MHz, δ/ppm): 8.90 (m, 6H, bipy), 8.78 (m, 6H, bipy), 8.41 (m, 6H, bipy), 7.90 (m, 6H, bipy), 5.96 (s, 6H, CH_2N^+), 2.62 (m, 6H, CH_2Me), 1.10 (m, 9H, Me).

Synthesis of 2a. 1,3,5-Tri(bromomethyl)-2,4,6-triethylbenzene[74] (1.00 g, 2.27 mmol) and ethyl nicotinate (1.19 g, 7.79 mmol) were dissolved in acetonitrile (120 cm^3) and the mixture refluxed for 6 h. The pale yellow solution was evaporated to dryness to leave a yellow powder which was washed with diethyl ether and then recrystallised from chloroform–hexane. Yield 2.03 g, 2.27 mmol, 100%. Anal. Calc. for $C_{39}H_{48}Br_3N_3O_3$: C, 52.37; H, 5.41; N, 4.70. Found: C, 52.36; H, 5.31; N, 4.55%. FAB-MS m/z 814 [M·Br$_2$]$^+$, 734 [M·Br]$^{\bullet+}$. ^{1}H NMR (D_2O, 400 MHz, J/Hz, δ/ppm): 9.35 (s, 3H, py), 9.10 (d, 3H, J = 8.1, py), 8.89 (d, 3H, J = 6.3, py), 8.25 (dd, 3H, J = 6.3 & 8.1, py), 6.19 (s, 6H, CH_2), 4.50 (q, 6H, J = 7.2, OCH_2Me), 2.68 (q, 6H, J = 7.4, Et), 1.39 (t, 9H, J = 7.4, OCH_2CH_3), 1.19 (t, 9H, J = 7.2 Et).

Synthesis of 2b. A tenfold excess of ammonium hexafluorophosphate (0.94 g, 5.59 mmol) dissolved in water (200 cm^3) was added dropwise to a stirred solution of **2a** in water (200 cm^3) over 1 h. The product was isolated as a white powder by filtration, washed with water and dried. Yield: 0.51 g, 0.46 mmol, 83%. FAB-MS m/z 800 [M·PF$_6$]$^{\bullet+}$, 944 [M·(PF$_6$)$_2$]$^+$. ^{1}H NMR: (CD_3CN, 360 MHz, δ/ppm): 9.33 (s, 3H, py), 9.00 (d, 3H, J = 8.1, py), 8.52 (d, 3H, J = 6.3, py), 8.17 (dd, 3H, J = 6.3 & 8.1, py), 5.97 (s, 6H, CH_2), 4.51 (q, 6H, J = 7.1, OCH_2Me), 2.56 (q, 6H, J = 7.6, Et), 1.42 (t, 9H, J = 7.1, OCH_2CH_3), 1.06 (t, 9H, J = 7.6, Et).

Results and discussion

Host **1** comprises three cationic bipyridinium 'arms' linked *via* a triethyl benzene core. The incorporation of the ethyl groups has been shown in related systems to result in an approximately 10–15 kJ mol^{-1} preference for an alternating conformation around the hexasubstituted aryl ring,[58] imparting a preorganised cone-shaped binding pocket. The lower part of the host cavity is expected to be an electrostatically attractive anion-binding pocket by virtue of its proximity to all three pyridinium nitrogen atoms. Cation **1** is readily prepared in high yield as the tribromide salt (**1a**) by slow addition of 1,3,5-tris(bromomethyl)triethylbenzene[74] to a tenfold excess of 4,4′-bipyridyl in CH_2Cl_2. In contrast, solid state grinding of a mixture of the two reactants leads to a polymeric product. Similar polymer arises from stoichiometric reaction in solution. The structural complementarity of $\mathbf{1}^{3+}$ with Br$^-$ and PF$_6^-$ was probed by X-ray crystal structure determinations of salts **1a** and hexafluorophosphate salt **1b**.

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† CCDC reference numbers 289341 (**1b**), 289342 (**1b**·3H$_2$O), 289343 (**1c**), 289344 (**2a**) and 290379 (**1a**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516027h

Compound **1a** forms a remarkable co-crystal of two entirely different forms of $[\mathbf{1}\subset \mathrm{Br}]^{2+}$, namely a solvated complex (form I) in which **1** acts as a second sphere ligand for hydrated bromide, Fig. 1a, and a solvent-free form (form II) in which host cation **1** acts as a first sphere ligand for bromide, interacting with the anion *via* CH···Br⁻ hydrogen bonds (Fig. 1b). This latter form is reminiscent of the structure of the unsubstituted pyridinium analogue.[29]

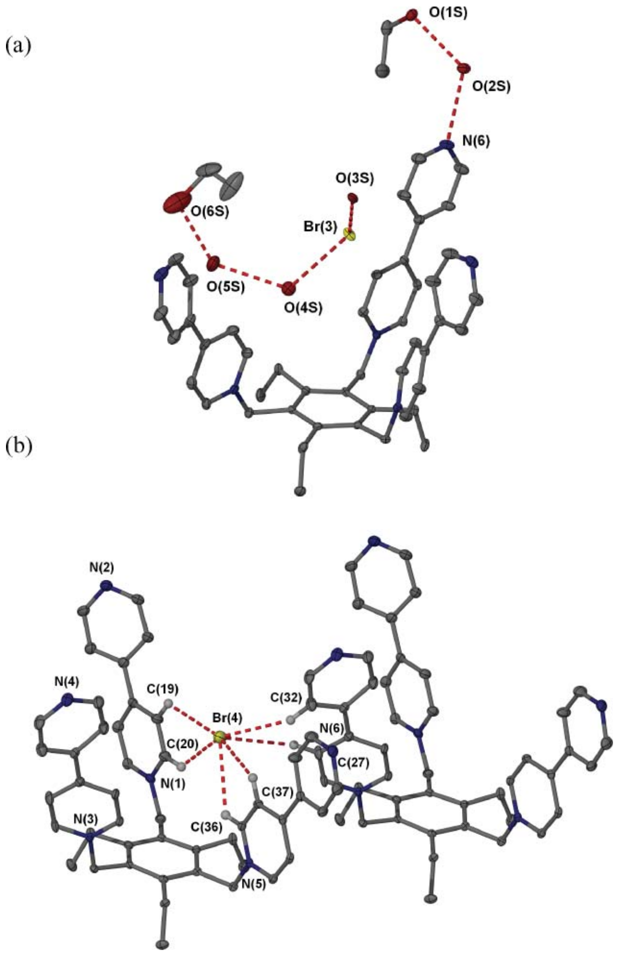


Fig. 1 (a) Structure of solvated $[\mathbf{1a}\subset \mathrm{Br}]^{2+}$ showing positions of included water and ethanol. Selected O···Br distances: 3.222, 3.444 Å. (b) Solvent free $[\mathbf{1a}\subset \mathrm{Br}]^{2+}$ incorporating CH···Br interactions 2.660–2.977 Å.

The host conformation deviates dramatically from the ideal C_{3v} symmetry with two bipyridinium arms essentially co-planar in both forms. In the form II this facilitates CH···Br interactions but this is clearly not the sole reason for the adoption of this conformation and it is also linked to the mutually interpenetrating π-stacking[75–85] between pairs of cation **1** in the solid state. The contrast between forms I and II in this system perhaps provides a fascinating 'snapshot' of the anion inclusion process as the anion is gradually desolvated and coordinated by the host. Clearly however in neither form is there any particular structural complementarity between Br⁻ and **1**.

Treatment of **1a** with NH_4PF_6 in water results in the formation of an immediate precipitate of the solvent-free hexafluorophosphate salt **1b**. Recrystallisation from water–acetonitrile repeatedly gives compound **1b** as an acetonitrile solvate in the chiral hexagonal space group $P6_3$ immediately suggesting the adoption of a threefold-symmetric conformation, in contrast to **1a**. This indeed proves to be the case with the chiral molecule situated upon a crystallographic threefold axis. One PF_6^- anion is deeply included within the molecular cavity. The Flack parameter[73] suggests that spontaneous resolution into the observed *P* enantiomer has occurred. The adoption of this chiral conformation is apparently a direct result of the binding mode of the PF_6^- guest species in $[\mathbf{1}\subset PF_6]^{2+}$ (Fig. 2) and the twisting of the bipyridyl moieties necessary to avoid unfavorable steric interactions between the *meta* pyridyl protons. Since PF_6^- is achiral then, statistically, an equal number of the opposite *M* crystals would be expected.[86] What is immediately clear from examination of the structure, however, is that a racemic mixture of *M* and *P* forms cannot pack efficiently together because of the mutual intercalation of the hosts about a second, independent PF_6^- anion, Fig. 3.

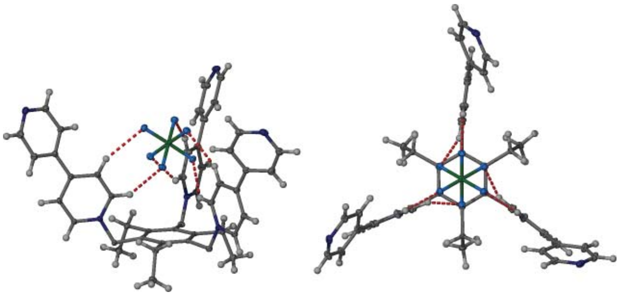


Fig. 2 Encapsulation of PF_6^- by cation **1** in a threefold symmetric conformation in **1b**. The achiral PF_6^- imposes a rigid threefold symmetric structure on the lower pyridinium rings *via* CH···F interactions (H···F distances 2.39 and 2.53 Å). The helical 'twist' in each bipyridyl unit arises from unfavorable steric interactions between the *meta* pyridyl protons.

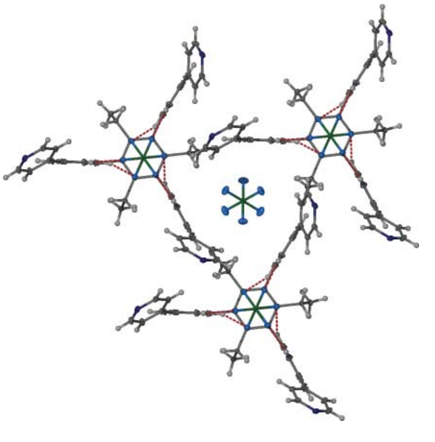


Fig. 3 Crystal packing in **1b** showing the mutual intercalation of the hosts to form edge-to-face π-stacking[11] interactions.

In the highly symmetrical **1b** the structure is dominated by CH···anion and by stacking interactions. The CH···F interactions are expected to be individually weak, however, and only assume particular structural importance in the absence of other, stronger competing interactions (*cf* **1a** forms I and II). Indeed crystallisation of **1b** from aqueous methanol, however, generates a hydrate of **1b** namely $\mathbf{1b}\cdot 3H_2O$. The structure of this second form retains the same essential features of hexagonal **1b** with anion inclusion within the '3-up' cavity by CH $\cdots$ F interactions, however the molecular conformation is of much lower symmetry, apparently in response to the packing demands of the water sheet, which interacts with the pyridine N atoms, and with sideways intercalation of the bipyridinium units, Fig. 4.

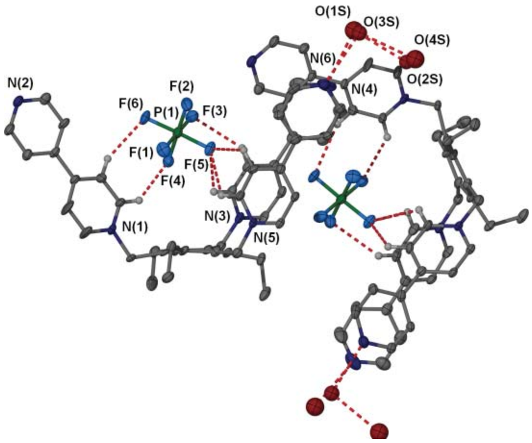


Fig. 4 Structure of **1b**$\cdot$3H_2O showing the lower symmetry host conformation and interdigitated packing, dominated by the poorly resolved water sheet.

The solution anion binding properties of host **1** were examined by ^{1}H NMR titration with a wide variety of anions. No significant changes to the spectrum of **1b** were observed on addition of up to ten molar equivalents of Cl^-, Br^-, I^-, HSO_4^-, SO_4^{2-}, $H_2PO_4^-$, $CH_3CO_2^-$ or NO_3^- in MeCN-d_3 solution. Similarly (^{n}Bu$_4$N)PF$_6$ showed no evidence of displacing Br^- when titrated against **1a** suggesting that 'inorganic' anions of this type do not strongly associate with **1** in a relatively competitive solvent. Experiments in less competitive solvents were not feasible because of the host's insolubility. Interestingly however, a number of significant changes to the ^{1}H NMR spectrum of **1b** were observed in the presence of aromatic anions. Addition of 10 equivalents of 9-anthracenecarboxylate and 2-naphthoate resulted in small (up to 0.23 ppm) shifts to the resonances assigned to the *ortho*-pyridyl protons, while negligible shifts were noted for anions and polyanions containing a single aryl ring (terephthalate, isophthalate and 1,3,5-benzenetricarboxylate).

Slow evaporation of an aqueous methanol solution of **1** in the presence of the aromatic anion 9-anthracenecarboxylate resulted in the formation of crystals of formula **1**$\cdot$(PF$_6$)$_2$(9-anthracenecarboxylate)$\cdot$5H_2O (**1c**) which were characterized by X-ray crystallography. Surprisingly, the tris(bipyridinium) cation in **1c** adopts the unusual '2-up, 1-down' or partial cone conformation in which one bipyridinium unit is orientated in the opposite direction to the other two despite the alternation preference of the hexasubstituted ring. The mutual repulsions of the pyridinium groups apparently destabilise the '3-up' or cone conformation compared to related, neutral compounds. Two of the pyridinium groups still provide an anion binding pocket into which a disordered PF_6^- anion is included *via* CH $\cdots$ F interactions, as noted for **1b**. The interaction between the host cation and 9-anthracene carboxylate anion is of the edge to face type and is characterised by CH $\cdots$ π and remarkably short, charge-assisted[87] CH $\cdots$ O interaction, C(30) $\cdots$ O(1) 3.178 Å; ∠CHO 175°, Fig. 5a. The unusual conformation allows intercalation of one pyridyl group between a pair of pyridyl substituents on an adjacent molecule. The resulting pairwise stack of hosts is approximately the same dimensions as the parallel $PF_6^- \cdots$ 9-anthracenecarboxylate $\cdots$ water stack, Fig. 5b.

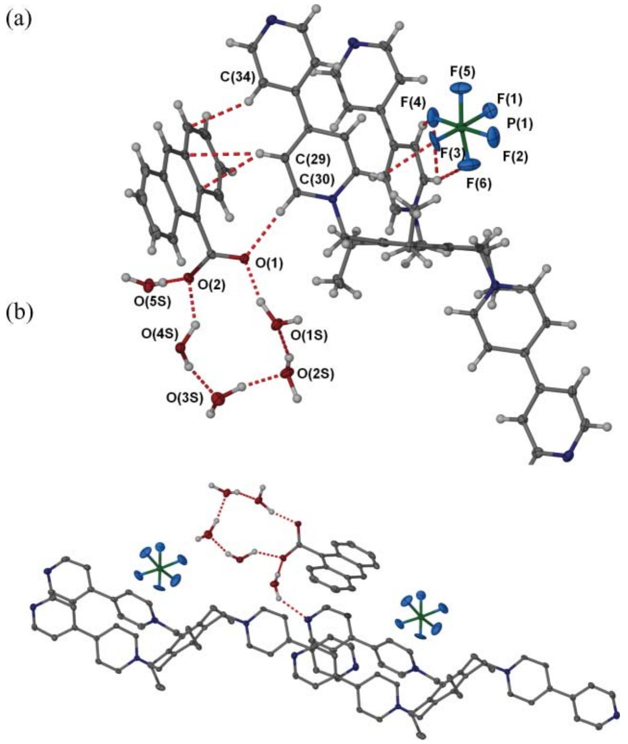
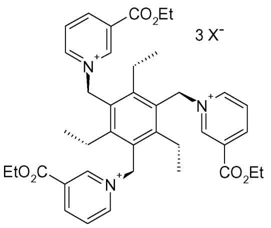


Fig. 5 X-Ray crystal structure of **1**$\cdot$(PF$_6$)$_2$(9-anthracenecarboxylate)$\cdot$5H_2O (**1c**) showing (a) CH $\cdots$ π and CH $\cdots$ O interactions and (b) interdigitated stacking in the 2-up, 1-down conformer (30% ellipsoids).

This interaction with anions capable of taking part in π-stacking interactions (inter-host stacking interactions are observed in the crystal structures of both **1a** and **1b**) is particularly intriguing since titration of **1a** with the disodium salt of adenosine triphosphate Na$_2$ATP in deuterated water–acetonitrile (1 : 1 v/v) also results in significant changes to the pyridyl proton resonances. A good fit to a 1 : 1 binding model was obtained using the program EQNMR[88] which gave a modest binding constant of 70 M^{-1}, albeit in a highly competitive solvent. While it is likely that electrostatic interactions play a significant part in ATP^{2-} binding in this competitive medium, the evidence from other aryl anions and the lack of inorganic sulfate and phosphate binding suggests that π-stacking may also play a significant role in this selectivity pattern.

Given the results with hosts of type **1** we examined another related host, triester **2**, without any acidic hydrogen bond donor functionality, that might be expected to bind *via* CH $\cdots$ anion interactions. Compound **2** as the bromide salt (**2a**) is readily prepared in essentially quantitative yield by reaction of 1,3,5-tri(bromomethyl)-2,4,6-triethylbenzene[74] with ethyl nicotinate in acetonitrile. Counter anion metathesis with NaPF$_6$ smoothly yields the analogous hexafluorophosphate (**2b**). The FAB mass spectra of both salts showed clear peaks assigned to **2**$\cdot X^{\bullet+}$ and **2**$\cdot X_2^+$ (X = Br, PF$_6$) suggesting retention of the anion in the gas phase. Diffusion of diethyl ether into a chloroform solution of **2a** resulted in the isolation of the crystalline solvate **2a**·2CHCl$_3$ which was characterised by X-ray crystallography, Fig. 6.



2a X = Br
2b X = PF$_6$

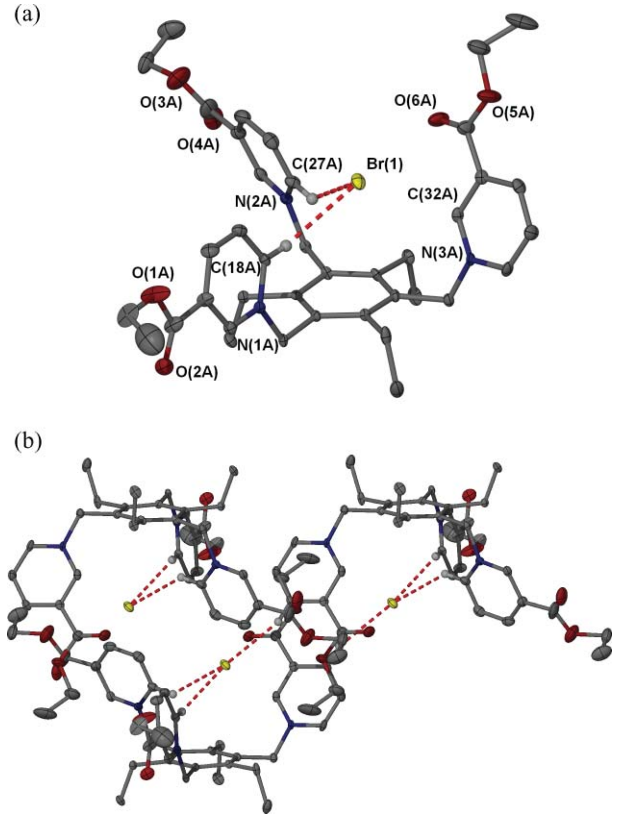


Fig. 6 X-ray crystal structure of **2**·Br$_3$·2CHCl$_3$ (**2a**) showing (a) CH · · · Br interactions and (b) intermolecular CH · · · Br$^-$ interactions and capsular stacking (30% ellipsoids, ester ethyl groups are disordered).

The X-ray structure of **2a** shows the usual 3-up (cone) conformation with all of the ethyl groups orientated on the opposite face of the compound to the pyridinium substituents. One bromide anion is held within the central cavity, forming two short CH · · · Br$^-$ interactions. This intra-cavity bromide is also apparently stabilised by a further such interaction from an adjacent host molecule, Fig. 6b, as well as forming a short Br · · · C(π) contact[22,89] of 3.39 Å that is not apparently a hydrogen bond. The remaining bromide anions form Cl$_3$CH · · · Br$^-$ hydrogen bonds with the enclathrated chloroform as well as further CH · · · Br$^-$ interactions with the acidic pyridinium and methylene groups of the host.

The greater solubility of host **2b** (hexafluorophosphate salt) allowed examination of its affinity for various anions in acetonitrile by NMR spectroscopy. Chemical shift changes upon addition of one equivalents of anion were pronounced for halides with $\Delta\delta = 1.32$ (Cl$^-$), 1.10 (Br$^-$) and 0.71 (I$^-$) ppm. Interestingly, the resonance most affected was the one assigned to the *ortho*-pyridinium protons attached to C(18A), C(27A) and C(32A) (Fig. 6a), suggesting that the X-ray structure of the bromide complex may be retained in solution. In comparison the resonance assigned to the proton *para* to the pyridinium nitrogen atom was essentially unaffected by addition of anions. The *ortho* resonance was unaffected by addition of BF$_4^-$ and ReO$_4^-$ but did show a smaller shift in the presence of NO$_3^-$ (0.54 ppm) and HSO$_4^-$ (0.52 ppm). A full ^{1}H NMR spectroscopic titration was undertaken for Br$^-$ for comparison with the X-ray data giving a binding constant of 838(3) M^{-1}, comparable to the value observed for the unsubstituted tris(pyridinium) host which also binds bromide by CH · · · anion interactions.[29]

Summary and conclusions

This work has shown that CH · · · anion interactions are both important and directional intercations in anion binding systems, particularly when acting collectively and in the absence of stronger, dominant hydrogen bonds. Optimal, multiple CH hydrogen bonds are apparently responsible for solid-state chiral induction and for complexation of anions in competitive media.

Acknowledgements

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