Pergamon

Tetrahedron 54 (1998) 949–968

TETRAHEDRON

Molecular Design using Electrostatic Interactions. 1. Synthesis and Properties of Flexible Tripodand Tri- and Hexa-cations with Restricted Conformations. Molecular Selection of Ferricyanide from Ferrocyanide

Peter J. Garratt* and Ashley J. Ibbett

Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ , U.K.

John E. Ladbury and Ronan O'Brien

Department of Biochemistry and Molecular Biology, University College London, Gower Street, WC1E 6BT, U.K.

Michael B. Hursthouse and K. M. Abdul Malik

U.K.SERC Crystallography Service, Department of Chemistry, University of Wales, Cardiff Park Place, Cardiff, CF1 3TB, U.K.

Received 29 September 1997; accepted 13 October 1997

Abstract: 1,3,5-Tri- and hexa-cations derived from 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene and DABCO or quinuclidine have been prepared and their interaction with polyanions in aqueous solution investigated by ^{1}H NMR titration and by isothermal titration calorimetry. The results from the two techniques are compared and the behaviour of these comparatively simple systems in water is shown to be complex. The trication **3b** forms a crystalline precipitate with ferricyanide but not with ferrocyanide and can select for the one anion in the presence of the other. The structure of the ferricyanide salt **3e** has been determined by X-ray crystallography

Introduction

Molecular recognition has developed as a prime focus of modern chemistry over the last two decades, with an increasing complexity in host molecular structure and a greater understanding of the factors leading to high binding affinities.[1] Interactions in water, where host-guest binding can be greatly enhanced, have attracted special interest because of their relation to biological recognition processes.[2] Hydrophobicity and release of bound solvent to the bulk phase contribute to this increase of binding affinity in water,[3] together with van der Waal's interactions and newly recognised effects, such as π-cation interactions.[4] In most of these studies, the host molecules have surface polar groups for interaction with the solvent and a cavity which is, at least in part, apolar. The binding of the guest molecule then involves desolvation of the guest and host cavity and the general and specific binding of the guest within the host. In biological systems, a considerable number of recognition processes involve an interaction of a small, charged molecule with a charged protein and electrostatic forces make a major contibution to the initial stages of the binding process.[5-7] In order to explore this type of interaction we have designed multiple charged host molecules without a binding cavity so that any host-guest recognition would represent a surface effect. The compounds were designed such that their conformational stability is enhanced by steric interaction, thus providing a longer lifetime for the host-guest complex. It was supposed that both charge and shape matching would be required for high binding affinities.

We now describe the synthesis of a number of polycations based on hexasubstituted benzene and detail how these systems form complexes with polyanions in water. We also report that the symmetrically substituted trication **3b** can specifically select the ferricyanide ion from the ferrocyanide ion in aqueous solution and describe the structure of the resultant salt.

0040-4020/98/$19.00
PII: S0040-4020(97)10351-9

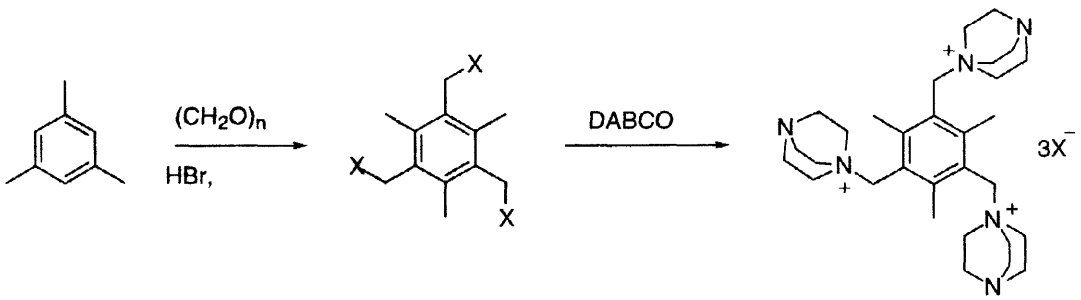
Results and Discussion

Synthesis.

Since we wished both to maximise the effect of electrostatic interaction in the molecule and allow some stability between different conformations, we chose to explore the properties of hexasubstituted benzenes with the charged systems in the 1,3,5-positions. For comparison, we also prepared the corresponding 1,3,5-trisubstituted benzene derivatives in which the bolstering effects of the 2,4,6-substituents would be absent and which would be expected to be conformationally flexible. Tabushi [8,9] and Diederich [10,11] and their respective co-workers had previously used 1,4-diazabicyclo[2.2.2]octane (DABCO) for the formation of cationic ammonium salts as anion receptors, it having among its advantages a symmetrical structure and thus simple spectra, and we chose also to use this as the cationic source.

The trichloride **2a** was treated with DABCO to give the trication **3a** (Scheme 1). The tribromide **2b**, prepared from 1,3,5-trimethylbenzene (**1**) by treatment with paraformaldehyde and HBr by the method of van der Made,[12] was similarly treated with DABCO to give the corresponding bromide salt **3b**. Both of these salts are soluble in water and are deliquescent. The mass spectrum of **3a** showed a signal for the relative molecular mass minus bromide ion and the ^{1}H NMR spectrum in D_2O showed signals for two sets of DABCO methylene groups (δ 3.68, 3.22), and signals for the methylene protons (δ 4.94) and the methyl groups (δ 2.70). The ^{13}C NMR spectrum showed the expected six signals and no evidence for conformational isomerism was seen. The salts **3a** and **3b** could be converted to the corresponding tetraphenylborate **3c** or hexafluorophosphate **3d** salts by treatment of the aqueous solution with sodium tetraphenylborate or ammonium hexafluorophosphate, respectively. These salts are soluble in acetone and the hexafluorophosphates could now be completely purified and characterised. The ^{1}H NMR spectrum of **3d** in acetone-d6 showed signals at δ 5.08 (s, 6H), 3.65 (t, 18H), 3.20 (t, 18H) and 2.86 (s, 9H), and the ^{13}C NMR spectrum showed six signals at δ 148.5, 129.4, 66.2, 54.4, 47.2, and 23.5. The corresponding trications **4a - d** without the methyl substituents on the benzene ring were prepared from 1,3,5-tris(bromomethyl)benzene in the same way.

Scheme 1



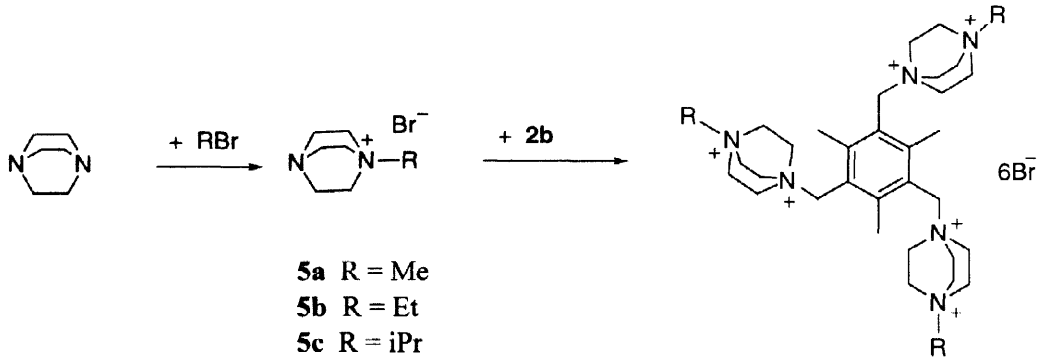
2a X = Cl
2b X = Br

3a X = Cl
3b X = Br
3c X = BPh_4
3d X = PF_6

Attempts to alkylate the nitrogens of the three DABCO moieties in the salts **3a - d** were unsuccessful, either incomplete alkylation occurring or, under more vigorous conditions, decomposition. Consequently, DABCO was alkylated with a number of alkyl bromides to give the corresponding alkyl-DABCO salts **5a - e** which were then treated with the tribromide **2b** to give the corresponding hexacations

6a - e (Scheme 2). These cations were purified by conversion to their hexafluorophosphate salts (**6f - 6j**). The ^{1}H NMR spectrum of **6f** (R = Me, X = PF_6) showed singlets at δ 2.98 and 3.68 for the two sets of methyl protons, triplets at δ 4.19 and 4.41 for the DABCO ethane bridges, and a singlet at δ 5.59 for the benzylic protons. The corresponding hexacations **7a - 7e** without the methyl groups on the benzene ring were prepared from 1,3,5-tris(bromomethyl)benzene.

Scheme 2

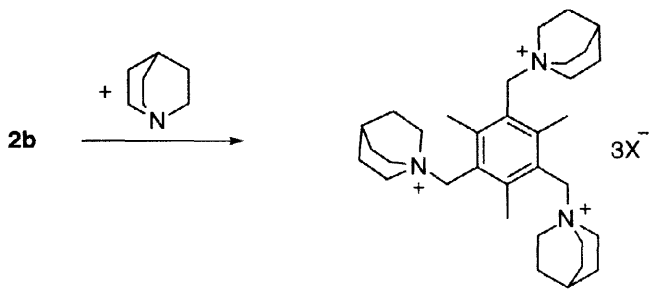


5a R = Me
5b R = Et
5c R = iPr
5d R = nPr
5e R = nBu

6a R = Me
6b R = Et
6c R = iPr
6d R = nPr
6e R = nBu

A similar sequence of reactions was carried out with quinuclidine as the base instead of DABCO, thereby producing a trication without further potential cationic sites. Treatment of **2a** with quinuclidine gave the trication **8a** which was purified as its hexafluorophosphate **8b** (Scheme 3). The ^{1}H NMR spectrum of **8b** shows the expected differences to the DABCO derivative **3d** with the methylene protons remote from the nitrogen at higher field than the corresponding protons in **3d**.

Scheme 3



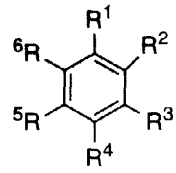
8a X = Br
8b X = PF_6

Complexation Studies.

The tripodand trications of type **3** and **8** were expected to be less conformationally mobile than the trications of type **4** [13] and one might expect that with selected polyanions of the correct shape the less conformationally free cations might be more strongly bound. The complexation of these ions was investigated by using the changes in ^{1}H NMR chemical shifts and by isothermal titration calorimetry.

^{1}H NMR Chemical Shift Measurements

The binding affinities of these trications as the halide salts were examined in D_2O with a series of sodium benzene carboxylates **9a - d** by examining the change in ^{1}H NMR chemical shift of the protons of the anion using the protocol described by Macomber. [14]



9a $R^1 = CO_2Na$; $R^{2-6} = H$
9b $R^{1,3} = CO_2Na$; $R^{2,4,5,6} = H$
9c $R^{1,3,5} = CO_2Na$; $R^{2,4,6} = H$
9d $R^{1,2,4,5} = CO_2Na$; $R^{3,6} = H$

Standardized solutions of trications and anions were prepared in D_2O and aliquots combined to give a constant volume of solution. The cation was initially considered to be the host and the ratio of host:guest was varied stepwise from 5:1 to zero, the latter providing the initial position of the anion signals, and ^{1}H NMR spectra were taken at 7 relative concentrations. The concentration of host varied between 50 mM and 3 mM, and that of the guest was kept constant at 10 mM. The plots of chemical shift difference against the ratio of host-guest concentrations were then fitted by iterative curve-fitting procedures, using data within the values 0.2 and 0.8 of the parameter p of Weber,[15] and association constants were derived from these curves. Typical titration curves are shown in Figure 1.

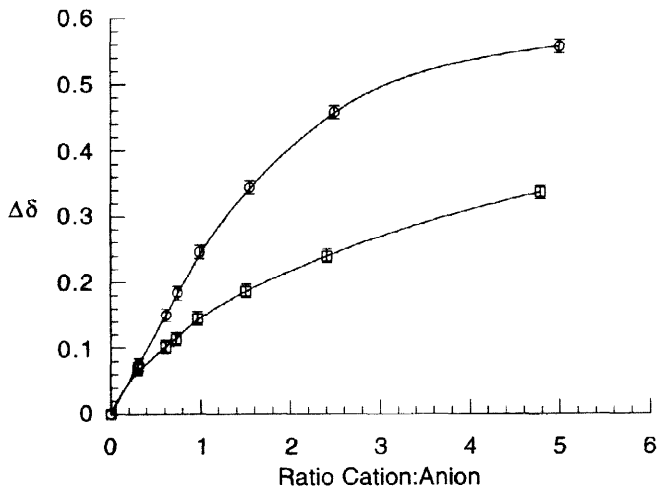


Figure 1: NMR titration of trications against constant concentration of anions.
□ Trication **3b** against dianion **9b**. ○ Trication **3b** against trianion **9c**.

Since the protons of the cation also exhibit chemical shift changes during complexation the chemical shift change for the benzylic and methyl protons of the cation were also determined. Typical titration curves are shown in Figure 2. Comparison of Figures 1 and 2 clearly shows that the process of complexation is not reflected by the chemical shifts of the two components in the same way. Whereas in the case of the cation

proton signals the change in shift is virtually over by the time 1:1 equivalence is reached, with the anion protons the effect continues to much higher host:guest ratios. In order to show that this was not an artefact of the order of addition, an experiment was conducted where the role of host and guest was reversed and the same results were obtained.

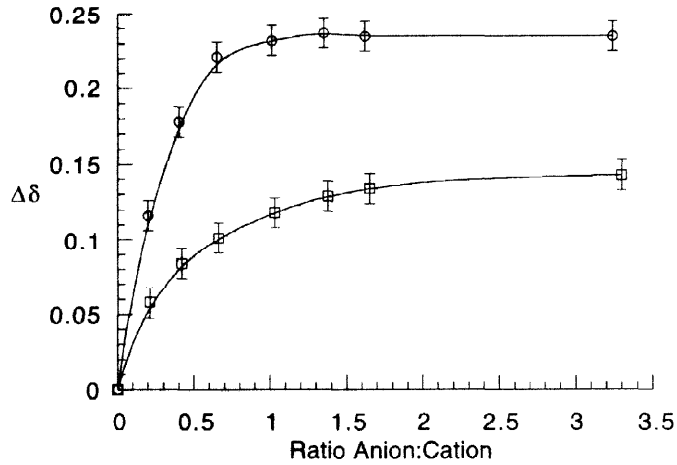


Figure 2: NMR titration of anions against constant concentration of trication.
□ Dianion **9b** against trication **3b**. ○ Trianion **9c** against trication **3b**.

A similar series of experiments were carried out with the hexacations. The cation and anion protons again exhibited changes in the chemical shifts similar to those observed for the trication/anion combinations.

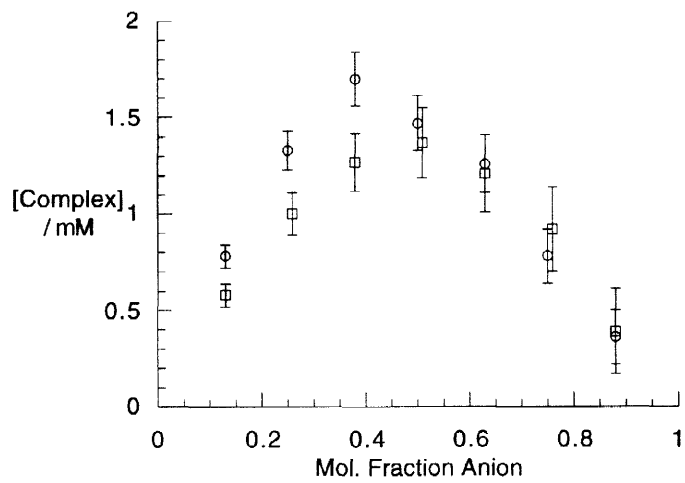


Figure 3: Job plots of trication **3b** with dianion **9b** and trianion **9c**.
□ Trication **3b** with dianion **9b**. ○ Trication **3b** with trianion **9c**.

In order to examine the stoichiometry of binding between the host and guest, Job plots were obtained from separate experiments in which the concentration of ions was constant with different ratios of host and guest.[16] All of the host:guest combinations showed symmetric curves with maxima at equivalent

concentrations of the two components, indicating that 1:1 complexes had been formed, except for the combinations of **3b** with **9a**, **3b** with **9c**, and **8a** with **9c** for which, in each case, the maximum is found for a larger mole fraction of the cation. The two systems **3b**:**9c** and **8a**:**9c** are those in which the electronic charges are balanced in the complex and yet these deviate from the 1:1 stoichiometry, both showing a maximum at *ca.* 3:2. These are shown in Figure 3.

Association constants and Free Energies of Association determined from the ^{1}H NMR chemical shift changes of the anion protons in those complexes showing 1:1 stoichiometry in the Job plots are shown in Table 1.

Table 1. Association Constants and Free Energies of Association determined from the ^{1}H NMR chemical shift changes of the anion protons.

Cation	Anion	K_a (Anion)	ΔG kJ mol^{-1}
3b	**9b**	67	-10.4
3b	**9d**	170	-12.7
4b	**9c**	47	-9.5
6b	**9c**		-16.5
6c	**9c**	5357	-21.8

Isothermal Titration Calorimetry

Because of this deviation from 1:1 stoichimetry between those combination of cations and anions with the best complementarity as regards charge interactions, some of these binding interactions were studied using isothermal titration calorimetry. In this method the enthalpy provides a direct probe of the extent of interaction. A series of injections of one component, which is placed in an automated syringe, into the other, which is placed in the calorimeter cell, is made. A titration is thus performed in which the concentrations of the interacting components is such that over a series of injections the binding site(s) of the component in the calorimeter becomes saturated. From this titration a direct determination of the molar enthalpy is obtained. The binding constant, K_B, can be determined from the profile of the titration curve, which is dictated by the binding equilibrium. From these parameters a complete thermodynamic characterization of the interaction is determined on the basis of the following relationship: [17,18]

$$-RT \ln K_B = \Delta H - T\Delta S = \Delta G.$$

Trication 3b with trianion 9c

Since this would appear to have the best stereo-complimentarity of the systems investigated, it was chosen for initial study. Isothermal titration calorimetry measures the total enthalpy for a given process and thus, if additional equilibria are present in the concentration regime adopted for the experiment, the heats associated with these equilibria are incorporated in the data. In many cases it is possible to deconvolute the heat effects arising from several events. In the case of the trication-trianion interaction the curves indicates that the complex formed on addition of the trianion to the trication does not occur with a simple 1:1 stoichiometry, a finding in accordance with the ^{1}H NMR observations. It appears that larger complexes are

more stable which probably results from interaction of the monomeric units. The data for titrations performed at 20 °C over a range of concentrations is shown in Table 2 and the graphs of these titrations are shown in Figure 4. There is a small effect of concentration of the cation on the observed curve which could result from the anion induced oligomerization of the cation in the cell. This is not unexpected since solvation of the largely hydrophobic interacting molecules is due to the presence of charge which, on complex formation, is less able to interact with solvent. The results are shown in Table 2.

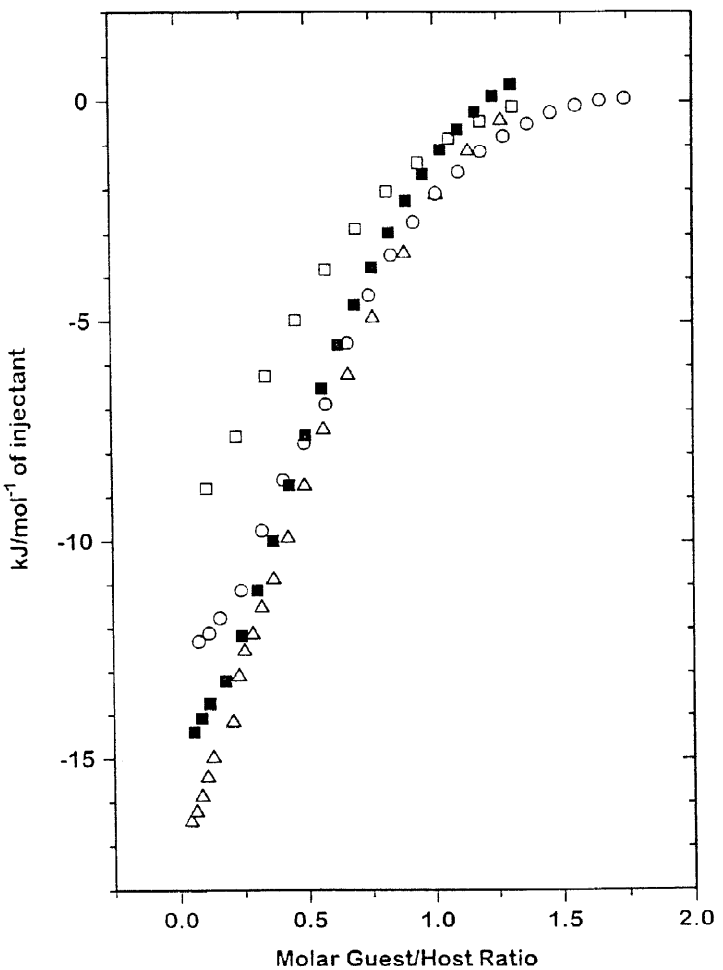


Figure 4. Isothermal titration calorimetric studies of trication **3b** with trianion **9c.** Trianion **9c** was added in a series injections to trication **3b** at 20 °C at various relative concentrations.
□ 30 mM into 3 mM; ○ 40 mM into 4.5 mM;△ 56 mM into 4.5 mM

The mean stoichiometry, N, of this reaction was determined as 0.6. The mean binding constant, K_B, was found to be 972 M^{-1}, with a large SD, and the mean enthalpy of reaction, ΔH, was -21.5 ±3.9 kJ mol^{-1}. Although the errors in these determinations are in the range expected for a system of this type in which the interaction is weak and in which other processes are occurring, there appears to be some effect due to the concentration of interacting species. From the equation a mean value for ΔG of -16.8±1.1 kJ mol^{-1} was derived.

Presuming a 1:1 complex occurs then three salt bridges are formed. Assuming these contribute equally to the thermodynamics of binding, the value of the enthalpy for salt bridge formation, $\Delta H/n$ (where n = 3 salt

bridges), is -7.2 kJ mol^{-1}. The mean value of ΔG for the formation of a salt bridge is -16.8/3 kJ mol^{-1}, that is -5.6 kJ mol^{-1}. This is very similar to the value of ΔG/n determined by Schneider *et al.*,[19] from ^{1}H NMR titration studies, who suggested a value of -5 ± 1 kJ mol^{-1}.

Table 2. Titration of trication 3b with trianion 9c at various concentrations

Conc., mM Syringe	Conc., mM Cell	Stoichiometry N	K_B, M^{-1}	ΔH kJ mol^{-1}
30	3	0.526	1070	-17.7
40	4.5	0.621	1720	-16.7
40	6	0.619	990	-21.2
56	9.6	0.619	585	-25.8
56	9.6	0.597	496	-26.0

Trication 3b and tetraanion 9d

The interaction is too weak for an accurate determination of the thermodynamic parameters to be made using ITC. Unlike the reaction of **3b** with **9c**, this reaction is endothermic and any interaction must be entropy driven.

Hexacations 6 with trianion 9c

The additional charged groups present on the hexacation compared to the trication add to the complexity of the titration and the titration curve appears to incorporate an additional interaction (Figure 5). This is attributed to the trianion induced association of the hexacation giving rise to higher order complexes. As the trianion is added to the calorimetric cell containing the hexactions, the huge excess of positively charged host molecules could result in structures involving a network of molecules in which the guest trianion binds a number of hexacation molecules. As further anions are added these networks dissociate to give rise to smaller intermolecular complexes. The titration curves are too complex for reliable fitting and hence no thermodynamic data is reported.

Hexacation 6d with tetraanion 9d

For this reaction a value of 1.63 for N was determined. K_B was 1170 M^{-1} and the reaction was endothermic, ΔH having a value of +11.7±2.8 kJ mol^{-1}, although again these values show some concentration dependence. From these determinations the values of -17.4±0.9 kJ mol^{-1} for ΔG was derived. The binding in this system is again entropic in character. The stoichiometry of the reaction suggests that the model is more complex than that taken to derive these results. The large increase in entropy in this system may derive from the release of complexed water molecules to the bulk environment.

From these results there does seem to be a significant difference in the nature of the **3b**/ **9c** interaction when compared with those of the other systems investigated by isothermal calorimetry.

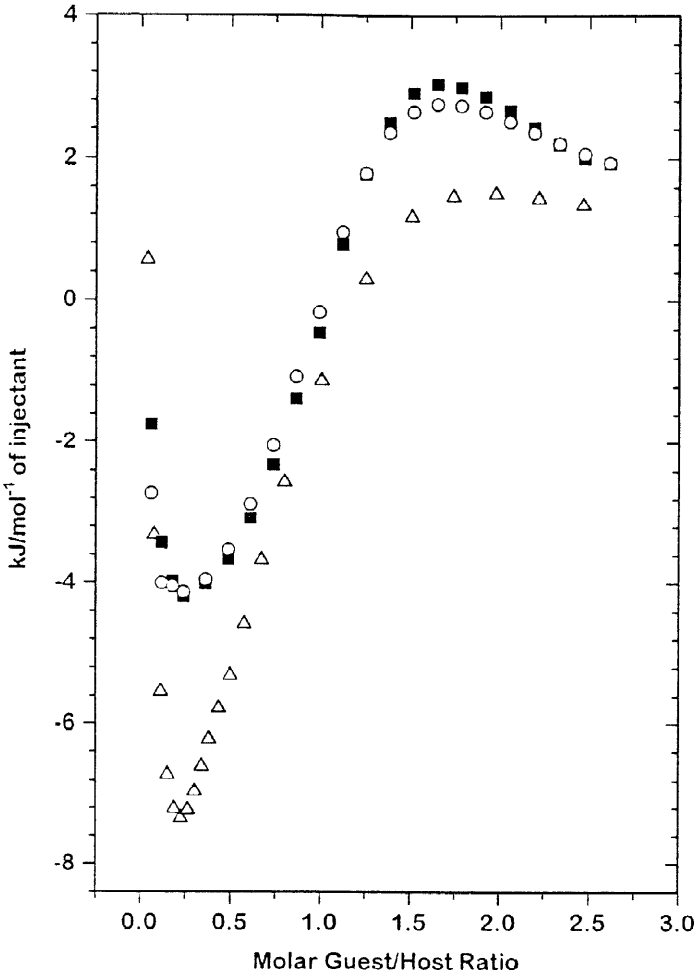


Figure 5. Isothermal titration calorimetric studies of hexacation **6d** with trianion **9c**. Trianion **9c** was added in a series of injections to hexacation **6d** at 20 °C at various relative concentrations □ , ○ 40 mM into 3 mM; △ 120 mM into 12 mM

Comparison of results from ^{1}H NMR titrations and Isothermal Titration Calorimetry

The two systems with the assumed best-fit with regard to charge equivalence , **3b** + **9c** and **4b** + **9c** show much the largest change in chemical shift of the anion protons ($\Delta\delta \sim 0.5$). The first system, however, does not appear to form a 1:1 complex and the second, because of the slow attainment of maximum $\Delta\delta$, shows a smaller association constant than those combinations with much smaller chemical shift changes. Since isothermal titration calorimetry shows that the combination **3b**/**9c** is more tightly bound than the other trication complexes, we may be observing an association in which, after the initial binding, further arrangement of the two ligands together with the solvent and other counter-ions occurs to give a tighter ion pair,[20,21] so that the final chemical shift does not reflect the actual chemical shift of the initially formed ion pair. The larger value found for the combination of **3b** with the monoanion **9a** may also be due to a more complex situation with more than one molecule of **9a** involved, as is suggested from the Job plot which indicates a value of 3.

Salt Precipitation

A solution of **3b** (X = Br) in water was treated with an equimolar solution of potassium ferricyanide and on standing yellow-orange crystals precipitated. The crystals showed a band at 2110 cm^{-1} in the IR spectrum indicative of the presence of the ferricyanide ion. An X-ray structural analysis of the crystals at 140 K showed that they were of **3e** (X = $Fe^{III}(CN)_6.8H_2O$) and illustrated the interaction of the trication in its all-cis conformation with the trianion, as shown in Figure 6.

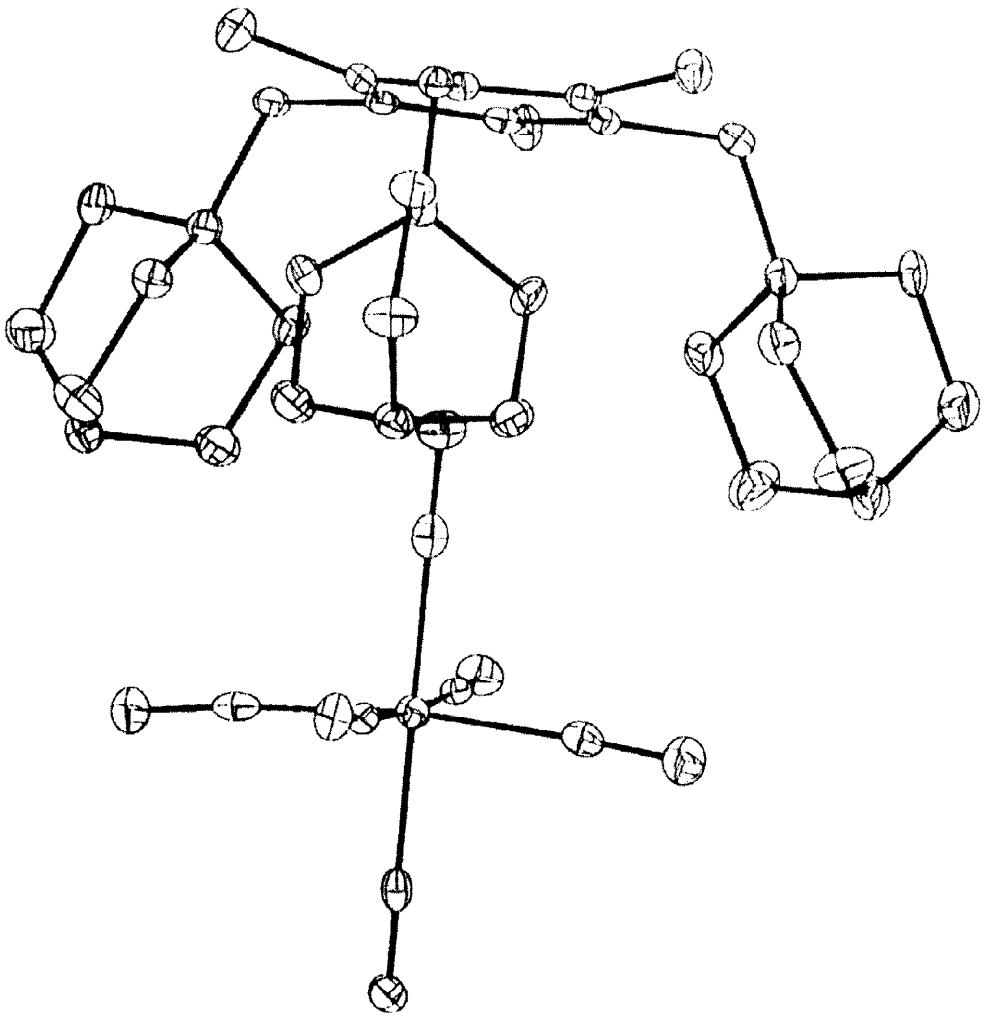


Figure 6. Crystallographic structure of **3e**, $[Fe(CN)_6]$ $[C_{30}H_{51}N_6]$.

Addition of a solution of **3b** (X = Br) to a solution of potassium ferrocyanide gave no crystalline precipitate even after prolonged standing, while addition of **3b** (X = Br) to a solution containing a mixture of ferri- and ferrocyanide gave crystals of the ferricyanide complex as shown by the IR spectrum. The residual solution showed a diminution of the CN stretching band due to the ferricyanide compared to that of ferrocyanide (2043 cm^{-1}), although the effect was not as great as the amount of precipitate would have indicated, possibly because of oxidation of the ferrocyanide. The addition of a solution of **4b** (X=Br) to potassium ferricyanide gave no precipitate after prolonged standing, again indicating the importance of the methyl substituents in prolonging the lifetime of the all-cis conformation of **3b** in the complex, thus allowing

a substantial concentration of the complex and the occurrence of nucleation. The quinuclidine analogue of **3b**, the trication **8a**, also gave crystals when treated with ferricyanide but not with ferrocyanide. In this case, however, we were unable to obtain crystals of the complex suitable for X-ray crystallographic analysis.

Solid State ^{13}C NMR Spectroscopy

We were surprised to observe that the solid state ^{13}C NMR spectrum of **3e** (X = $Fe^{III}(CN)_6.8H_2O$) recorded using magic-angle spinning and cross-polarisation, showed well resolved peaks at similar chemical shifts to the solution NMR spectrum of **3d** (X = PF_6). This indicates that the interaction between the paramagnetic iron atom and the organic trication is small. The most likely reason for this is that the paramagnetic coupling is reduced by rapid reorientation of the DABCO groups within the crystals at room temperature. This theory is supported by two observations. Firstly, peaks from the DABCO environments are still observed in the solid state ^{13}C NMR spectrum even after a 40 ms period of interrupted ^{1}H decoupling and, secondly, the linewidth ($\Delta\upsilon_{1/2}$) of the peak observed in the solid state ^{1}H NMR spectrum is only 350 Hz (recorded using a magic-angle spinning speed of 4.5 kHz).

Conclusions

These comparatively simple polycations exhibit a number of interesting features and pose a number of questions regarding the interactions of ions in aqueous solution. Restricting the conformational mobility of the polycation clearly changes its behaviour and allows it to interact at all cationic centres at the same time with a complementary polyanion. This is most strikingly seen in the precipitation of the ferricyanide salts of the hexasubstituted trications derived from either DABCO or quinuclidine, which does not occur with the corresponding trisubstituted benzene analogues. Charge matching is probably the dominant factor in the interactions of these polycations, although the shape of the polyanion component is also of importance. We had hoped that these systems would be of sufficient simplicity that a value for a salt-bridge between a cationic and anionic charge could have been measured or estimated with some accuracy. As the results from the isothermal calorimetry show, however, the interaction between the designed ions, the spectator counterions and the water molecules in these systems is already complex. It would appear that, when the concentration of the polycation is high compared to the polyanion, networks are formed in which the polyanion species is shared by more than one polycation. Increasing the concentration of the polyanion leads to regrouping of these species and eventually, in favourable cases, to formation of a system in which there approximates a one-to-one correspondence between the polycation and polyanion. As these changes occur it seems likely that water molecules are displaced from solvation sites in the charged species to the bulk water. The spectator ions are themselves not indifferent, as we have shown by measuring the effects of salt concentration on the ^{1}H NMR chemical shifts. When the complete process is explored by ITC then the system with the best complementarity, **3b** with **9c**, has a much greater enthalpy of binding and higher binding constants than the others. We continue to explore related polycation and complementary polyanion systems in order to clarify further the interactions that occur in these intriguing systems.

Experimental Section

Melting points were determined on a Reichert melting point apparatus and are uncorrected. Mass spectra were recorded on either a VG micromass 305 electron impact (EI) or VG-ZAB SE fast atom

bombardment (FAB) mass spectrometer with Finnigan Incos II data system at University College London. In some cases overloaded spectra were recorded in order to see the parent-ion, and in this case neither the relative intensities nor a base peak are recorded. For hexabromide salts a complex splitting pattern is observed in the parent-ion and in such cases only the most intense peak in the group is noted. ^{1}H and ^{13}C NMR spectra recorded at 400 MHz and 100 MHz respectively on a Varian VXR-400 instrument, with residual protic solvent as the internal standard, except where D_2O was used as the solvent. In the latter case the spectrometer was referenced to 3-(trimethylsilyl)propionic-*2,2,3,3-d*4 acid, sodium salt before and after insertion of the sample to be examined. IR spectra were recorded on a Perkin-Elmer 1605 FT-IR spectrophotometer as KBr pellets. Microanalyses were carried out by the microanalytical section of the Chemistry Department, University College London.

Chemical reagents were purchased from Aldrich Chemical Co., Lancaster Synthesis, ACROS and BDH. Diethyl ether and tetrahydrofuran (sodium and benzophenone) were distilled under an atmosphere of nitrogen immediately prior to use. All other solvents and reagents were used as received unless otherwise stated.

Analytical thin layer chromatography was performed on pre-coated aluminium backed plates (Merck Kieselgel 60 F_{254}) and visualised using ultraviolet light (254 nm), iodine or potassium permanganate.

2,4,6-Tris(bromomethyl)mesitylene (2b). A solution of hydrogen bromide in acetic acid (45% w/v, 17.5 mL) was added rapidly to a mixture of mesitylene (3.02 g, 25.1 mmol), paraformaldehyde (2.51 g, 83.6 mmol) and glacial acetic acid (25 mL). The mixture was stirred for 20 h at 95 °C and then poured into water (100 mL). A precipitate formed which was removed by filtration on a glass frit and dried under vacuum. Recrystallisation from chloroform/light petroleum gave white needles of **2b** (8.62 g, 21.6 mmol, 86%), mp 184-186 °C (lit. [14]186 °C).

Monoalkylated DABCO

General Procedure. The bromoalkane was added via a syringe to a solution of DABCO in acetonitrile over a period of 15 min. The resultant mixture was stirred for either 4-6 h or overnight, after which time the solution was poured into diethyl ether (400-700 mL) and stirred for 1 h. A precipitate formed which was removed by filtration and dried *in vacuo* .

N-Methyl-DABCO bromide (5a). Bromomethane in diethyl ether (2.0 M solution, 6.0 mL, 12 mmol) was added to a solution of DABCO (2.50 g, 22.3 mmol) in acetonitrile (40 mL) . The mixture was stirred for 4 h and then poured into diethyl ether (400 mL) and stirred for 30 min. The precipitate formed was removed by filtration and dried *in vacuo* to give **5a** as a white hygroscopic powder (2.23 g, 10.8 mmol, 90%), mp 253-255 °C (dec.). ^{1}H NMR (D_2O) δ 3.09 (s, 3H), 3.23 (t, 6H, J = 7.4 Hz), 3.43 (t, 6H, J = 7.6 Hz); ^{13}C NMR (D_2O) δ 46.8, 54.2, 56.6; FAB-MS *m/z* 335 (7.9), 333 (8.1) ($[2M-Br]^+$), 127 (100) ($[M-Br]^+$).

N-Ethyl-DABCO bromide (5b). DABCO (2.78 g, 24.8 mmol) and 1-bromoethane (1.00 mL, 13.4 mmol) in acetonitrile (40 mL) were reacted as described in the general procedure to give **5b** as a white hygroscopic powder (2.47 g, 11.2 mmol, 83%), mp 190-192 °C. ^{1}H NMR (D_2O) δ 1.38 (t, 3H, J = 7.1 Hz), 3.25 (br, 6H), 3.41 (m, 8H); ^{13}C NMR (D_2O) δ 9.8, 47.0, 54.3, 62.8; FAB-MS *m/z* 363 (7.5), 361 (7.7) ($[2M-Br]^+$), 141 (100) ($[M-Br]^+$).

N-2-Propyl-DABCO bromide (5c). DABCO (5.05 g, 45.0 mmol) and 2-bromopropane (2.50 mL, 26.6 mmol) in acetonitrile (100 mL) were reacted as described in the general procedure to give **5c** as a white hygroscopic powder (6.13 g, 26.0 mmol, 98%), mp 231-233 °C (lit. 228 °C). ^{1}H NMR (D_2O) δ 1.38 (d, 6H, J = 6.7 Hz), 3.19 (t, 6H, J = 7.3 Hz), 3.40 (t, 6H, J = 7.3 Hz), 3.57 (heptet, 1H, J = 6.6 Hz); ^{13}C NMR (D_2O) δ 18.2, 47.1, 51.9, 69.2; FAB-MS *m/z* 391 (6.1), 389 (4.8) ($[2M-Br]^+$), 155 (100) ($[M-Br]^+$).

N-1-Propyl-DABCO bromide (5d). DABCO (2.48 g, 22.1 mmol) and 1-bromopropane (1.00 mL, 11.3 mmol) in acetonitrile (30 mL) were reacted as described in the general procedure to give **5d** as a white hygroscopic powder (2.18 g, 9.3 mmol, 82%), mp 144-146 °C. ^{1}H NMR (D_2O) δ 0.98 (t, 3H, J = 7.3 Hz), 1.79 (sextet, 2H, J = 8.2 Hz), 3.21 (m, 8H) 3.41 (br t, 6H); ^{13}C NMR (D_2O) δ 12.8, 17.8, 47.0, 54.9, 68.8; FAB-MS *m/z* 390 (14.3), 388 (14.0) ($[2M-Br]^+$), 155 (100) ($[M-Br]^+$).

N-1-Butyl-DABCO bromide (5e). DABCO (2.61 g, 23.3 mmol) and 1-bromobutane (1.00 mL, 9.2 mmol) in acetonitrile (100 mL) were reacted as described in the general procedure to give **5e** as a white hygroscopic powder (1.88 g, 7.5 mmol, 82%), mp 128-130 °C. ^{1}H NMR (D_2O) δ 0.96 (t, 3H, J = 7.4 Hz), 1.39 (m, 2H), 1.75 (m, 2H), 3.21 (t, 6H, J = 6.5 Hz), 3.27 (t, 2H, J = 8.1 Hz), 3.42 (t, 6H, J = 6.9 Hz); ^{13}C NMR (D_2O) δ 15.6, 22.0, 26.0, 47.0, 54.9, 67.3; FAB-MS *m/z* 418 (2.4), 416 (2.4) ($[2M-Br]^+$), 169 (100) ($[M-Br]^+$).

Trications

General Procedure. A mixture of the aromatic trihalide and the amine were stirred in acetonitrile at room temperature for 24-36 h during which time precipitation occurred. The flask contents were poured into diethyl ether (400-700 mL) and stirred for 1 h. The precipitate was removed by filtration, washed with diethyl ether (3x50 mL) and acetonitrile (3x15 mL), and then dried *in vacuo* . The hexafluorophosphate salt was obtained by dissolving the halide product in water (*ca.* 5% w/v) and then adding a saturated aqueous solution of ammonium hexafluorophosphate until no further precipitation occurred. The precipitate was removed by filtration, dissolved in acetone and dried over potassium carbonate. Evaporation of the solvent, followed by recrystallisation of the residue from a mixture of acetonitrile and methanol yielded the hexafluorophosphate salt.

2,4,6-Tris(DABCO-N-methyl)mesitylene trichloride (3a). 2,4,6-Tris(chloromethyl)mesitylene (0.30 g, 1.35 mmol) and DABCO (3.00 g, 26.8 mmol) were reacted in acetonitrile (100 mL) as described in the general procedure to give **3a** as a hygroscopic white powder (0.71 g, 1.18 mmol, 94.4%), mp 252-255 °C (dec.). ^{1}H NMR (D_2O) δ 2.67 (s, 9H), 3.20 (br, 18H), 3.64 (br), 4.92 (s, 6H); ^{13}C NMR (D_2O) δ 23.8, 47.4, 54.6, 66.5, 129.6, 149.7; FAB-MS *m/z* 567 (0.9), 566 (0.2), 565 (2.2) ($[M-Cl]^+$), 113 (100).

2,4,6-Tris(DABCO-N-methyl)mesitylene tribromide (3b). A solution of 2,4,6-tris(bromomethyl)-mesitylene (1.98 g, 4.96 mmol) and DABCO (5.85 g, 52.2 mmol) in acetonitrile (150 mL) was treated as outlined in the general procedure to give **3b** as a hygroscopic white powder (3.22 g, 4.4 mmol, 88%), mp 227-229 °C (dec.). ^{1}H NMR (D_2O) δ 2.70 (s, 9H), 3.22 (br t, 18H), 3.68 (br t, 18H), 4.94 (s, 6H); ^{13}C NMR (D_2O) δ 23.5, 47.2, 54.4, 66.2, 129.4, 149.5; FAB-MS *m/z* 657 (7.5), 655 (13.9), 653(7.0) ($[M-Br]^+$), 137 (100).

2,4,6-Tris(DABCO-N-methyl)mesitylene tri(hexafluorophosphate) (3d). The tribromide **3b** (0.22 g, 0.30 mmol) was converted to the hexafluorophosphate salt as outlined in the general procedure to yield colourless plates, which upon removal from the mother liquor and drying *in vacuo* gave **3d** (0.21 g, 0.23 mmol, 75%) as a white solid, mp 234-236 °C (dec.). ^{1}H NMR (d$_6$-acetone) δ 2.86 (s, 9H), 3.20 (br t, 18H), 3.65 (br t, 18H), 5.08 (s, 6H); ^{13}C NMR (d$_6$-acetone) δ 21.8, 46.0, 53.0, 64.4, 128.1, 148.5; FAB-MS *m/z* 785 (34.0) ([M-PF$_6$]$^+$), 320 (8.6) ([M-2PF$_6$]$^{2+}$), 192 (100). Anal. Calcd for $C_{30}H_{51}N_6F_{18}P_3.3H_2O$: C, 36.57; H , 5.83; N, 8.53. Found: C, 36.59; H, 5.68; N, 8.44.

1,3,5-Tris(DABCO-N-methyl)benzene tribromide (4a). A solution of 1,3,5-tris(bromomethyl)-benzene (0.19 g, 0.53 mmol) in acetonitrile (35 mL) was added dropwise to a solution of DABCO (1.04 g, 9.27 mmol) in acetonitrile (30 mL). The solution was stirred for 48 h during which time a precipitate formed. The contents of the flask were poured into ether (350 mL) and stirred for 10 minutes. The precipitate was removed by filtration under nitrogen and dried *in vacuo* to give **4a** as a white hygroscopic solid (0.35 g, 0.50 mmol, 95%), mp 255-258 °C (dec.). ^{1}H NMR (D$_2$O) δ 3.23 (t, 18H, J = 7.1 Hz), 3.60 (t, 18H, J = 7.1 Hz), 4.68 (s, 6H), 7.88 (s, 3H); ^{13}C NMR (D$_2$O) δ 46.9, 54.7, 69.5, 131.4, 142.4; FAB-MS *m/z* 615 (34.6), 613 (67.6), 611 (37.2) ([M-Br]$^+$), 112 (100).

1,3,5-Tris(DABCO-N-methyl)benzene tri(tetraphenylborate) (4c). The tribromide **4a** was dissolved in water (25 mL) and to the resulting solution was added sodium tetraphenylborate (0.20 g, 0.58 mmol) in water (25 mL). A precipitate formed which was removed by filtration and dried *in vacuo*. After dissolution of the material in acetonitrile followed by filtration and removal of the solvent under reduced pressure, **4c** was isolated as an off-white solid (0.67 g, 0.47 mmol, 89%), mp 143-146 °C (dec.). ^{1}H NMR (d$_6$-acetone) δ 3.03 (t, 18H, J = 7.1 Hz), 3.26 (t, 18H, J = 7.1 Hz), 4.55 (s, 6H), 6.78 (t, 12H, J = 7.2 Hz), 6.91 (t, 24H, J = 7.4 Hz), 7.16 (br m, 24H), 7.68 (s, 3H); ^{13}C NMR (d$_6$-acetone) δ 44.7, 51.7, 65.5, 121.5, 125.3, 128.6, 135.5, 139.4, 163.3; FAB-MS *m/z* 1092 (5.0) ([M-BPh4]$^+$), 112 (100).

2,4,6-Tris(Quinuclidine-N-methyl)mesitylene tribromide (8a). A solution of 2,4,6-tris-(bromomethyl)mesitylene (0.45 g, 1.13 mmol) and quinuclidine (0.46 g, 4.14 mmol) in acetonitrile (40 mL) were treated as outlined in the general procedure to yield **8a** as a hygroscopic white powder (0.76 g, 1.03 mmol, 92%), mp 267-270 °C (dec.). ^{1}H NMR (D$_2$O) δ 2.01 (br, 18H), 2.18 (m, 3H), 2.66 (s, 9H), 3.66 (br, 18H), 4.77 (s, 6H); ^{13}C NMR (D$_2$O) δ 21.3, 23.5, 26.4, 57.2, 65.8, 129.9, 149.0; FAB-MS *m/z* 654 (11.5), 652 (22.1), 650 (10.5) ([M-Br]$^+$), 541 (28.8), 112 (100).

2,4,6-Tris(Quinuclidine-N-methyl)mesitylene tri(hexafluorophosphate) (8b). The tribromide (**8a**) (0.30 g, 0.41 mmol) was converted to the hexafluorophosphate salt as outlined in the general procedure to yield **8b** as colorless plates, which upon removal from the mother liquor and drying *in vacuo* gave a white solid (0.30 g, 0.32 mmol, 79%), mp 290-292 °C (dec.). ^{1}H NMR (d$_6$-acetone) δ 2.04 (m, 18H), 2.13 (m, 3H), 2.82 (s, 9H), 3.75 (t, J = 7.9 Hz, 18H), 4.96 (s, 6H); ^{13}C NMR (d$_6$-acetone) δ 19.4, 21.3, 24.2, 55.1, 63.7, 128.0, 147.6; FAB-MS *m/z* 782 (37.0) ([M-PF$_6$]$^+$), 319 (24.5) ([M-2PF$_6$]$^{2+}$), 137 (100). Anal. Calcd. for $C_{33}H_{54}N_3F_{18}P_3$: C, 42.73; H, 5.87; N, 4.53. Found, C, 42.48; H, 5.85; N, 4.73.

Hexacations

General Procedure

A mixture of the aromatic trihalide and amine were stirred in acetonitrile at room temperature for 24-72 h during which time precipitation of a white solid occurred. This precipitate was removed by filtration, washed with acetonitrile (3x20 mL), and then dried *in vacuo* . The hexafluorophosphate salt was obtained by dissolving the halide product in water (*ca.* 5% w/v), followed by addition of a saturated aqueous solution of ammonium hexafluorophosphate until no further precipitation occurred. This precipitate was removed by filtration, dissolved in acetone and dried over potassium carbonate. Evaporation of the solvent, followed by recrystallisation of the residue from a mixture of acetonitrile and methanol, gave the hexafluorophosphate salt.

2,4,6-Tris(N'-methyl-DABCO-N-methyl)mesitylene hexabromide (6a). 2,4,6-Tris(bromomethyl)-mesitylene (0.20 g, 0.50 mmol) and N-methyl-DABCO bromide (0.52 g, 2.51 mmol) in acetonitrile (40 mL) were treated as described in the general procedure to give **6a** as a white powder (0.49 g, 0.48 mmol, 96%), mp 234-236 °C (dec.). ^{1}H NMR (D_2O) δ 2.78 (s, 9H), 3.41 (s, 9H), 4.06 (t, 18H, J = 7.0 Hz), 4.31 (t, 18H, J = 7.2 Hz), 5.27 (s, 6H); ^{13}C NMR (D_2O) δ 23.8, 53.9, 55.4, 56.4, 67.2, 129.7, 151.3; FAB-MS *m/z* 939 ($[M-Br]^+$), 860 ($[M-2Br]^+$), 460.

2,4,6-Tris(N'-methyl-DABCO-N-methyl)mesitylene hexa(hexafluorophosphate) (6f). The hexa-bromide **6a** (0.25g, 0.25 mmol) was converted to the hexafluorophosphate salt as outlined in the general procedure to yield, after drying *in vacuo*, **6f** as a white solid (0.29g, 0.21 mmol, 84%), mp 236-239 °C (dec.).^{1}H NMR (d6-acetone) δ 2.98 (s, 9H), 3.68 (s, 9H), 4.19 (t, 18H, J = 7.0 Hz), 4.41 (t, 18H, J = 7.0 Hz), 5.59 (s, 6H); ^{13}C NMR (d6-acetone) δ 21.2, 51.8, 53.3, 54.1, 65.1, 127.6, 150.2; FAB-MS *m/z* 1265 ($[M-PF_6]^+$), 1120 ($[M-2PF_6]^+$), 460.

2,4,6-Tris(N'-ethyl-DABCO-N-methyl)mesitylene hexabromide (6b). 2,4,6-Tris(bromomethyl)-mesitylene (0.34 g, 0.85 mmol) and N-ethyl-DABCO bromide (0.73 g, 3.30 mmol) in acetonitrile (45 mL) were treated as described in the general procedure to give **6b** as a white powder (0.86 g, 0.81 mmol, 95%), mp 222-225 °C (dec.). ^{1}H NMR (D_2O) δ 1.46 (t, 9H, J = 7.3 Hz), 2.80 (s, 9H), 3.71 (q, 6H, J = 7.3 Hz), 4.00 (t, 18H, J = 7.1 Hz), 4.32 (t, 18H, J = 7.1 Hz), 5.29 (s, 6H); ^{13}C NMR (D_2O) δ 9.8, 23.6, 53.6, 53.7, 63.9, 67.0, 129.5, 151.0; FAB-MS *m/z* 983 ($[M-Br]^+$), 901 ($[M-2Br]^+$), 459

2,4,6-Tris(N'-ethyl-DABCO-N-methyl)mesitylene hexa(hexafluorophosphate) (6g). The hexabromide **6b** (0.30 g, 0.28 mmol) was converted to the hexafluorophosphate salt as outlined in the general procedure to yield, after drying *in vacuo*, **6g** as a white solid (0.34 g, 0.23 mmol, 84%), mp 247-249 °C (dec.). ^{1}H NMR (d6-acetone) δ 1.45 (t, 9H, J = 7.2 Hz), 2.95 (s, 9H), 3.94 (q, 6H, J = 7.3 Hz), 4.11 (t, 18H, J = 7.2 Hz), 4.38 (t, 18H, J = 7.0 Hz), 5.59 (s, 6H); ^{13}C NMR (d6-acetone) δ 7.9, 21.5, 51.6, 52.1, 61.9, 65.1, 128.0, 150.2; FAB-MS *m/z* 1307 (1.3) ($[M-PF_6]^+$), 581 (0.8) ($[M-2PF_6]^{2+}$), 141 (100). Anal. Calcd. for $C_{36}H_{66}N_6F_6P_{36}$ C: 29.76; H, 4.58; N, 5.78. Found: C, 29.10; H, 4.60; N, 5.39.

2,4,6-Tris(N'-2-propyl-DABCO-N-methyl)mesitylene hexabromide (6c). 2,4,6-Tris-(bromomethyl)-mesitylene (0.08 g, 0.20 mmol) and N-2-propyl-DABCO bromide (0.17 g, 0.72 mmol) in acetonitrile (25

mL) were treated as described in the general procedure to give **6c** as a white powder (0.18 g, 0.16 mmol, 81%), mp 220-223 °C (dec.). ^{1}H NMR (D_2O) δ 1.48 (d, 18H, J = 6.5 Hz), 2.78 (s, 9H), 3.96 (br t, 18H), 4.18 (br, 3H), 4.28 (br t, 18H), 5.28 (s, 6H); ^{13}C NMR (D_2O) δ 18.3, 23.8, 51.5, 53.8, 66.9, 71.4, 129.8, 151.1; FAB-MS *m/z* 1023 (2.7) ($[M-Br]^+$), 473 (2.5) ($[M-2Br]^{2+}$), 155 (100).

2,4,6-Tris(N'-2-propyl-DABCO-N-methyl)mesitylene hexa(hexafluorophosphate) (6h). The hexabromide **6c** (0.22 g, 0.30 mmol) was converted to its hexafluorophosphate salt as outlined in the general procedure to yield, after drying *in vacuo*, **6h** as a white solid (0.26 g, 0.17 mmol, 87%), mp 251-253 °C (dec.). ^{1}H NMR (d_6-acetone) δ 1.52 (d, 18H, J = 5.7 Hz), 2.95 (s, 9H), 4.10 (br, 18H), 4.21 (br, 3H), 4.36 (br, 18H), 5.60 (s, 6H); ^{13}C NMR (d_6-acetone) δ 15.7, 21.1, 49.4, 51.6, 64.3, 68.6, 128.0, 149.1; FAB-MS *m/z* 1349 ($[M-PF_6]^+$), 1204 ($[M-2PF_6]^+$), 602 ($[M-2PF_6]^{2+}$). Anal. Calcd. for $C_{39}H_{72}N_6F_6P_{36}.H_2O$ C: 30.96; H, 4.93; N, 5.56. Found: C, 30.81; H, 4.76; N, 5.57

2,4,6-Tris(N'-1-propyl-DABCO-N-methyl)mesitylene hexabromide (6d). 2,4,6-Tris-(bromomethyl)-mesitylene (0.20 g, 0.50 mmol) and N-1-propyl-DABCO bromide (0.84 g, 3.63 mmol) in acetonitrile (45 mL) were treated as described in the general procedure to give **6d** as a white powder (0.51 g, 0.46 mmol, 90%), mp 205-207 °C (dec.). ^{1}H NMR (D_2O) δ 1.00 (t, 9H, J = 7.2 Hz), 1.85 (m, 6H), 2.77 (s, 9H), 3.55 (m, 6H), 4.00 (t, 18H, J = 7 Hz), 4.29 (t, 18H, J = 7 Hz), 5.27 (s, 6H); ^{13}C NMR (D_2O) δ 12.4, 18.2, 23.8, 53.9, 54.3, 67.1, 69.5, 129.7, 151.2; FAB-MS *m/z* 1023 ([M-Br]+), 944 ($[M-2Br]^+$),473 ($[M-2Br]^{2+}$).

2,4,6-Tris(N'-1-propyl-DABCO-N-methyl)mesitylene hexa(hexafluorophosphate) (6i). The hexabromide **6d**(0.45 g, 0.41 mmol) was converted to the hexafluorophosphate salt as outlined in the general procedure to yield, after drying *in vacuo*, **6i** as a white solid (0.47 g, 0.31 mmol, 77%), mp 224-226 °C (dec.).^{1}H NMR (d_6-acetone) δ 1.02 (t, 9H, J = 7.3 Hz), 1.86 (m, 6H), 2.95 (s, 9H), 3.80 (br, 6H), 4.12 (br t, 18H), 4.40 (br t, 18H), 5.58 (s, 6H); ^{13}C NMR (d_6-acetone) δ 10.4, 11.3, 21.5, 52.1, 52.3, 65.1, 67.2, 128.1, 150.8; MS FAB-MS *m/z* 1349 ($[M-PF_6]^+$), 1203 ($[M-2PF_6]^+$), 602 ($[M-2PF_6]^{2+}$). Anal. Calcd. for $C_{39}H_{72}N_6F_6P_{36}$ C: 31.34; H, 4.85; N, 5.62. Found: C, 30.81; H, 4.76; N, 5.54

2,4,6-Tris(N'-1-butyl-DABCO-N-methyl)mesitylene hexabromide (6e). 2,4,6-Tris(bromomethyl)-mesitylene (0.20 g, 0.50 mmol) and N-1-butyl-DABCO bromide (0.93 g, 3.73 mmol) in acetonitrile (45 mL) were treated as described in the general procedure to give **6e** as a white powder (0.52 g, 0.45 mmol, 90%), mp 203-206 °C (dec.). ^{1}H NMR (D_2O) δ 0.98 (t, 9H, J = 7.3 Hz), 1.42 (m, 6H), 1.82 (m, 6H), 2.78 (s, 9H), 3.60 (m, 6H), 4.00 (t, 18H, J = 6.6 Hz), 4.30 (t, 18H, J = 6.6 Hz), 5.27 (s, 6H); ^{13}C NMR (D_2O) δ 15.3, 21.5, 23.5, 26.0, 53.6, 54.0, 66.8, 67.9, 129.4, 150.9; FAB-MS *m/z* 1067 ($[M-Br]^+$), 986 ($[M-2Br]^+$).

2,4,6-Tris(N'-1-butyl-DABCO-N-methyl)mesitylene hexa(hexafluorophosphate) (6j). The hexabromide **6e** (0.37 g, 0.32 mmol) was converted to the hexafluorophosphate salt as outlined in the general procedure to yield, after drying *in vacuo*, **6j** as a white solid (0.40 g, 0.26 mmol, 81%), mp 243-245 °C (dec.). ^{1}H NMR (d_6-acetone) δ 0.96 (t, 9H, J = 7.3 Hz), 1.44 (m, 6H), 1.82 (m, 6H), 2.94 (s, 9H), 3.85 (br m, 6H), 4.12 (br t, 18H), 4.43 (br t, 18H), 5.60 (s, 6H); ^{13}C NMR (d_6-acetone) δ 4.4, 15.9, 20.8, 21.8, 52.1, 52.2, 65.1, 65.8, 128.0, 150.3; FAB-MS *m/z* 1391 (2.2) ($[M-PF_6]^+$), 623 (1.6) ($[M-2PF_6]^{2+}$), 169 (100). Anal. Calcd. for $C_{42}H_{78}N_6F_6P_{36}$ C: 32.82; H, 5.12; N, 5.47. Found: C, 32.41; H, 5.23; N, 5.24

1,3,5-Tris(N'-methyl-DABCO-N-methyl)benzene hexabromide (7a). 1,3,5-Tris(bromomethyl)benzene (0.18 g, 0.50 mmol) and N-methyl-DABCO bromide (0.38 g, 1.83 mmol) in acetonitrile (30 mL) were treated as described in the general procedure to give **7a** as a white powder (0.40 g, 0.41 mmol, 81%), mp 228-231 °C (dec.). ^{1}H NMR (D_2O) δ 3.44 (s, 9H), 4.11 (t, J = 6.9 Hz, 18H), 4.28 (t, J = 6.8 Hz, 18H), 5.08 (s, 6H), 8.16 (s, 3H); ^{13}C NMR (D_2O) δ 53.7, 55.3, 56.1, 69.7, 131.3, 143.2; FAB-MS *m/z* 899 ($[M-Br]^+$), 693.

1,3,5-Tris(N'-methyl-DABCO-N-methyl)benzene hexa(hexafluorophosphate) (7f). The hexabromide **7a** (0.34 g, 0.35 mmol) was converted to the hexafluorophosphate salt as outlined in the general procedure to yield, after drying *in vacuo*, **7f** as a white solid (0.44 g, 0.32 mmol, 93%), mp 261-263 °C. ^{1}H NMR (d_6-acetone) δ 3.65 (s, 9H), 4.29 (m, 36H), 5.21 (s, 6H), 8.20 (s, 3H); ^{13}C NMR (d_6-acetone) δ 52.2, 53.6, 54.3, 67.9, 129.8, 141.5; FAB-MS *m/z* 1223 ($[M-PF_6]^+$), 1077 ($[M-2PF_6]^+$), 539 ($[M-2PF_6]^{2+}$). Anal. Calcd. for $C_{30}H_{54}N_6F_{36}P_6$: C, 26.33; H, 3.98; N, 6.14. Found: C, 26.17; H, 4.04; N, 6.06.

1,3,5-Tris(N'-ethyl-DABCO-N-methyl)benzene hexabromide (7b). 1,3,5-Tris(bromomethyl)benzene (0.19 g, 0.53 mmol) and N-ethyl-DABCO bromide (0.51 g, 2.31 mmol) in acetonitrile (35 mL) were treated as described in the general procedure to yield **7b** as a white powder (0.46 g, 0.45 mmol, 85%), mp 232-235 °C (dec.). ^{1}H NMR (D_2O) δ 1.46 (t, 9H, J = 6.2 Hz), 3.71 (br q, 6H, J = 7.1 Hz), 4.04 (br, 18H), 4.26 (br, 18H), 5.08 (s, 6H), 8.17 (s, 3H); ^{13}C NMR (D_2O) δ 9.9, 53.5, 53.8, 64.0, 69.6, 131.4, 143.2; FAB-MS *m/z* 939 ($[M-Br]^+$), 859 ($[M-2Br]^+$), 363.

1,3,5-Tris(N'-ethyl-DABCO-N-methyl)benzene hexafluorophosphate (7g). The hexabromide **7b** (0.29 g, 0.28 mmol) was converted to the hexafluorophosphate salt as outlined in the general procedure to yield, after drying *in vacuo*, **7g** as a white solid (0.36 g, 0.26 mmol, 90%), mp 282-284 °C. ^{1}H NMR (d_6-acetone) δ 1.47 (t, 9H, J = 7.2 Hz), 3.89 (q, 6H, J = 7.3 Hz), 4.16 (br t, 18H), 4.28 (br t, 18H), 5.22 (s, 6H), 8.26 (s, 3H); ^{13}C NMR (d_6-acetone) δ 7.9, 51.5, 52.1, 62.0, 67.7, 129.8, 141.4; FAB-MS *m/z* 1265 ($[M-PF_6]^+$), 1120 ($[M-2PF_6]^+$), 560 ($[M-2PF_6]^{2+}$), 459. Anal. Calcd. for $C_{33}H_{60}N_6F_{36}P_6$: C, 28.10; H, 4.29; N, 5.96. Found: C, 28.10; H, 4.30; N, 5.73.

1,3,5-Tris(N'-2-propyl-DABCO-N-methyl)benzene hexabromide (7c). 1,3,5-Tris(bromomethyl)benzene (0.19 g, 0.53 mmol) and N-2-propyl-DABCO bromide (0.60 g, 2.55 mmol) in acetonitrile (35 mL) were treated as described in the general procedure to give **7c** as a white powder (0.44 g, 0.41 mmol, 78%), mp 242-245 °C (dec.). ^{1}H NMR (D_2O) δ 1.49 (d, 18H, J = 5.8 Hz), 4.00 (br, 18H), 4.22 (br, 21H), 5.05 (s, 6H), 8.15 (s, 3H); ^{13}C NMR (D_2O) δ 18.0, 51.1, 53.8, 69.3, 71.3, 131.4, 143.0. FAB-MS *m/z* 983 ($[M-Br]^+$), 901 ($[M-2Br]^+$), 452 ($[M-2Br]^{2+}$).

1,3,5-Tris(N'-2-propyl-DABCO-N-methyl)benzene hexa(hexafluorophosphate) (7h). The hexabromide **7c** (0.31 g, 0.29 mmol) was converted to the hexafluorophosphate salt as outlined in the general procedure to yield, after drying *in vacuo*, **7h** as a white solid (0.37 g, 0.26 mmol, 87%), mp 227-229 °C. ^{1}H NMR (d_6-acetone) δ 1.55 (d, 18H, J = 6.4 Hz), 4.17 (br, 18H), 4.25 (br, 21H), 5.22 (s, 6H), 8.29 (s, 3H); ^{13}C NMR (d_6-acetone) δ 15.5, 48.8, 51.7, 66.9, 68.9, 129.4, 140.8; FAB-MS *m/z* 1307 ($[M-PF_6]^+$), 1162 ([M-

$2PF_6]^+$), 581 ($[M-2PF_6]^{2+}$). Anal. Calcd. for $C_{36}H_{66}N_6F_{36}P_6$: C, 29.76; H, 4.58; N, 5.78. Found: C, 29.80; H, 4.64; N, 5.96.

1,3,5-Tris(N'-1-propyl-DABCO-N-methyl)benzene hexabromide (7d). 1,3,5-Tris(bromomethyl)benzene (0.17 g, 0.48 mmol) and N-1-propyl-DABCO bromide (0.44 g, 1.87 mmol) in acetonitrile (30 mL) were treated as described in the general procedure to give **7d** as a white powder (0.33 g, 0.31 mmol, 78%), mp 235-238 °C (dec.). ^{1}H NMR (D_2O) δ 1.03 (t, 9H, J = 7.1 Hz), 1.88 (br, 6H) 3.58 (br t, 6H, J = 8.1 Hz), 4.06 (br, 18H), 4.26 (br, 18H), 5.08 (s, 6H), 8.17 (s, 3H); ^{13}C NMR (D_2O) δ 12.5, 18.3, 54.0, 54.2, 69.6, 69.8, 131.6, 143.4; FAB-MS *m/z* 983 ($[M-Br]^+$), 902 ($[M-2Br]^+$).

1,3,5-Tris(N'-1-propyl-DABCO-N-methyl)benzene hexa(hexafluorophosphate) (7i). The hexabromide **7d** (0.11 g, 0.10 mmol) was converted to the hexafluorophosphate salt as outlined in the general procedure to yield, after drying *in vacuo*, **7i** as a white solid (0.11 g, 0.08 mmol, 73%), mp 261-263 °C. ^{1}H NMR (d_6-acetone) δ 0.99 (t, 9H, J = 7.3 Hz), 1.91 (m, 6H), 3.75 (m, 6H), 4.18 (br, 18H), 4.28 (br, 18H), 5.20 (s, 6H), 8.24 (s, 3H); ^{13}C NMR (d_6-acetone) δ 10.4, 16.2, 52.1, 52.2, 67.3, 67.7, 129.8, 141.4; FAB-MS *m/z* 1307 (42.9) ($[M-PF_6]^+$), 581 (12.2) ($[M-2PF_6]^{2+}$), 155 (100). Anal. Calcd for $C_{36}H_{66}N_6F_{36}P_6$: C, 29.76; H, 4.58; N, 5.78. Found: C, 29.67; H, 4.57; N, 5.85.

1,3,5-Tris(N'-1-butyl-DABCO-N-methyl)benzene hexabromide (7e). 1,3,5-Tris(bromomethyl)benzene (0.17 g, 0.48 mmol) and N-1-butyl-DABCO bromide (0.43 g, 1.73 mmol) in acetonitrile (30 mL) were reacted as described in the general procedure to give **7e** as a white powder (0.38 g, 0.34 mmol, 72%), mp 242-245 °C (dec.). ^{1}H NMR (D_2O) δ 0.96 (t, 9H, J = 7.3 Hz), 1.41 (q, 6H, J = 7.2 Hz), 1.81 (br, 6H), 3.60 (m, 6H), 4.03 (br, 18H), 4.23 (br, 18H), 5.04 (s, 6H), 8.13 (s, 3H); ^{13}C NMR (D_2O) δ 15.3, 21.5, 26.1, 53.8, 53.9, 68.0, 69.6, 131.4, 143.1. FAB-MS *m/z* 1023 (1.4) ($[M-Br]^+$), 169 (100).

1,3,5-Tris(N'-1-butyl-DABCO-N-methyl)benzene hexa(hexafluorophosphate) (7j). The hexabromide **7e** (0.23 g, 0.21 mmol) was converted to the hexafluorophosphate salt as outlined in the general procedure to yield, after drying *in vacuo*, **7j** as a white solid (0.22 g, 0.15 mmol, 71%), mp 272-274 °C (dec.). ^{1}H NMR (d_6-acetone) δ 0.94 (t, 9H, J = 7.3 Hz), 1.42 (m, 6H), 1.88 (m, 6H), 3.83 (m, 6H), 4.23 (br, 18H), 4.28 (br, 18H), 5.21 (s, 6H), 8.23 (s, 3H); ^{13}C NMR (d_6-acetone) δ 13.3, 19.5, 24.1, 51.7, 51.9, 65.6, 67.4, 129.5, 141.1; FAB-MS *m/s* 1349 ($[M-PF_6]^+$), 601 ($[M-2PF_6]^{2+}$). Anal. Calcd. for $C_{39}H_{72}N_6F_{36}P_6$: C, 31.34; H, 4.85; N, 5.62. Found: C, 30.74; H, 5.18; N, 5.28.

NMR Titrations

Stock solutions were prepared containing (i) host and guest (typically 50 mM and 10 mM respectively) and (ii) guest (typically 10 mM). Aliquots of these solutions were combined to give eight samples with varying ratios of host and guest. The quantities of each solution used were generally as follows, where the first figure in each series refers to the quantity of the mixed host-guest stock solution in mL, the second figure refers to the quantity of pure guest stock solution in mL, and the third figure refers to the corresponding host:guest ratio: 0.80, 0.00, 5.0; 0.40, 0.40, 2.5; 0.25, 0.55, 1.6; 0.16, 0.64, 1.0; 0.12, 0.68, 0.8; 0.10, 0.70, 0.6; 0.05, 0.75, 0.3; 0.00, 0.80, 0.0.

Isothermal Titration Calorimetry

All samples were dissolved in HPLC grade water. Calorimetric measurements were made at 25 °C using an MCS ITC (MicroCal Inc., Northampton, MA, USA). The heats of dilution were determined in separate experiments by titration of the injection of the component in the syringe into water and the injection of water into the component in the calorimetric cell. The heats derived from these control experiments were subtracted from the total heats of reaction before data analysis. In the systems in which no oligomerization of the interacting components occurs the heats of dilution are approximately constant during the course of the titration. It was thus possible to clearly identify interactions where the unbound components were associated.

To assess the effects of possible protonation, experiments were performed in 5 mM MOPS at pH 7.0. No differences in data were, however, observed from those obtained in water.

X-ray Crystallography

Crystal data for $[C_{30}H_{51}N_6][Fe(CN)]_6 \cdot 8H_2O$, M_r = 851.87, Monoclinic, $P2_1/n$, a = 16.436(5), b = 19.551(6), c = 13.111(4) Å, b = 90.80(2)°, U = 4213(2)Å^3, Z = 4, D_c = 1.343 g cm^{-3}, m(Mo-Ka) = 4.22 cm^{-1}, $F(000)$ = 1828, T = 140 K. Crystallographic measurements were made using a FAST area detector diffractometer and Mo-Ka radiation (l = 0.71069Å), following previously described procedures.[22] The structure was solved by direct methods (SHELX-S)[23] and refined on F_o^2 by full-matrix least-squares (SHELXL-93)[24] using all 6291 unique data (632 parameters) to final wR (on F^2) = 0.0927 and R (on F) = 0.0545. The non-hydrogen atoms were anisotropic; the hydrogens on water molecules were all experimentally located and refined with O-H distance constrained at 0.95(1) Å, the -CH_3 and -CH_2- hydrogens were included in riding model; U_{iso}(H) free to refine.

Acknowledgement. AJI thanks the Engineering and Physical Science Research Council (U.K.) for a postgraduate award. We thank Dr R. Wrigglesworth (SIMR) and Dr A. Sella for valuable discussions and Professor J. H. Ridd for his advice and help and the provision of computer programs to determine association constants. We thank ULIRS service for the solid state NMR spectra and Dr P. Barrie for his guidance in their interpretation. JEL is a Wellcome Trust Research Career Development Fellow.

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