Molecular Recognition Using Highly Charged Podands

A thesis presented to the University College London in partial fulfilment of the requirements for the degree of Doctor of Philosophy

by

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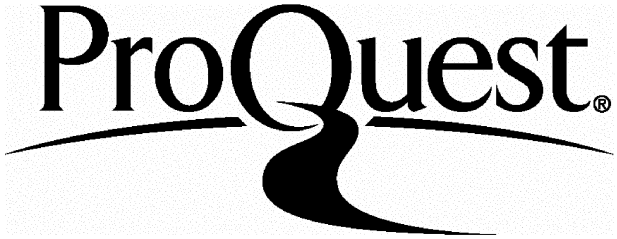

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To My Parents and Grandmother

also

In loving memory of My Grandfather

Abstract

This thesis describes the syntheses and host-guest properties of some anion receptors. These have been designed as mimics for the initial interactions of peptides with small molecules which mainly involves electrostatic binding. Treatment of substituted bromomethyl benzenes and naphthalenes with 1,4-diazabicyclo[2.2.2]octane (DABCO) gave a series of polycations with different substitution patterns. These patterns ensured different degrees of conformational freedom and "restricted" molecules were compared with "non-restricted" analogues. Nuclear Magnetic Resonance techniques were extensively used to investigate the behaviour of these polycations with simple anionic guests. Association constants and stoichiometries of the complexes were determined using NMR titrations and Job's plots, respectively.

Specific recognition of ferricyanide over ferrocyanide was observed with these polycations. X-ray crystal structure analysis on some of the resulting complexes revealed interesting information regarding the conformation adopted by these polycations. The crystal structure also indicated that structured water molecules were involved in cation-anion binding.

The syntheses of polycationic thiols and their electrochemical behaviour attached to a gold electrode are described. Treatment of ω-bromoundecanethiol with DABCO gave the corresponding N-mono-thioundecanyl DABCO precursor. On treatment of this precursor with substituted bromomethyl benzenes, a series of polycationic thiol derivatives was obtained. The kinetics of electrode processes were studied by cyclic voltammetry, in which the current is monitored as the potential of the electrode is changed. The redox potentials of potassium ferrocyanide and sodium bromide in phosphate buffer were examined.. Such self-assembled monolayers (SAMs) are permeable to electrolytes but show some inhibition of redox processes at the electrode. Inhibition of oxidation of ferrocyanide and enhancement of oxidation of bromide were observed, the extent of these effects varying with the structure of the attached species. A model to explain these results is advanced.

Acknowledgements

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Finally, I would like to thank my parents, my family and my fiancée for their support and patience during the past years.

Contents

Glossary

ADP	adenosine diphosphate
AMP	adenosine monophosphate
ATP	adenosine triphosphate
br	broad unresolved signal
br-d	broad doublet
br-m	broad multiplet
br-s	broad singlet
br-t	broad triplet
$CDCl_3$	deuterated chloroform
CV	cyclic voltammogram
d	doublet
DABCO	1,4-diazabicyclo[2.2.2]octane
D_6-DMSO	deuterated dimethylsulfoxide
DIPAD	diisopropyl azodicarboxylate
D_2O	deuterium oxide
FAB	fast electron bombardment
IR	infra-red
J	coupling constant
K	association constant
m	multiplet
MCPBA	m-chloroperbenzoic acid
Mp	melting point
MS	mass spectroscopy
NMR	nuclear magnetic resonance
s	singlet
SAM	self-assembling monolayer
t	triplet
THF	tetrahydrofuran

1 Introduction

"Molecular Recognition" is the basis of many biochemical processes but it is only during the last two decades that the attention of organic chemists has turned towards the design and synthesis of molecules that can recognise other molecules. This type of recognition is normally achieved through a reversible formation of a complex between a large organic molecule (the host) and a comparatively smaller species (the guest). Distinction between two different guests is based upon different association constants of the complexations[1].

$$H + G_1 \rightleftharpoons HG_1 \qquad K_1$$

$$H + G_2 \rightleftharpoons HG_2 \qquad K_2$$

$$H + G_1 + G_2 \rightleftharpoons HG_1 + G_2 \qquad K_1 > K_2$$

Since the formulation of the lock-and-key analogy by Emil Fischer[2] more than 100 years ago, molecular recognition has been one of the most important concepts in structural biology and also has an influence on the theory of host-guest complexes and crystal packing. If we neglect dynamic aspects and remain in the framework of the rigid-body approximation, we may consider the association between host and guest molecules as fitting a key into its lock.

Within the static model a theory of molecular recognition must be able to define the terms "lock", "key" and "fit". The definition of the first two terms is straightforward. The "lock" refers to the crevice inside or on the surface of a molecular entity (host) accommodating the "key", a whole molecule or part of it (guest). The definition of the term "fit" is more complicated. In our terminology, "fit" means the combination of at least three types of interactions: steric, hydrophobic and electrostatic. Steric fit means that interacting atoms may not approach each other beyond their van der Waals radii and, simultaneously, the crevice should be filled densely by reducing the free space between interacting atoms to a maximum. The term "hydrophobic fit" corresponds to the association trend between apolar groups in an aqueous medium. Electrostatic fit requires the maximum ionic and polar interaction between host and guest molecules[3]. The latter is known to be an important element in many biological processes[4] and is described in the following sections.

1.1 Electrostatic Effects

Electrostatic interactions play a central role in a variety of biological processes. A detailed characterisation of the strength and nature of these interactions require an understanding of the physical chemical properties of the molecules in aqueous solution. Coulombic forces largely dominate the long range electrostatic interaction between ions which means that they are likely to be primarily responsible for the departure from ideality in ionic solutions and to dominate all the other contributions to non-ideality. This domination is the basis of the Debye-Hückel theory of ionic solutions, which was derived by Peter Debye and Erich Hückel in 1923[5].

Since oppositely charged ions attract each other, cations and anions are not uniformly distributed in solutions: anions are more likely to be found around cations, and vice versa. Overall the solution is electrically neutral, but near any given ion there is an excess of counter ions, the ions of opposite charge. Averaged over time, more counter ions than like ions pass by any given ion, and they come and go in all directions. This time-averaged sphere around a given ion has a net charge equal in magnitude but opposite in sign to that on the central ion, and is called its ionic atmosphere. The energy of any given central ion is lowered as a result of its Coulombic interaction with its ionic atmosphere. This model leads to the result that at low concentrations the ionic activity coefficient can be calculated from the Debye-Hückel limiting law given by Equation 1.

$$\log \gamma_{\pm} = - |z_+ z_-| \, A I^{1/2} \tag{1}$$

where A is a constant and is equal to 0.509 (mol kg^{-1})$^{1/2}$ for an aqueous solution at 25 °C, $\gamma_{\pm}$ is the mean activity coeffient of the ions, z_+ and z_- are the ionic charges and I is the ionic strength of the solution. The reason why the term limiting law is applied to Equation 1 is that all solutions are expected to conform in the limit of arbitrarily low molality. However, when the ionic strength of the solution is too high for the limiting law to be valid, it is found that the activity coefficent could be estimated from the extended Debye-Hückel law (Equation 2).

$$\log \gamma_{\pm} = - \frac{|z_+ z_-| \, A I^{1/2}}{1 + B I^{1/2}} \tag{2}$$

where B is second constant. Although B can be interpreted as a measure of the closest approach of the ions, it is best considered as an adjustable parameter. However, this equation still remains very poor near concentration of 1 mol kg^{-1}.

1.1.1 Ionisation of Acids

In the ionisation of an acid, a proton is removed against the electrostatic force created by the incipient negative charge that is then left behind on the anion. When a second proton is removed from a symmetrical polybasic, the second proton must be removed not only against a similar force, but also against the additional force created by the negative charge derived from the first ionisation. Thus, for example, the ionisation of the second proton that is removed in the ionisation of the monoanion of phosphoric acid in water takes place in the presence of a residual negative charge. Because of the extra electrostatic work required to remove a proton from this anionic residue, the second ionisation constant of phosphoric acid is less than the first by a factor of about 10^5. The example of phosphoric acid provides a measure of the possible magnitude of electrostatic effects.

Bjerrum[6] calculated the work of removing the second proton from a symmetrical dibasic acid in the electrostatic field of the negative charge left over from the first ionisation as

$$\Delta\Delta F = Ne^2/Dr = RT \ln(K_1/4K_2) \quad (3)$$

where N is the Avagadro's number, e is the electronic charge, r is the distance between the protons of the dibasic acid, and D is the dielectric constant of water.

In 1932, Eucken[7] published the corresponding electrostatic formula for the effect of a dipole on the ionisation constant of a substituted acid, that is

$$\Delta\Delta F = Ne\,\mu\cos\theta/Dr^2 = RT \ln(K_{substituted}/K_{unsubstituted}) \quad (4)$$

where μ is the dipole moment of the substituent, θ is the angle the moment makes with the line joining its centre to the ionising proton, D is the dielectric constant of empty space taken as 1.00.

Neither equation, that for water[6] nor that for empty space[7], worked very well. In particular, Bjerrum's formula was wildly wrong for small molecules such as phosphoric acid; it grossly underestimated the electrostatic effect[8].

1.1.2 Kirkwood-Westheimer Model

In 1938, Kirkwood and Westheimer[9,10] introduced a model in which the charges or dipoles were contained in a sphere or prolate ellipsoid of low dielectric constant, representing the molecule, surrounded by water of dielectric constant 80. They then worked out the electrostatics by classical physics (Figure 1.1).

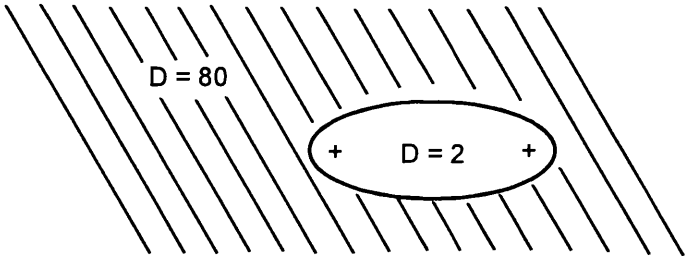
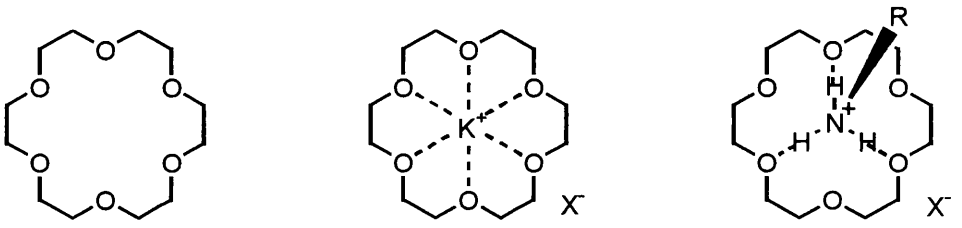


Figure 1.1 – Kirkwood-Westheimer model

Although this is a simplified model, it is less crude than that of Bjerrum, who placed the charges directly in water, or that of Eucken, who replaced the water by empty space. It has, at least, the advantage of consistency for both charges and dipoles. The equations have the same form as those of Bjerrum and of Eucken, but with an effective dielectric constant, D_E, substituted for the dielectric constant in those equations; all the mathematical complexity relates to the calculation of the effective dielectric constant. More recently, other investigators have sought simpler equations to calculate the effective dielectric constant for charges immersed in proteins. They have come up with semi-empirical formulae that are useful and quite satisfactory for this important application. In 1988, Pickersgill[11] reported that the charge-charge interaction energies in small proteins can be calculated using simple distance-dependant effective dielectric model. Mehler and co-workers successfully modelled the electrostatically dependant properties of charged groups in proteins by the use of a screened electrostatic potential[12,13].

1.2 Molecular Recognition

In 1987, Cram, Pedersen and Lehn shared the Nobel Prize in chemistry for their pioneering work in the molecular recognition area. The discovery of crown ethers by Pedersen[14-16] and their subsequent development by others, particularly Cram and co-workers[17,18], has been well documented. 18-Crown-6 **1** has been shown to form complexes with potassium cations **2**, alkylammonium cations **3**, and a number of other species. Binding to cationic guests is through electrostatic interactions, and although binding to alkylammonium cations is often depicted as involving specific hydrogen bonding as shown in **3** it is perhaps more satisfactory to think of this binding as net attraction between the array of negative and positive charges presented by the guest cation and the crown ether.

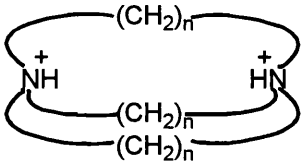


1 **2** **3**

These early reports provided the starting point for the field of host-guest chemistry, also known as molecular recognition. In 1974, Cram[19] stated that 'In host-guest chemistry, the host molecule is the larger, and the guest molecule is the smaller of the two. The host molecule must "recognise" by complexing best those guest molecules that contain the array of binding sites and steric features that complement those of the host. The self-evident postulate that two objects cannot occupy the same space at the same time indicates that host and guest, the host and guest must be compatible with respect to shape if they are to complex. The simple attraction of positive and negative charges accounts for much of the binding between host and guest molecules'.

1.2.1 Artificial Anion Hosts

About 30 years ago, the non-covalent encapsulation of halide anions into a preformed molecular cage **4** was observed by Simmons and co-workers[20-22]. The spherical anion is held there by an array of hydrogen bonds within a cavity formed in a bicyclic molecular framework **5**.



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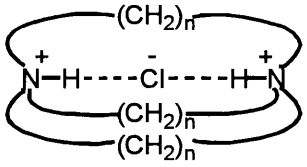


5

The origin for the discrimination of the simple tetrahedral oxyanions phosphate and sulfate by their respective binding proteins was thus traced back to the ability of the phosphate to act as a hydrogen-bond donor in a delicately balanced network of hydrogen bonds deeply buried in the interior of the protein[23,24]. In spite of this growing insight into anionic binding, the construction of hosts evolved more rapidly, presumably owing to better established concepts for ligand design.

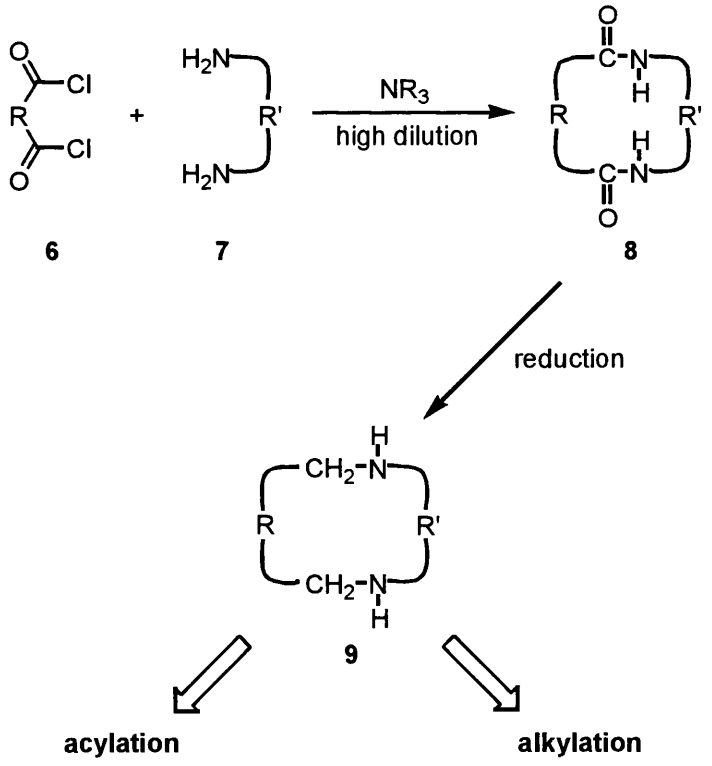
1.2.2 Azonia Compounds

Cationic hosts capable of forming ion pairs with anions in solution are most easily prepared by protonation of suitable basic compounds. Since many anions possess some basic properties as well, host-guest binding in these cases depends on relative proton affinities in interconnected multiple equilibria. In water as a solvent, protonation equilibria are readily established and the corresponding pKa values of individual groups may be determined from titration curves. It is no surprise, therefore, that water was the solvent of choice to study anion binding to a great variety of protonated polyaza compounds. Due to the high dielectric permittivity and high hydrogen-bond donor-acceptor ability of water, electrostatic ion pairing is hampered to the extent that significant association at moderate concentrations can only be observed with multiply charged species. On the other hand, the mutual interaction rapidly increases with number of charges so that great thermodynamic stability can be attained on complexation of highly charged ions. Of course, the state of protonation depends on pH and, as a general rule, several differently protonated species constitute the ensemble of hosts at any given value of pH. As a corollary, the host-guest association observed in the actual experiment is an integral event that may be divided by regression calculation into singular contributions from all of the species involved. In this case, the respective association constants may contain relatively large errors. Moreover, it is not straightforward to derive information about complex structures from the analysis of trends in the binding constants. Relating the binding effect to host structure is essential for selectivity development which contributes the basis of molecular design.

In 1968, Park and Simmons[22] made a significant contribution when they described a new type of ion pairing by which a halide guest occupied the central cavity offered by an organic cage

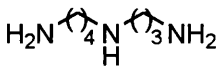
compound as in **5**. It was found that bromide ion is encapsulated by **4** less favourably than chloride, and no encapsulation of iodide ion was detected. This suggests that the size of the cavity is an important factor for halide encapsulation.

This result had a lasting effect on the further development of host-guest chemistry with anions. Guided by the high interest in azacrown ethers and cryptands as cation complexing agents, the convenient preparations of this class of compounds have been found[25,26]. Following the work of Stetter[27], azamacrocycles could be readily obtained by condensing an α,ω-dicarboxylic acid chloride **6** with an open-chain α,ω-diamine **7** using high dilution conditions (Scheme 1.1). In general, moderate to fair yields of macrocyclic bisamides **8** were obtained which in turn were reduced by $LiAlH_4$ or borane/THF to afford the secondary amines **9**. Further elaboration by alkylation or acylation led to the formation of lariat compounds or polycyclic cryptands that were amenable to protonation and thus could serve as anion hosts.



Scheme 1.1

Biological linear polyamines such as spermine **10** or spermidine **11** are well known to bind phosphate or polyanions in water at neutral pH values[28,29], but due to the accumulated charge and flexible nature they most likely adopt an extended conformation.



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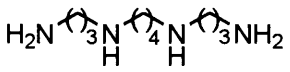
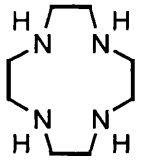


11

Polyprotonated azacrown ethers possess a greater charge density and consequently present a higher Coulombic attraction for anion association. On the basis of this concept, it is only rational to place as many ammonium groups as is synthetically feasible in close vicinity in order to maximise the electrostatic attraction for the anionic guest. Limitations, however, arise when the distance between cationic centres becomes too small. The experimental determination of the pKa constants for the two most acidic protonation steps pKa_3 and pKa_4 in the series **12-14** reveals that very low pH values are required to convert di- or tricationic ammonium salts to tetracationic species if the separation of charge is less than that provided by a propane spacer unit (Table 1.1).



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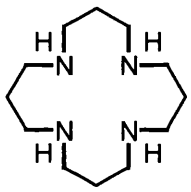

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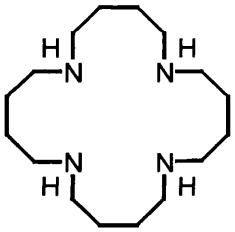


14

	pKa_1	pKa_2	pKa_3	pKa_4
12	10.7	9.7	1.7	< 1
13	10.8	9.6	6.9	5.4
14	11.8	11.4	10.6	8.9

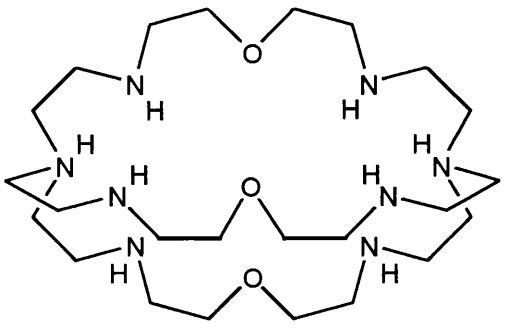
Table 1.1

Aiming at the complexation of biologically important anions under physiological pH conditions, the diminution of host volume by using ethylene connections of cationic centres is not a viable route. Rather, an increase in nominal charge by enlargement of the marcocycle[30,31] or through annexing amino-functionalised side arms pending from smaller azacrown compounds[32] has been carried out.

	logarithms of stability constant (log K_s)		
	12	**13**	**14**
oxalate^{2-}	3.8	3.7	4.7
sulfate^{2-}	4.0	4.0	4.5
fumarate^{2-}	2.2	2.9	2.6
squarate^{2-}	3.2	3.6	3.4
citrate^{3-}	4.7	7.6	5.8
1,3,5-benzenetricarboxylate^{3-}	3.5	6.1	3.8
$Co(CN)_6^{3-}$	3.9	6.0	3.3
AMP^{2-}	3.4	4.1	4.7
ADP^{3-}	6.5	7.5	7.7
ATP^{4-}	8.9	8.5	9.1

Table 1.2 – Selected logarithms of stability constants for anion binding by polyammonium macrocycles 12, 13 and 14 in water[31]

Pertinent binding data with a variety of anions are collected in Table 1.2[31], where logarithm of the stability constant is shown as log K_s. Coulombic interactions apparently dominate host-guest binding as can be seen from the increase in complex stability with charge. At the same time, only a moderate dependence of the stabilities on structure can be noted.



15

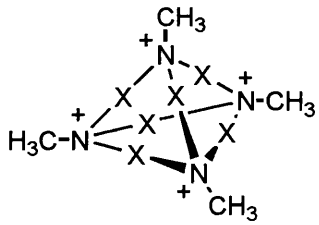
The hexaprotonated form of bicyclic cryptate **15** gives rather stable complexes with a variety of well solvated anions in aqueous solution (Table 1.3)[33-36].

	log K_s
	15
F^-	4.1
Cl^-	3.0
Br^-	2.6
I^-	2.2
N_3^-	4.3
SO_4^{2-}	4.9
Oxalate^{2-}	5.0
Malonate^{2-}	3.1
AMP^{2-}	3.9
ATP^{4-}	8.0

Table 1.3 – Logarithms of stability constants for anions with macrocycle 15[33-36]

Comparing the log K_s values it became apparent that strong binding is based on an inclusion process by which the guest anion penetrates into the molecular cavity of the host that is expanded by the electrostatic repulsion of the positive charges[34,35]. Several X-ray crystal structures confirmed that the guest is fixed by an oriented set of hydrogen bonds in the host cavity[34,36]. Viewing the ellipsoidal shape of the cavity and the topology of nitrogen hydrogen-bonding sites, it seems plausible that the azide anion having an optimal complementarity to the host cavity shows extraordinarily high complex stability. Spherical anions, such as halides, fit less well, and the decrease in binding going from fluoride to iodide argues in favour of hydrogen bonding as a major binding force.

The study of anion binding using protonated polyaza hosts is severely hampered by the requirement of quite acidic conditions, thus preventing any study involving basic anions. In addition, switching the solvent may shift the pK_a values and may diminish the total charge by deprotonation, thereby affecting anion complexation. Nitrogen quaternisation might offer a remedy to this situation, but since hydrogen bonding contributes a major share of the total interaction in the protonated host species, it was not at all clear that peralkylation of nitrogen sites would still give useful anion hosts. This concept was put to test by the synthesis of the macrotricyclic quaternary ammonium salts **16** and **17**, prepared by methylation of the parent tertiary amines[37-40].

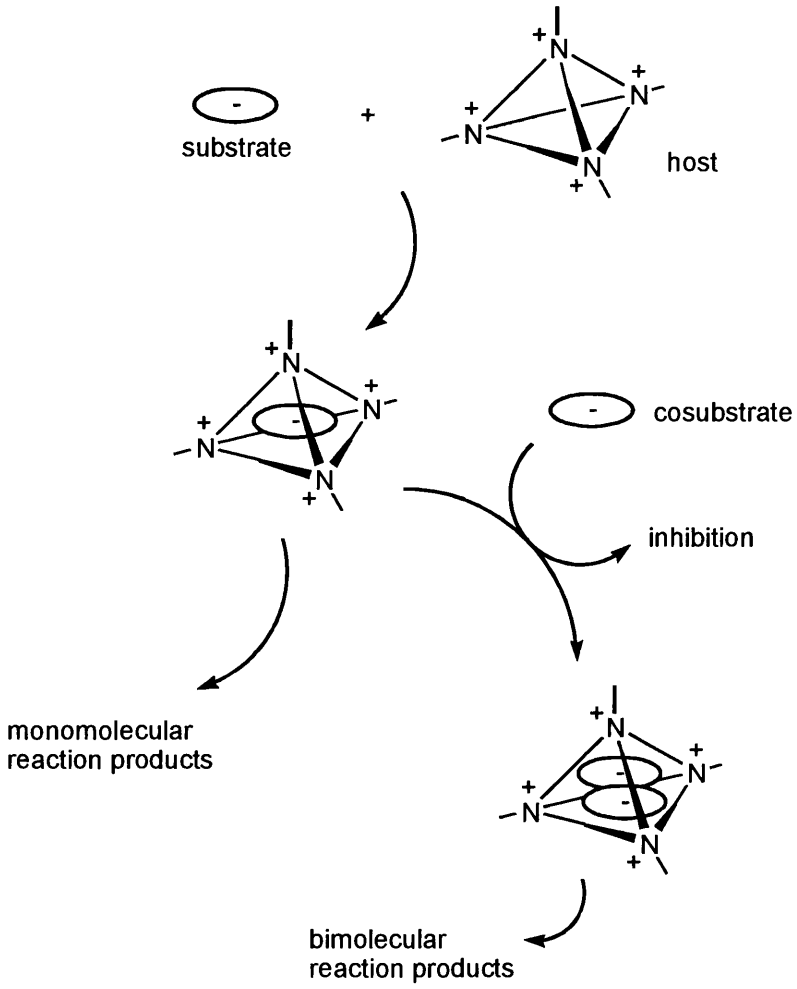


16 X = -$(CH_2)_6$-

17 X = -$(CH_2)_8$-

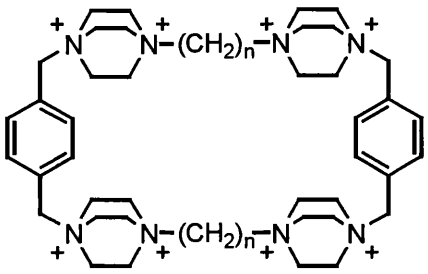
Both quaternary ammonium compounds were freely soluble in water without detectable aggregation and proved to be hosts for a broad variety of anions in water, always adhering to 1:1 host-guest stoichiometry[39-41]. On the basis of NMR titration data, as well as X-ray crystal structures of **17** with iodide[42], guest binding occurred by inclusion complexation. Iodide fits rather comfortably into the smaller tetrahedral host **16**. The good fit allows efficient stabilisation by dispersion interactions with this halide ion which becomes apparent also in preferential transport of iodide over chloride in membrane carrier studies[43]. Larger anions such as *p*-nitrophenolate cannot be complexed by **16** but only by the bigger host **17**, thus providing additional evidence for an encapsulation process. The quaternary ammonium inclusion hosts are chemically stable compounds and opened the option to study reacting systems depending on host-guest binding without interference from pH effects.

In the monomolecular case, the reacting anion may form an inclusion complex with the host which results in a change in the molecular environment and can translate into a change in reaction rate in complete analogy to any ordinary solvent effect. The ground and transition states of the reaction undergone by the substrate will be affected to different extents, and overall catalysis or inhibition of the reaction may result. The same reasoning applies in bimolecular reactions. It is obvious that the first reaction partner by virtue of its encapsulation into the host's cavity, is shielded from attack by the second substrate, and the corresponding reaction is thus inhibited. If, however, the cavity is spacious enough to incorporate both reaction partners simultaneously, one may observe rate acceleration (Scheme 1.2)



Scheme 1.2

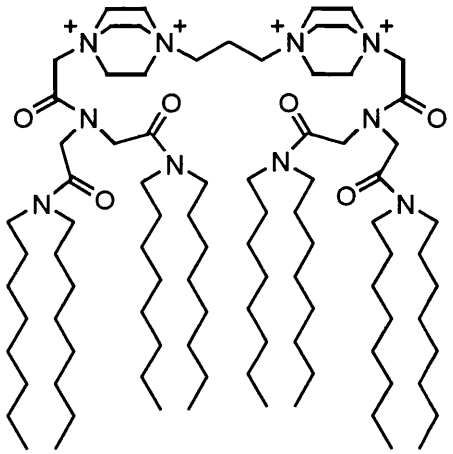
In order to maximise Coulombic binding while conserving the option for stacking interactions with aromatic guest moieties, the octacationic cyclophanes **18** were designed[44].



18 n = 3, 4, 5

Small inorganic anions, such as chloride and bromide, bind inside the cavity, as evidenced by a crystal structure. Large organic anions such as ATP or naphthalenesulfonates, however, do not penetrate the host, but rather bind from the outside. As a corollary, the binding constants with

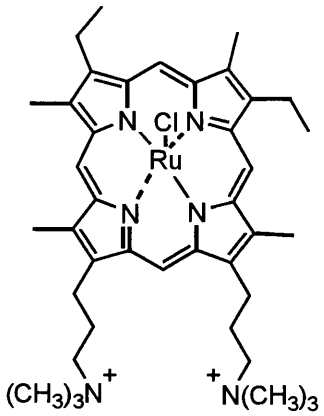
ATP do not vary appreciably with the ring size and in absolute terms are of the same magnitude as found with tetracationic quaternary ammonium cyclophanes. The use of diazabicyclo[2.2.2]octane (DABCO) building blocks in the construction of host **18** was inspired by the success of this moiety to serve as membrane transfer agent for ATP and other nucleotides after quaternisation with hydrophobic moieties[45-47]. Thus the tetracation **19**, like several other compounds of similar design, formed 1:1 complexes with nucleotide triphosphates and extract ATP from very dilute aqueous solution into chlorohydrocarbon phases[46]. Their use in membrane transport, however, was severely hampered by their detergenic properties leading to disruption of liposome vesicles.



19

1.2.3 Oligopyrrole-Derived Receptors

When complexing metal cations, chelating ligands may not fully satisfy the coordination needs of the central atom but leave a site open for additional ligation of another species that will be readily exchangable. This dedicated single-point interaction between binding partners does not meet the definition of a host-guest relationship. More modes of interaction have to intentionally be added to generate a true host compound which extend well beyond the first ligation sphere of the metal. Examples, such as **20**, encompass polypyrrole complexes as metalloporphyrins that have been investigated for anion selective sensing and transport[48].



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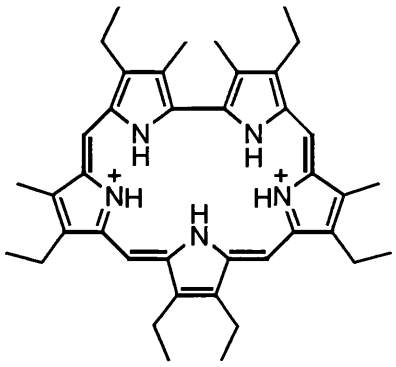
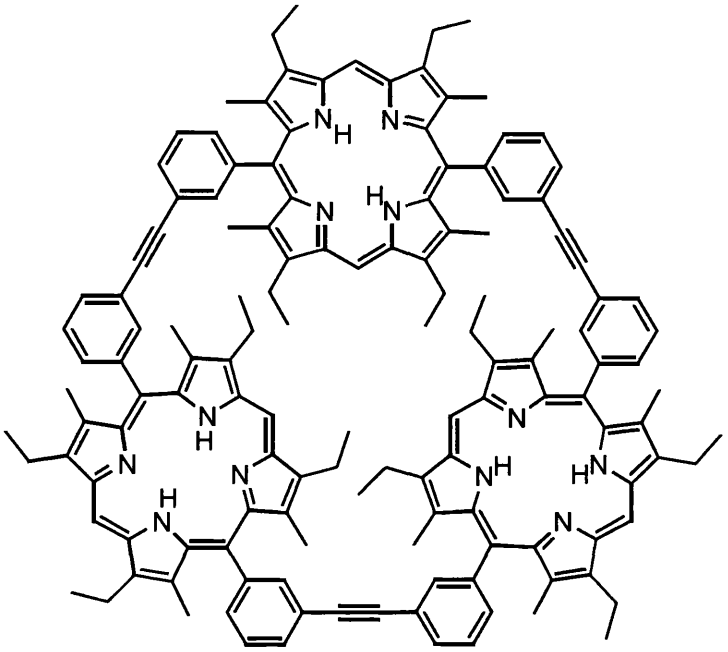


21

The anion-binding capacity of porphyrins is totally dependent on the presence of the metal ion. The free tetrapyrrolic ligand has no anion-binding power due to the small size of the porphyrin cavity which does not allow the use of the convergent N-H dipoles for anion stabilisation[49]. Expansion of the porphyrin cavity by the incorporation of more pyrrolic or other spacer moieties appeared as a rational remedy. Sessler and co-workers prepared a large number of ring extended porphyrins among which the sapphyrins were shown to possess anion-binding properties[49,50]. Sapphyrin **21** contains an unique disposition for anion inclusion based on its planar pentapyrrolic skeleton of aromatic character which forces three N-H bonds to point with their positive ends towards the centre of a cavity. Another two protons may be added to form a symmetric array of hydrogen-bonding sites that is almost perfectly predisposed for anion encapsulation. It was found that the diprotonated sapphyrin **21** formed a very stable complex with fluoride in methanol solution. The X-ray crystal structure shows a fluoride guest completely encircled by the dicationic aromatic macrocycle. For steric reason, the larger halides chloride and bromide cannot be bound in this inclusion mode[51].

Following a building block approach, Sanders *et al.* used prophyrins as construction elements. The giant cage molecule **22** was obtained by covalent connection of three porphyrin macrocycles and formed a hexaprotonated cation $[\mathbf{22}\bullet H_6]^{6+}$ with acid[52]. When this compound was dissolved with the cluster anions $[PW_{12}O_{40}]^{3-}$ or $[SiW_{12}O_{40}]^{4-}$ in *m*-nitrobenzyl alcohol matrix and subjected to fast atom bombardment (FAB) mass spectroscopy, signals corresponding to 1:1 host-guest complexes were observed. Since small anions, which should be at least as volatile as the big cluster anions, could not be detected in the host-guest complexes with protonated **22**, it suggests that it is the complementarity in size, shape and charge that cause host-guest association of $[\mathbf{22}\bullet H_6]^{6+}$ and the observed anions. This system holds the record in size for guest encapsulations.



22

1.2.4 Guanidinium-Based Receptors

The guanidinium group as present in the side chain of arginine is ubiquitous in enzymes that binds anionic substrates and is also involved in the stabilisation of protein tertiary structures via internal salt bridges with carboxylate functions. The reason for the strong interaction with oxyanions lies in the particular binding pattern featuring two parallel hydrogen bonds together with an electrostatic interaction (Figure 1.2), a structural motif that can be found in many crystal structures of enzyme complexes with oxyanionic substrates as well as in simple guanidinium salts.

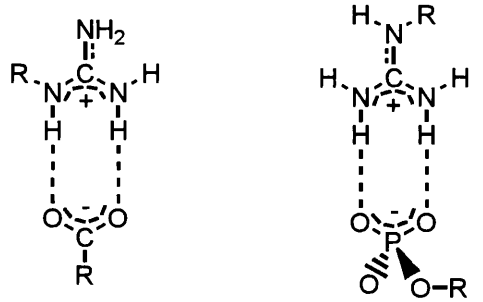
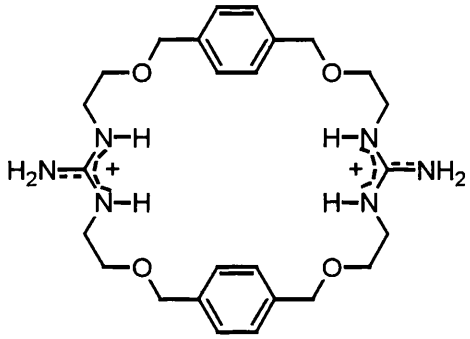


Figure 1.2 – Binding pattern of guanidinium groups with oxyanions

This type of binding appears to form the basis for the biological activity of quite a number of alkaloids and toxins[53,54]. Another feature which makes the guanidinium moiety an attractive anchor group in artificial receptors is the extremely high basicity of guanidine (pK_a = 13.5),

which guarantees protonation over a wide pH range. On the other hand, the exploitation in host-guest chemistry is hampered by the very effective solvation of the guanidinium function in water and its lower charge density as compared to that of ammonium-based receptors, leading to weaker electrostatic interactions. In spite of these disadvantages, the attractive features of the guanidinium group have led to the development of an appreciable number of artificial guanidinium-based receptors for anions[55].

The first examples of macrocyclic guanidinium-based receptors were reported by Lehn *et al.*[56] who synthesised compounds **23** and **24**. Both of these compounds showed only weak complexation with PO_4^{3-} which was thought to be governed by electroststaic interactions. This was confirmed by a more extensive study of several polyguanidinium hosts which revealed that binding of phosphates and carboxylates was influenced by a macrocyclic as well as a chelate effect. Guest selectivity was primarily dependent on the charge density of the anions[57].



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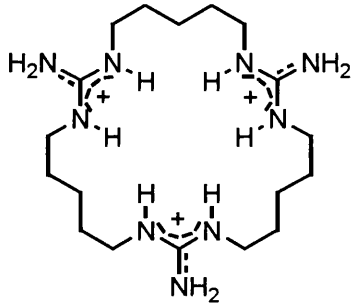
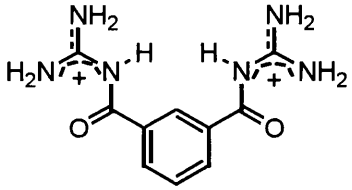


24

Simple bisguanidinium compounds like **25**, synthesised by Hamilton and co-workers[58], were found to complex phosphodiesters and gave rate enhancements for transesterification by a factor of 300[59]. A monoguanidinium receptor increased the reaction rate only 2.5-fold, indicating the importance of the cleft-like arrangement of the guanidinium groups in **25** for co-operative binding.



25

In order to improve the binding characteristics, the guanidinium group can be embedded in a bicyclic framework, which reduces hydration of the charged moiety by the accumulation of

hydrophobic hydrocarbon residues. Further manipulation of substituents could introduce other binding sites to increase specificity of guest binding (Figure 1.3). It was found that even the simple compound **26** formed an ion pair with *p*-nitrobenzoate of great stability in chloroform[60].

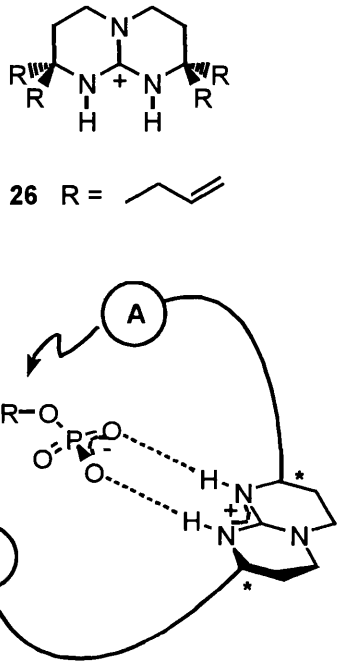
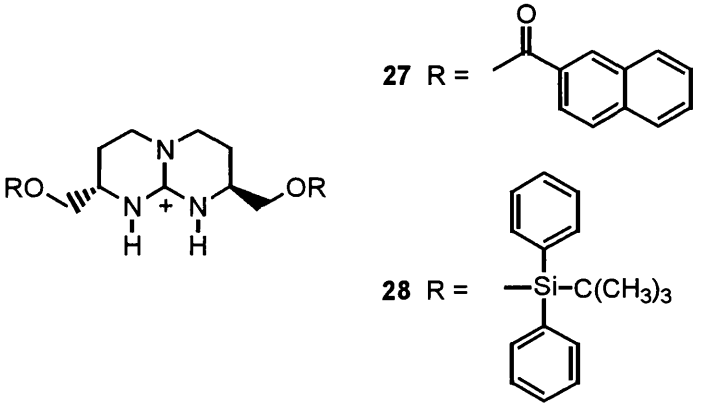


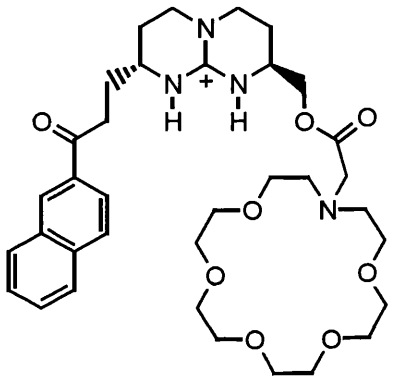
Figure 1.3 – The host-guest binding concept of chiral bicyclic guanidinium groups.

The first exploitation of the chirality of these bicyclic guanidines for enantioselective recognition was reported by de Mendoza and co-workers[61], who attached aromatic moieties to the parent framework to give receptor **27**. Aromatic carboxylic guests could interact with two different recognition sites comprising guanidinium-carboxylate ion pairing and aromatic π stacking. With chiral carboxylates, diastereomeric complexes were formed and it was found possible to extract N-acetyl- and N-BOC-tryptophan from a racemic aqueous solution into chloroform with moderate selectivity (17% diastereomeric excess).

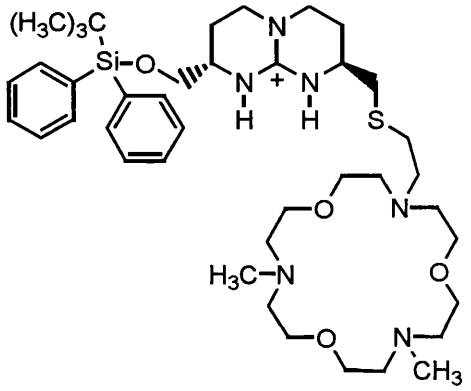


Even the parent anchor group **28** formed diastereomeric host-guest complexes with racemic aliphatic carboxylates such as N-acetylalanine or 2-methylbutyrate in acetonitrile[62]. Here, the bulky silyl ether groups seem to be sufficient to form a chiral cleft around the quanidinium binding site.

In order to recognise underivatised amino acids in their zwitterionic form, de Mendoza introduced host **29**, which is built upon **27**, but has an additional recognition site for the ammonium moiety[63]. In single-point liquid-liquid extraction experiments, selectivity for aromatic amino acids such as tryptophan and phenylalanine was found supporting a three-point binding mode.



29



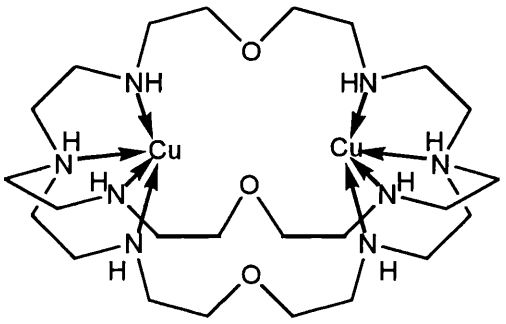
30

A similar receptor **30** was used by Schmidtchen and co-workers[64] in a more detailed study on the extraction of ^{14}C-labeled amino acids. Here, a triazacrown ether having an intrinsically better selectivity for the complexation of primary ammonium cations was attached by a stable thioether bridge to the guanidinium anchor function. For the first time, even quite hydrophilic amino acids such as serine and glycine could be transferred to the organic phase, with clean 1:1 host-guest stoichiometry. Maximum extractability was reached at pH 9, indicating that the amino acids were extracted in their zwitterionic forms.

1.2.5 Other Cationic Hosts

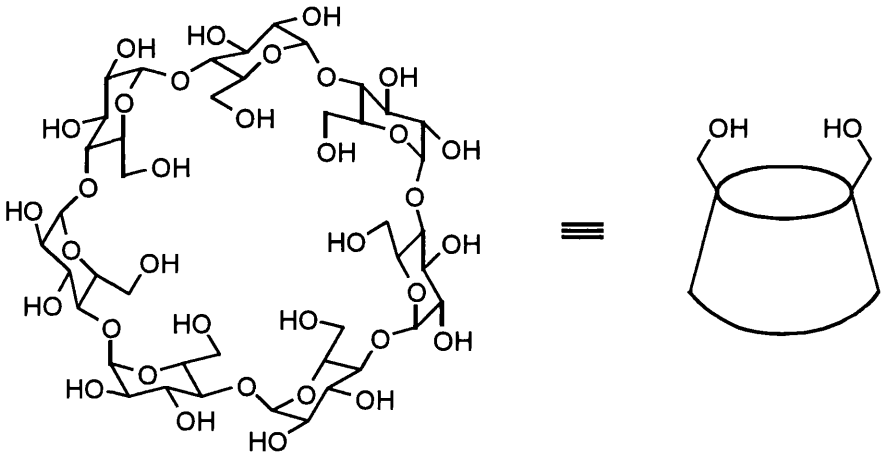
The overwhelming majority of organic host compounds interacting by charge attraction with anionic species are based on cationic nitrogen compounds. However, the introduction of positive charge into organic frameworks, as an alternative to protonation, can be very efficiently accomplished by metal cation ligation and in consequence requires the careful design of suitable coordination sites.

Azacrown ethers and cryptands after protonation make very successful anion hosts, and can serve in their basic form as ligands for a number of transition metal cations with well-defined coordination geometries. Bicyclic cryptate **15**, for instance, was shown to complex Cu(II) ions, one at each hemisphere of nitrogen sites, to give the binuclear complex **31** which, in spite of the presumed distorted tetrahedral ligation geometry of the metal ions, still contains a void space in the centre of the structure ready for encapsulation of an anion such as chloride[65].



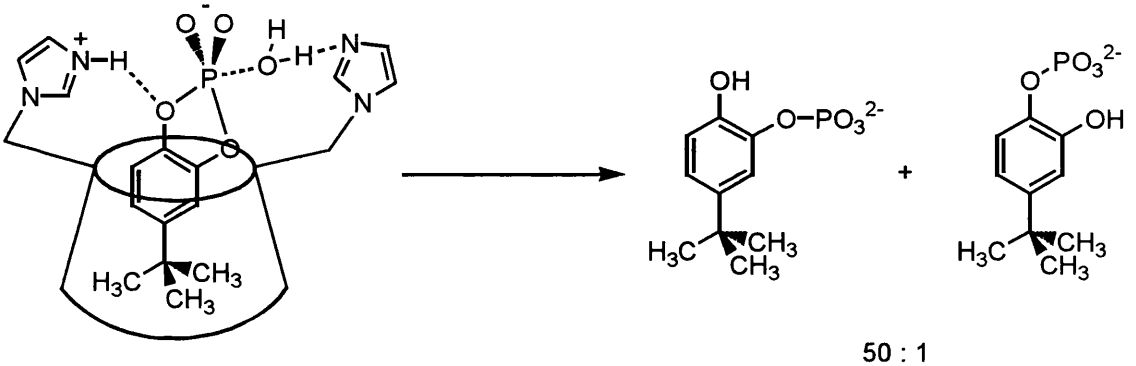
31

Cyclodextrins are an important class of natural hosts that have no known function in living systems[66]. β-Cyclodextrin **32** represents a classic example of a host compound for molecular recognition in water[67]. It provides cavities of variable size which offer a hydrophobic environment rimmed by arrays of highly hydrophilic hydroxy groups. As a general rule, guest molecules which are not well hydrated in water but are of the correct complementary size to fit into the molecular cavity will associate with this class of host compounds.



32

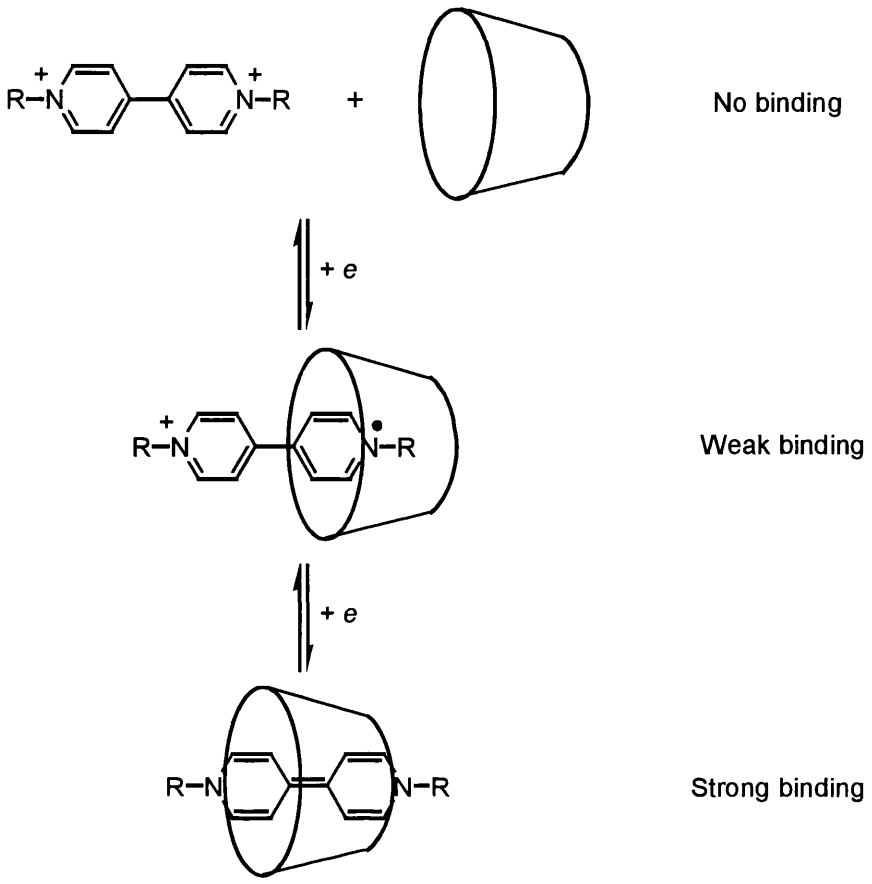
Breslow *et al.*[68,69] modified **32** with two imidazole heterocyces to give bisimidazolylcyclodextrin **33** which can catalyse the cleavage of anionic catechol phosphate and thus mimic certain nucleases. It also showed an impressive regioselectivity of phosphate cleavage which made this model resemble real enzymes (Scheme 1.3).



33

Scheme 1.3

Although cyclodextrins are not electroactive, they do form inclusion complexes with suitable redox active guests. For instance, **32** forms stable 1:1 complexes with ferrocene and ferrocene derivatives. Recently, Kaifer and Mirzoian[70] reported the cyclodextrin complexation of redox active guest, such as viologen[70] and cobaltocenium[71] derivatives. Due to their charge, these guests do not interact appreciably with cyclodextrins in their most stable oxidation states, that is 2+ for the viologens and 1+ for cobaltocenium. However, reduction considerably increases the affinity of these guests for the cyclodextrins. In the case of cobaltocenium[71], one-electron reduction yields the neutral cobaltocene, which, like ferrocene, is an excellent guest for inclusion by **32**. One electron reduction of the viologens leads to cation radical species that are not strongly bound by the cyclodextrins. In contrast, two-electron reduction yields uncharged guests which form very stable complexes with **32**[70] (Scheme 1.4). Kaifer[66] stated that 'Neutral subunits of appropriate size are strongly bound by the cyclodextrin hosts while charged subunits of similar size are not.'



Scheme 1.4

1.3 Water

1.3.1 Physical Properties of Water

Some of the notable physical properties[72] displayed by water are the following: (i) negative volume of melting; (ii) density maximum in the normal liquid range at 4 °C; (iii) isothermal compressibility minimum in the normal liquid range at 46 °C; (iv) numerous crystalline polymorphs; (v) high dielectric constant; (vi) anomalously high melting, boiling, and critical temperatures for low-molecular-weight substance that is neither ionic nor metallic; (vii) increasing liquid fluidity with increasing pressure; and (viii) high-mobility transport for H^+ and OH^- ions.

The key to understanding liquid water and its solutions lies in the concept of the hydrogen bond. In general terms it is found that specific attractions exist between electronegative atoms (such as nitrogen, oxygen, fluorine and chlorine) and hydrogen (or deuterium) atoms, particularly when the latter are themselves chemically bonded directly to electronegative atoms[72]. The water molecule, which contains two hydrogen atoms and one oxygen atom in a

non-linear arrangement, is ideally suited to engage in hydrogen bonding. It can act both as a donor and as an acceptor of hydrogens. This dual ability is illustrated by the crystal structure of ordinary hexagonal ice, a fragment of which is displayed in Figure 1.4.

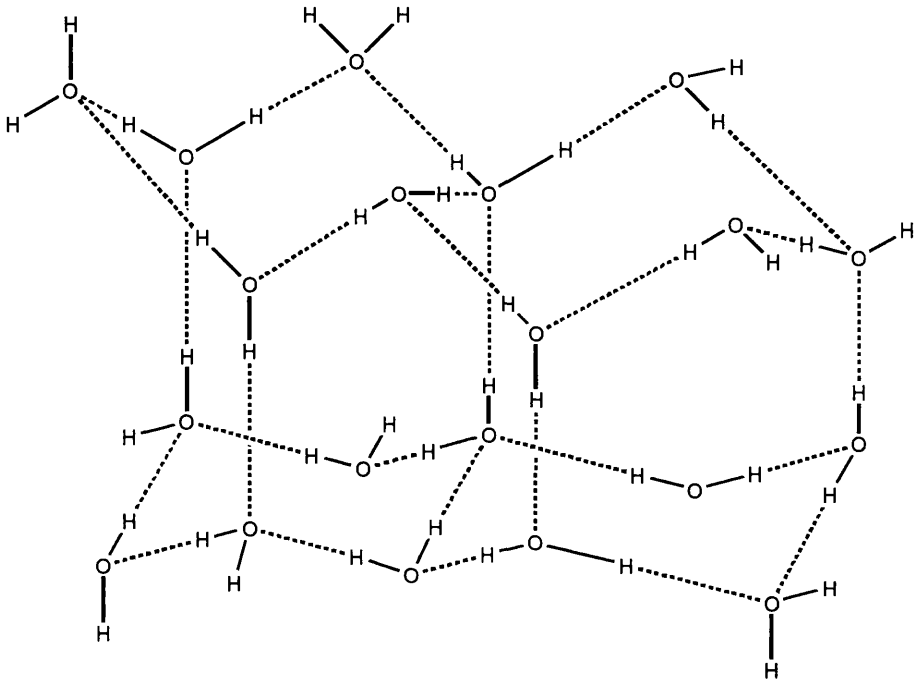


Figure 1.4 – Structure of hexagonal ice. Covalent bonds are shown as solid lines and hydrogen bonds as dashed lines.

Each water molecule in the crystal has four nearest neighbours to which it is hydrogen-bonded. It acts as hydrogen donor to two of the four and accepts hydrogens from the remaining two. These four hydrogen bonds are spatially arranged with local tetrahedral symmetry; that is the oxygen atoms of the neighbours occupy the vertices of a regular tetrahedral surrounding the oxygen atom of the central molecule.

The behavious of water toward nonpolar solutes has long been recognised as unusual. This peculiarity and its effects have given rise to the popular phrases "hydrophobic effect" and "hydrophobic bond"[72]. Typical nonpolar solutes are the noble gases, hydrocarbons such as methane and cyclopropane, and sulfur hexafluoride. None can readily hydrogen bond to water, and all are sparingly soluble. The process of isothermally dissolving such substances in water is accompanied by a significant negative entropy that quite naturally has been interpreted as a "structure-making" phenomenon in that solvent. Any acceptable molecular theory must account for this hydrophobic interaction.

Since nonpolar solutes occupy space, if a nonpolar solute molecule is to be placed in liquid water, the random hydrogen bond network must reorganise around it in such a way that

sufficient room is available to accommodate that molecule while at the same time not causing too much additional damage to the already defective hydrogen bond network. The crystal structures of the clathrate hydrates for many of these nonpolar substances show that such rearrangements are possible.

Computer simulation offers the best opportunity to understand details of the solvation process at the molecular level. Several studies[73,74] seem to agree that insertion of a single space-filling but otherwise essentially inert solute solute molecule spontaneously causes the network to rearrange toward formation of a local clathrate-like convex cage. The cage is usually far from perfect. Although there is some strengthening of hydrogen bonds in the cage relative to the case in pure water, substantial strain and disorder remain. Evidently the surrounding medium with its own strained and broken bonds exerts strong forces and torques on the solvent sheath, which cause geometric disruption[72].

The negative entropy for the solution of nonpolar molecules resides partly in the strengthening of the bonds in the imperfect solvation cage. But it is also related to the fact that molecules in that cage layer around the solute have markedly reduced orientational options. Because of the energetic advantage of having hydrogen bonds rather than of not having them, each solvation sheath water molecule strongly prefers to place its tetrahedral bonding directions (OH covalent bonds, and the lone pair directions) in a straddling mode (Figure 1.5). This arrangement permits bonding to other solvation layer water molecules and always avoids pointing one of the four tetrahedral directions inward toward the region occupied by the inert solute, which would waste a possible hydrogen bond[72]. Computer simulation unequivocally supports these orientational preferences.

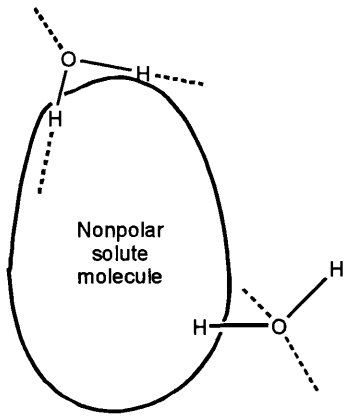
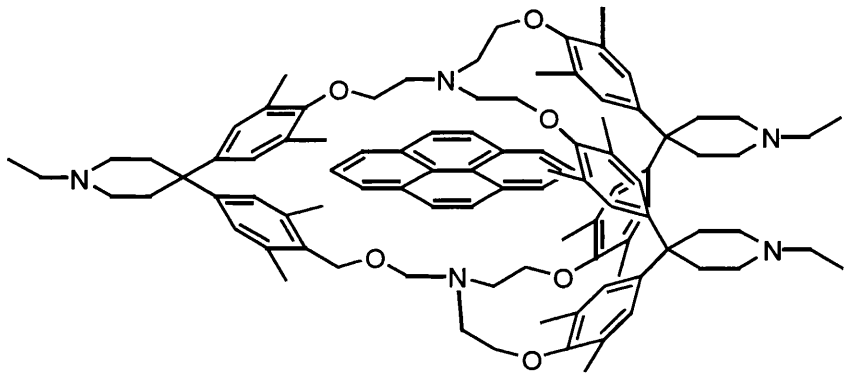


Figure 1.5 – Orientational preference for water molecules next to a nonpolar solute. In order to preserve intact the maximum number of hydrogen bonds, the water molecules tend to straddle the inert solute, pointing two or three tetrahedral directions tangential to the surface of the occupied space.

1.3.2 Complexation in Water

In 1990, Diederich *et al.*[75] studied the stablility of complex **34** in a total of 18 solvents including water. It was found that the complexation strength decreases steadily from water to nonaqueous polar solvents, to dipolar aprotic solvents, and finally to apolar solvents like carbon disulfide. The large difference in binding strength results almost exclusively from solvation



34

effects.

2,2,2-Trifluoroethanol is a solvent which comes close to water in its ability to promote apolar complexation[75]. Strong complexation is also observed in ethylene glycol and in formamide. Binding is strongest in solvents characterised by low molecular polarisabilities and by high cohesive interactions. Solvent molecules with high cohesive interactions interact more favourably with bulk solvent molecules than with the complementary apolar surfaces of free host and guest, and therefore, entropic energy is gained upon the release of surface-solvating molecules to the bulk during the complexation step. Water has the highest cohesive interactions and possesses by far the lowest molecular polarisability. Both effects taken together make it the best solvent for complexation[75].

A large number of studies of synthetic receptors in aqueous media have been well documented[76-79]. In water, a cation will be very well solvated. The binding cavities of the synthetic receptors must compete with aqueous solvation if a cation is to bind tightly. The importance of studies in aqueous media is that they can have significant implications for biological recognition. If a synthetic receptor can pull an organic cation out of water and into a nominally hydrophobic binding site, then perhaps nature can adopt a similar strategy[80].

Studies in aqueous media also present special challenges. One is the prominent role of the hydrophobic interaction. This large effect can often dominate binding studies in aqueous media, and establishing a significant contribution from other forces in the face of a strong hydrophobic

effect can be difficult. Also, in order to make synthetic receptors water soluble, one must often append polar groups that are typically charged. The possibility of conventional electrostatic interactions between cationic guests and these polar groups can complicate analysis of binding studies[80].

It was discovered that, in all cases, the deoxygenation of certain hydroxyl groups essentially abolished binding, and this brought attention to the fact that all the epitopes were amphiphilic in character[81]. In the case of complex oligosaccharides, the epitopes normally involved a cluster of two to four hydroxyl groups, and these were designated the key hydroxyl groups. Since, prior to complex formation, the polar groups of both the epitope and the receptor site were surely extensively hydrated, water molecules would have to be displaced for the complex to form[82,83]. In view of the directional demands for the formation of hydrogen bonds[84], a high degree of complementarity was necessary, otherwise dehydration would be energetically difficult and complex formation strongly discouraged[83]. For this reason, the water molecules of the hydration shell were considered a hindrance to access to the receptor site by non-complementary structures, and the hydrated polar gate concept was proposed[85]. Paraphrasing Emil Fischer[2], the hydrated polar groups within the combining site were viewed as a locked gate that could be opened only by the key polar groups of the epitope. In this context, water molecules are intimately connected to the specificity of binding. With regard to structural requirements for effective binding, it is noteworthy that simple monosaccharides often display low but detectable activities[86]. It was exciting to learn, through the use of deoxy congeners, that a strong recognition of an oligosaccharide normally involved key hydroxyl groups on more than one sugar unit[87]. It is also noteworthy that, in order to effect complementarity, stereoelectronically well stabilised water molecules are often occluded within the complex[88,89]. It was estimated that the cost in entropy for the imprisonment of a single water molecule can be as high as 2 kcal mol^{-1}[90].

Recently, Braga and co-workers[91] stated that water molecules can play an important role in stabilisation of organometallic solids by participating in both OH-O and CH-O interactions. They also suggested that hydrogen bonds, both of conventional OH-O and controversial CH-O types, afford a pattern of interactions in common between organics, organometallics and water that can be utilised to engineer crystalline materials on the basis of the complementarity between donors and acceptors. The study recently reported by Abe and co-workers suggested that water molecules reduce the number of ionic contacts between cationic and anionic species and consequently reduce the packing energy of crystals[92]. To sum up, the hydrogen-bond network certainly plays an important role in the stabilisation of the stacked molecular chains[91,93].

It should be stressed that the hydrogen-bond structure of water and its interactions with the surroundings still represent a key issue in the study of highly hydrated systems[94]. Additional information on water binding can be of some importance in the study of biological macromolecules[95].

1.4 Electrochemistry

Electrochemistry is primarily concerned with charge transfer at the boundary between an electronically conducting or semi-conducting phase and an ionically conducting phase, such as a liquid, molten or solid electrolyte. By extension, the subject has traditionally included the study of ionic equilibria and dynamic processes taking place within ionic electrolytes, particularly from the perspective of those processes determining the concentration of electroactive species at or near the electrode surface.

The overall electrochemical oxidation and reduction reactions of organic and organometallic molecules often comprise complex sequences of electrochemical and chemical steps. In the shorthand notation now universally used, an electrochemical step is designated with the identifier E and is defined as a step involving loss or gain of an electron at the electrode-solution interface. Chemical steps, designated with the letter C, can be surface chemical reactions involving reactants. Most investigators have concentrated on the chemical steps.

The types of chemical reactions that are encountered as steps in organic and organometallic electrode reactions are extremely diverse. A given reaction can be a protonation or deprotonation, bond cleavage, complexation or decomplexation, ligand exchange, nucleophilic or electrophilic attack, polymerisation, isomerisation, or conformational change. For example, the reduction of a quinone to the hydroquinone in a proton-donating medium requires two E steps and two C steps, the latter being protonations. Designating the quinone as a Q, one can write a substantial number of possible reaction sequences. However, for benzoquinone, it has been shown that only three reaction sequences are of importance, a CECE process in acidic media (pH < 2), an ECEC sequence at pH > 7, and an ECCE reaction at intermediate pH[96,97].

$$Q \xrightarrow{C} HQ^{+} \xrightarrow{E} HQ^{\bullet} \xrightarrow{C} H_2Q^{\bullet+} \xrightarrow{E} H_2Q \qquad \text{(CECE)} \qquad pH < 2$$

$$Q \xrightarrow{E} Q^{\bullet-} \xrightarrow{C} HQ^{\bullet} \xrightarrow{C} H_2Q^{\bullet+} \xrightarrow{E} H_2Q \qquad \text{(ECCE)} \qquad \text{intermediate pH}$$

$$Q \xrightarrow{E} Q^{\bullet-} \xrightarrow{C} HQ^{\bullet} \xrightarrow{E} HQ^{-} \xrightarrow{C} H_2Q \qquad \text{(ECEC)} \qquad pH > 7$$

The coexistence of the reactant and various intermediates in the layer of solution close to the electrode surface leads to the possibility of the simplest of all the homogeneous chemical reactions, an electron-transfer reaction. These solution electron-transfer (SET) reactions are the subject of this section. For example, in the ECEC scheme mentioned above, it is almost always the case that the neutral radical, HQ•, formed by protonation of the anion radical, is capable of being reduced by the anion radical itself.

$$HQ^{\bullet} + Q^{\bullet-} \longrightarrow HQ^{-} + Q$$

Thus, under certain circumstances, reduction of HQ• in solution (a C step) is essentially the exclusive route, completely dominating the direct reduction of HQ• at the electrode (an E step).

It was in the context of the ECE family of reactions that the importance of SET reactions was first demonstrated. The concept was introduced by Hawley and Feldberg[98,99], and Savéant and co-workers developed the theory in its most complete form[100,101]. SET reactions have been considered as steps in a variety of electrode reaction schemes, and in some cases they exert a dramatic influence on the current-potential-time response. The most frequently employed experimental techniques are the various types of voltammetry.

1.4.1 Cyclic Voltammetry

Cyclic voltammetry, which was employed in this project, was first introduced by Matheson and Nichols in 1938[102]. Since that time this technique has grown rapidly in popularity, not only as a means of obtaining a quick electrochemical spectrum of a charge transfer system, but also as a method for the detailed examination of reaction mechanisms.

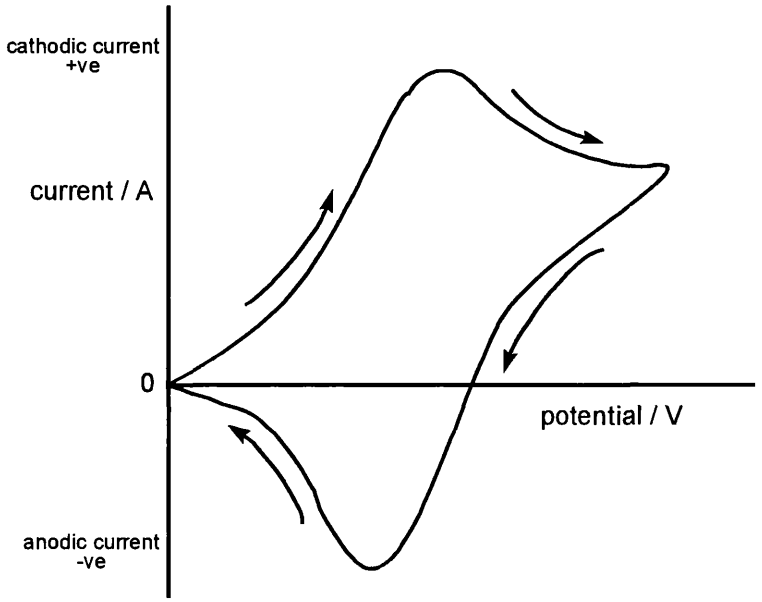


Figure 1.5 – typical cyclic voltammogram

Figure 1.5 shows a typical current/potential curve in a cyclic voltammetry experiment. Initially the potential is low and the cathodic current is due to the migration of ions in the solution. However, as the potential approaches the reduction potential of the reducible solute, the cathodic current grows. Soon after the potential exceeds the reduction potential, the current declines on account of the concentration polarisation of the electrode, since now there is a shortage of reducible solute close to the electrode. This initial half of the cyclic voltammetric curve is given by equation 5.

$$E = E_I - vt \tag{5}$$

where E_I is the initial potential selected so that no net charge transfer takes place at this potential and v is the sweep rate in volts sec^{-1}.

After the potential begins to fall there is a rapid change in current on account of the high concentration of oxidisable species close to the electrode. When the potential is close to the potential required to oxidise the reduced species, there is a substantial anodic current until all the oxidation is complete, and the current returns to zero. The overall shape of the curve gives details of the kinetics of the electrode process. For the reverse potential sweep, the potential E is given by equation 6.

$$E = E_I - 2\lambda v + vt \tag{6}$$

where λ is the time taken for completing the sweep in each direction.

1.4.2 Self-Assembling Monolayers

Interest in self assembling monolayers (SAMs) has focussed on a number of systems, including chlorosilanes on silicon[103,104], carboxylic acids on metal oxides[105] and organosulfur compounds on gold[106]. Sulphur-containing SAMs on gold surface have recently received much attention, it being well established that long-chain alkanethiols form well-organised, electrically insulating monolayers on the gold surface[107-109]. Most of the literature describes the properties of simple alkanethiols attached to the gold surface and it seemed probable that monolayers of polythiols in which a non-terminal methylene group is replaced by a positively charged group would exhibit new and different electrochemical properties. The packing of these charged alkanethiols on gold surfaces may also be quite different to that observed with the uncharged alkanethiols and this may also affect the behaviour of the monolayers.

The ability of a monolayer to block the electron transfer of a depolariser in solution is a measure of defectiveness. A freely diffusing electroactive species will react exclusively at defect sites of the monolayer. While uncharged monolayers with long alkane chains provides a substantial barrier for heterogeneous electron transfer[107], the apparent blocking behaviour can be dramatically affected by incorporating polar or ionic sites[110-113] into absorbents. Three effects can be expected. First, a repulsive interaction between ionic groups of the absorbate will destabilise the monolayer and promote permeability and defectiveness. Second, a positively charged monolayer will cause the double layer potential to be more positive compared to the double layer of a neutral monolayer. The effective potential difference driving the redox reaction will, therefore, be shifted to a more negative value. This shift in the potential difference leads to a decrease of the apparent heterogeneous rate constant (k_{app}) for the anodic reaction and to an increase of k_{app} of the cathodic reaction[113]. This behaviour is independent of the charge of the redox couple in solution. Third, the effective concentration of an ionic redox system, and thus k_{app}, is affected by the charge of the groups in the monolayer and by the charge of the electroactive species. A positively charged monolayer with terminal groups such as $-NR^{3+}$, (R = H, CH_3) will repel cationic species and more or less block the oxidation of $Ru(NH_3)_6^{3+}$. Such monolayers show no blocking behaviour to the negatively charged species $Fe(CN)_6^{3-}$[111,113], but this species is blocked by monolayers containing negatively charged groups (e.g. -COO)[110-113].

1.5 Aim of Project

Most studies of molecular recognition have concentrated on hydrogen bonding and π-stacking in non-aqueous environment. Electrostatic interaction in aqueous solution, however, is less well studied. In this project, we intended to synthesise a series of relatively simple anion receptors containing a number of positive charges through the use of quaternary ammonium centres. Using these positively charged receptors, we hoped to study their electrostatic complexation with simple organic anions in aqueous solution. To examine these interactions, we intended to use NMR titration and Job's method to determine their association constants and stoichiometries of the complexes. Using ferro- and ferricyanide as anions, we were interested to determine the selectivity of these receptors and to form crystals which could be studied in detail with X-ray crystallography.

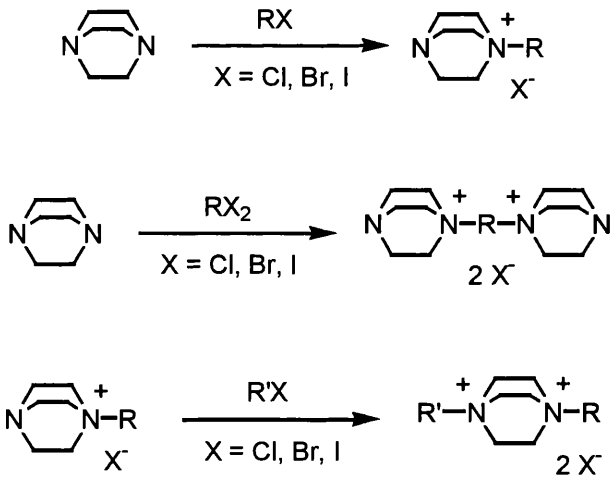
In many reports of sulfur containing self-assembling monolayers, electrically neutral long-chain alkane thiols have been used to attach to gold surface. Various techniques have been used to study such monolayers, such as voltammetry, optical ellipsometry, infrared spectroscopy and X-ray photoelectron spectroscopy. We were interested in attaching positively charged thiols to a gold surface and use cyclic voltammetry to study their electrochemical behaviour with different anionic species.

2 Results and Discussion

In this chapter, we describe the syntheses of a series of dications, trications and tetracations based on substituted benzenes and naphthalenes, and the preparation of a number of polyanionic compounds. The results of a series of NMR titrations and Job plots, providing the association constants and stoichiometries of different complexes, are also listed and discussed. Molecular recognition with these polycations, using potassium ferro- and ferricyanide, and cyclic voltammetry of related highly charged thiols on a gold surface are also described.

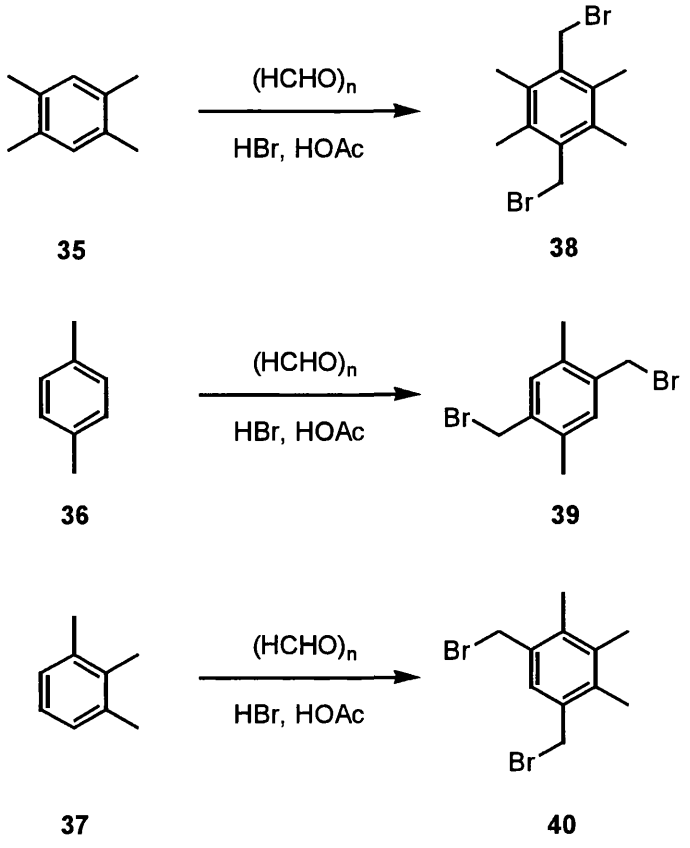
2.1 Syntheses of Dicationic Compounds

In order to introduce positive charges into these compounds, a commercially available base DABCO (1,4-diazabicyclo[2.2.2]octane) was used. It has been found that DABCO reacts readily with alkyl halides to give halide salts, resulting in a positively charged nitrogen atom on the DABCO[114,115]. It has also been shown that DABCO can further react so that both nitrogen atoms become positively charged[116] (Scheme 2.1).



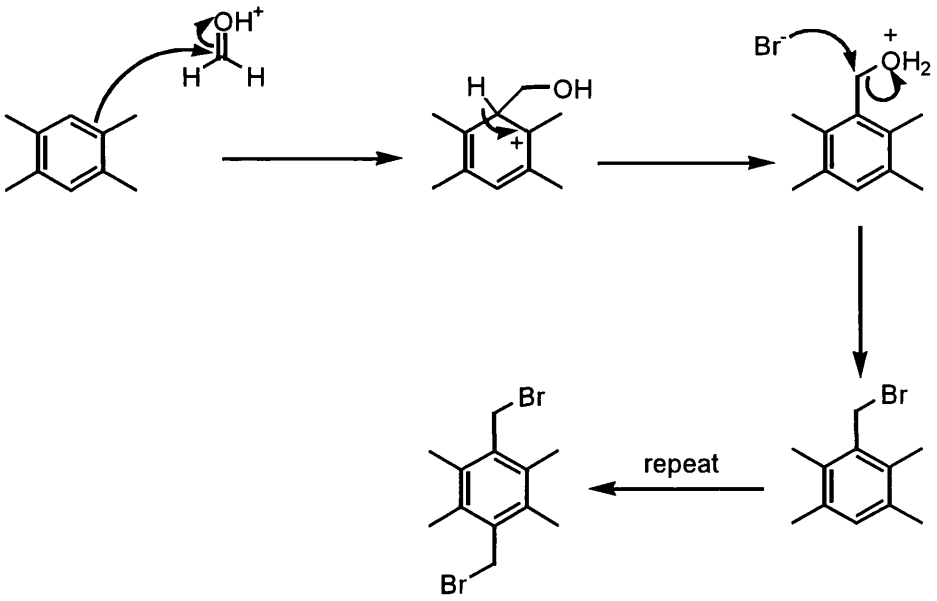
Scheme 2.1

In 1993, van der Made *et al.*[117] reported a procedure for bromomethylation of aromatic compounds by adding a solution of HBr in acetic acid to a mixture of paraformaldehyde, acetic acid and the aromatic compound. Using durene (1,2,4,5-tetramethylbenzene) (**35**), 1,4-xylene (1,4-dimethylbenzene) (**36**) and hemellitol (1,2,3-trimethylbenzene) (**37**) as starting materials, this method was used to obtain 3,6-bis(bromomethyl)-1,2,4,5-tetramethylbenzene (**38**), 2,5-bis(bromomethyl)-1,4-dimethylbenzene (**39**) and 4,6-bis(bromomethyl)-1,2,3-trimethylbenzene (**40**) in 68%, 46% and 36% yield, respectively (Scheme 2.2).



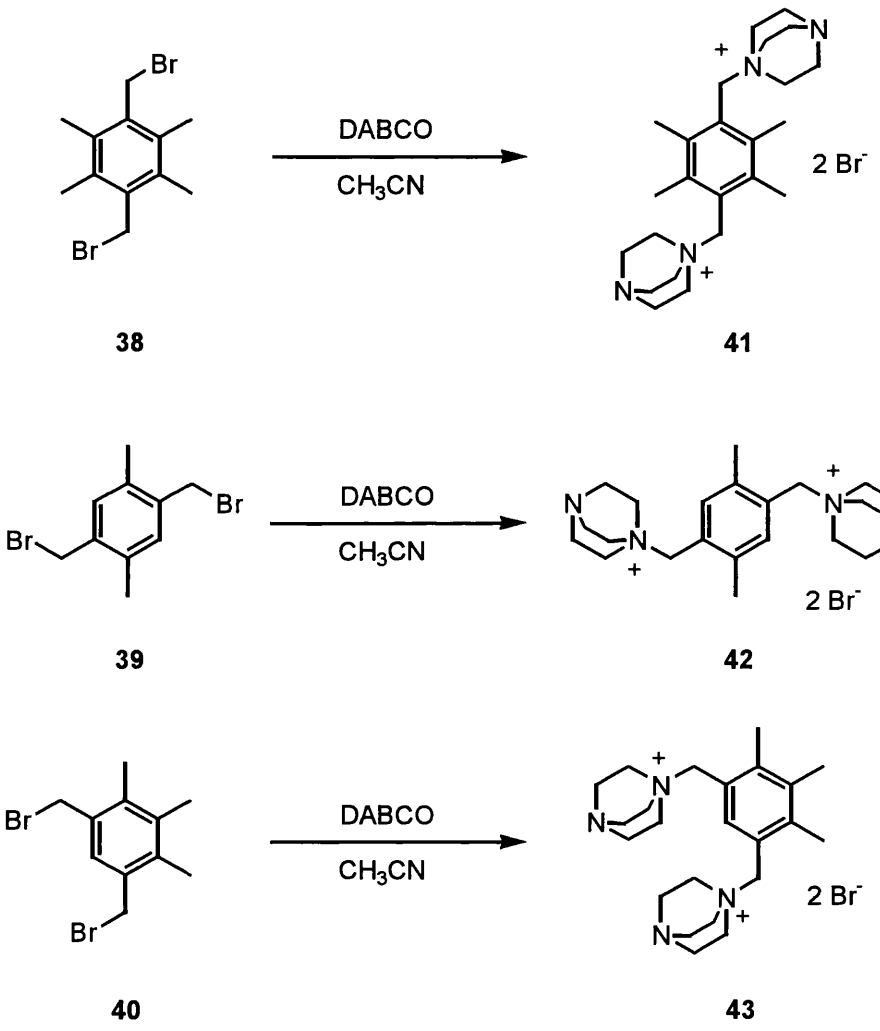
Scheme 2.2

A possible mechanism for this reaction is outlined in Scheme 2.3. Formaldehyde is first protonated and the resulting oxonium ions undergoes electrophilic attack by the benzene followed by re-aromatisation. The resulting benzyl alcohol is protonated and then substituted by bromide to give a mono-bromomethylated benzene. A similar, second substitution provides a second bromomethyl substitution.



Scheme 2.3

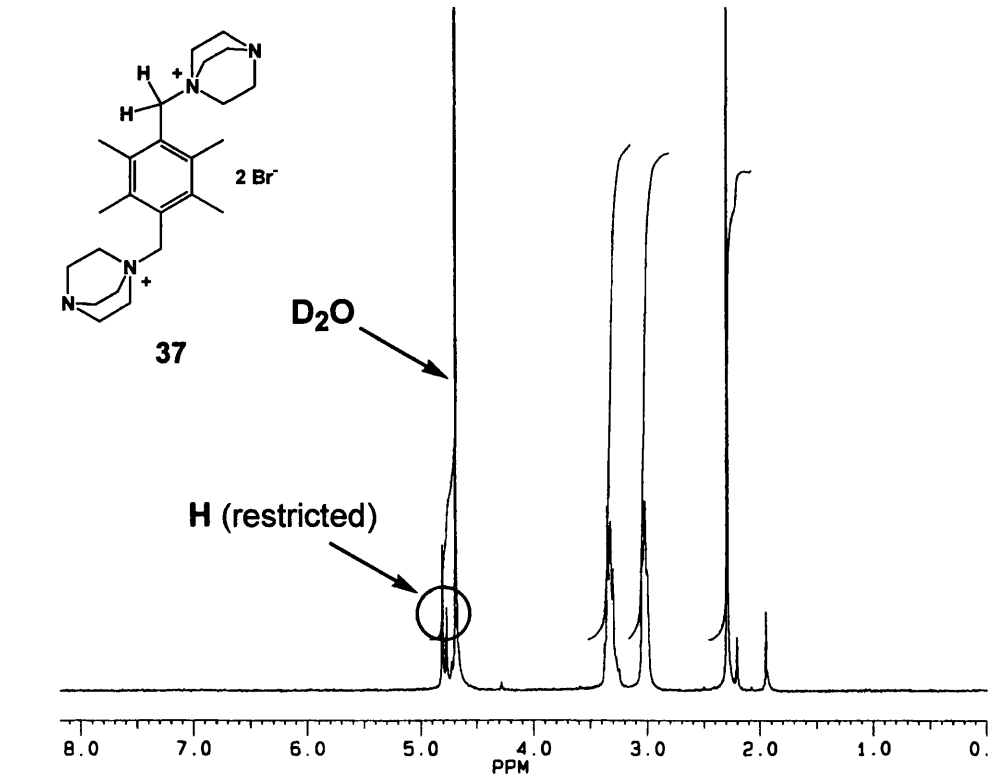
Treatment of the bromomethylated compounds **38**, **39** and **40** with DABCO in acetonitrile for 48 hours gave the tetraalkylammonium salts 3,6-bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide (**41**), 2,5-bis(DABCO-N-methyl)-1,4-dimethylbenzene dibromide (**42**) and 4,6-bis(DABCO-N-methyl)-1,2,3-trimethylbenzene dibromide (**43**) as white solids (Scheme 2.4).



Scheme 2.4

Fast atom bombardment (FAB) mass spectra of compound **41**, **42** and **43** showed ions corresponding to the loss of one bromide anion. The ^{1}H NMR spectra showed the correct number of protons according to the integration. Methylene signals were observed in the region δ 4.93-4.59, DABCO signals in the region δ 3.45-3.16 and methyl signals in the region δ 2.46-2.32. The ^{13}C NMR spectra showed the correct number of non-identical carbon atoms.

The ^{1}H NMR spectrum of compound **41**, however, was more complex than those of **42** and **43**, and the spectrum was interpreted by assuming that restricted rotation of the side chains was occurring in this compound on the NMR time scale at room temperature. The room temperature spectra of **41** and **42** are shown in Figure 2.2.



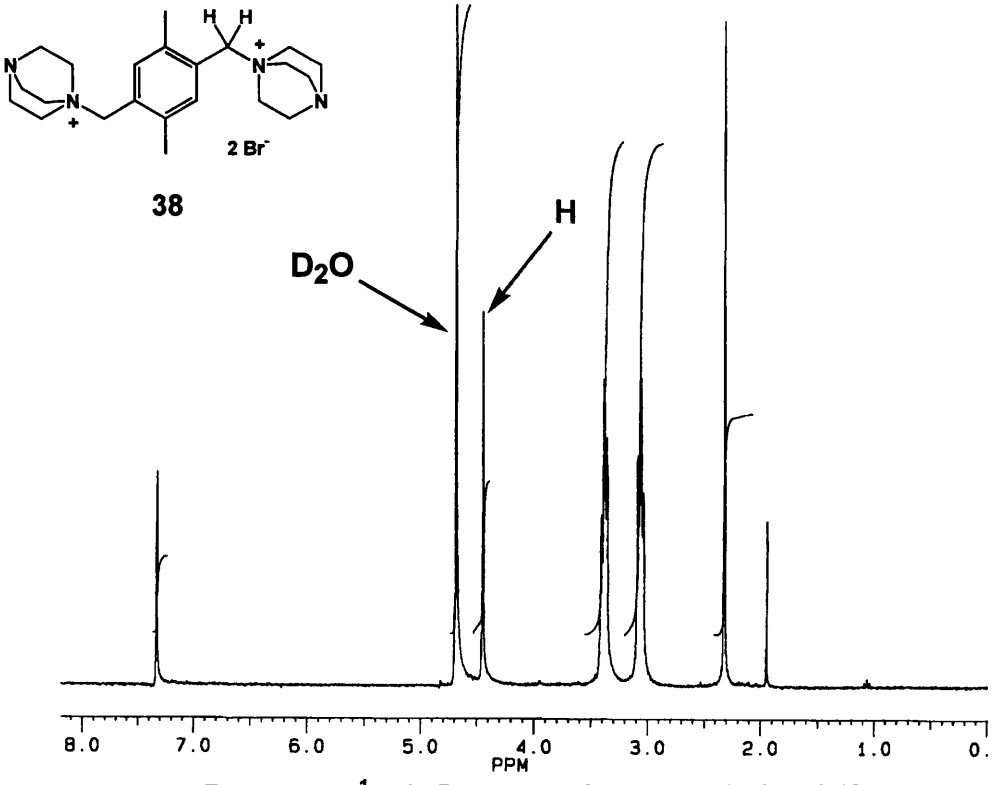
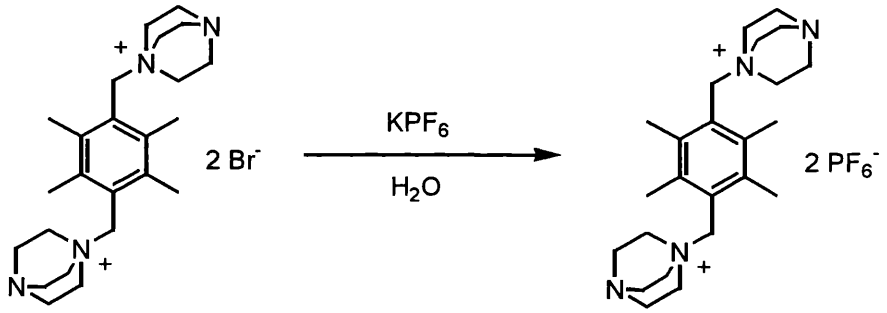


Figure 2.2 – ^{1}H NMR spectra of compound 41 and 42

The small signal adjacent to the methylene signal might be an impurity rather than a restricted conformation, and this should be resolved by variable temperature NMR. However, compound **41** was found to be only soluble in water or deuterium oxide which cannot be heated over 90 °C during a variable temperature NMR experiment. Thus, an alternative counter anion, hexafluorophosphate, was introduced to replace bromide ions in order to attempt to increase the solubility in organic solvents.

Compound **41** in aqueous solution was converted into its hexafluorophosphate salt **44** by addition of a saturated aqueous solution of potassium hexafluorophosphate, and it precipitated out of solution (Scheme 2.5).

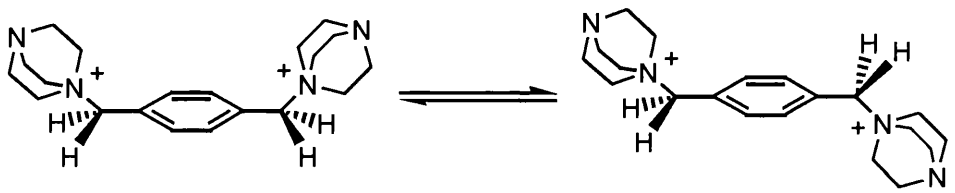


41 **44**

Scheme 2.5

With hexafluorophosphate as the counter anion, compound **44** is soluble in dimethyl sulfoxide which, with a boiling point of 189 °C, can be heated to a much higher temperature than deuterium oxide during a variable temperature NMR experiment.

Variable temperature NMR was performed on compound **44** using deuterated dimethyl sulfoxide on a Varian VXR-400 NMR spectrometer. After heating to 100 °C, the temperature was brought back down to room temperature and no decomposition of the compound was observed. This procedure was carried out twice to ensure that this result could be reproduced. From the resulting spectra, it can be seen that the coalescence temperature for the diastereotopic methylene protons in **44** (Scheme 2.6) is approximately 90 °C. The rotational barrier was calculated to be approximately 80 $kJmol^{-1}$. The changes in the appearance of the methylene signal from room temperature to 100 °C are shown in Figure 2.2.



Scheme 2.6 – Rotation of benzylic groups (2,3,5,6 methyl groups not shown)

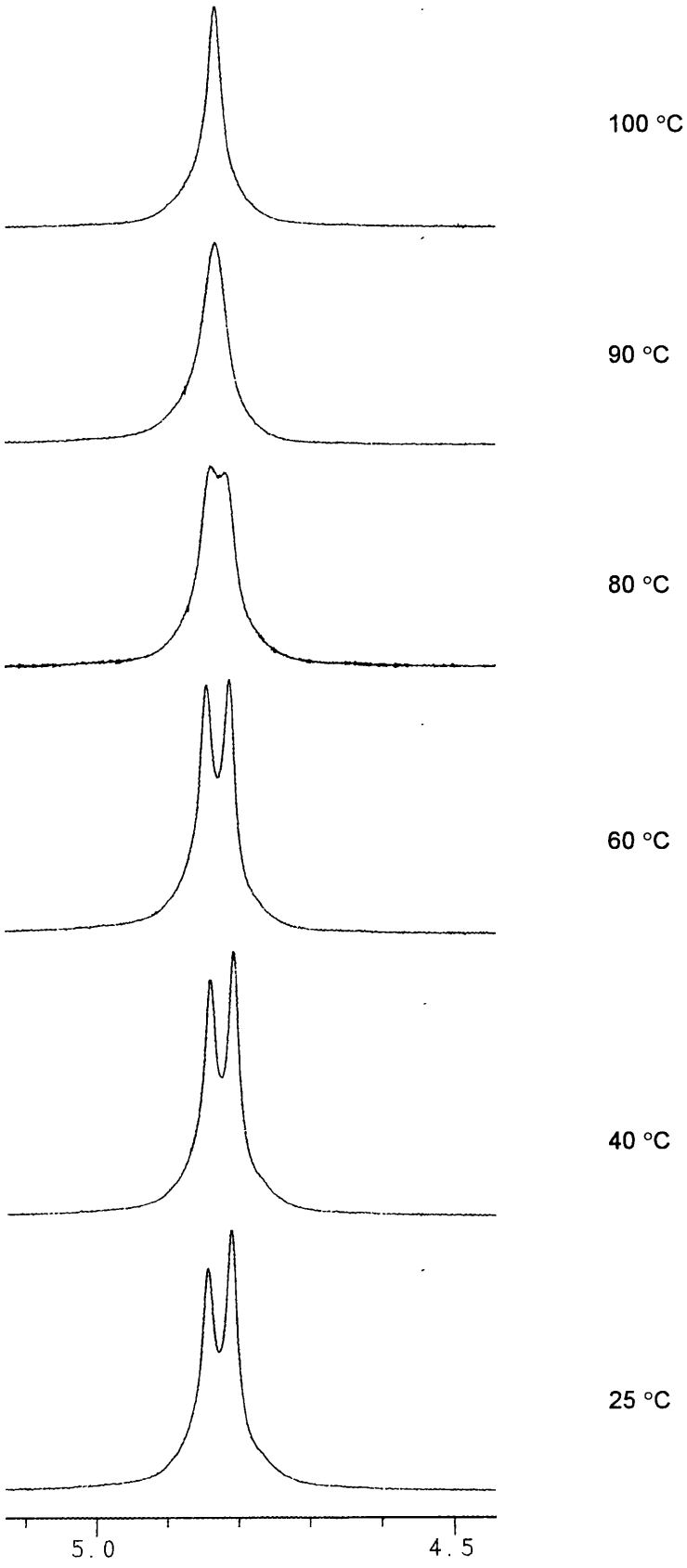
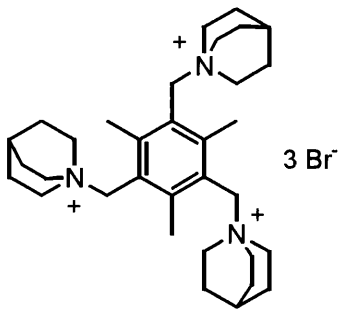


Figure 2.2 – NMR signals for the CH_2- group in 44 at various temperatures

2.2 Syntheses of Tricationic Compounds



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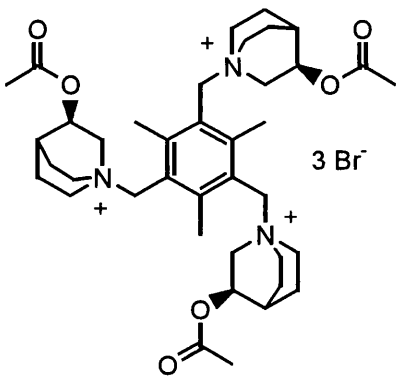
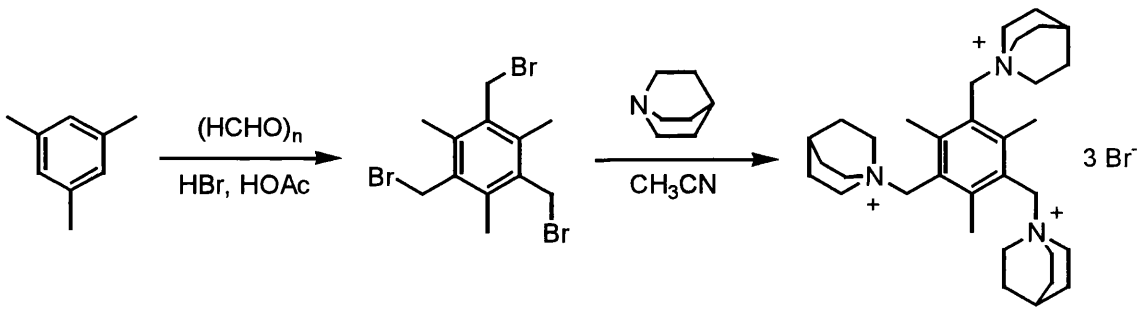


46

Compound **45** was made by a similar method to that described previously for the dicationic compounds. 2,4,6-Tris(bromomethyl)-1,3,5-trimethylbenzene (**47**) was prepared from 1,3,5-trimethylbenzene (**48**) by reacting with HBr, paraformaldehyde and acetic acid. On treating compound **47** with quinuclidine in acetonitrile, compound **45** was obtained as a white solid in 52% overall yield (Scheme 2.7).

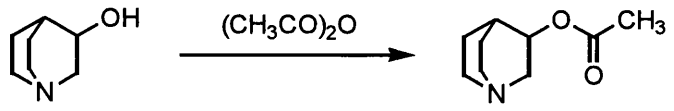


48 47 45

Scheme 2.7

The FAB mass spectrum of **45** showed a 1:2:1 triplet at *m/z* 652 for $C_{33}H_{54}N_3{}^{79}Br^{81}Br$ which has the correct isotope pattern for two bromine atoms and corresponds to the loss of one bromide ion. The integration of the ^1H NMR spectrum showed the correct number of protons with the appropriate chemical shifts and the ^{13}C NMR showed the correct number of non-identical carbon atoms.

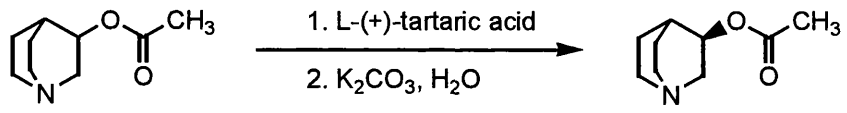
Compound **46** was made in an attempt to demonstrate that it was possible to use such polycations to distinguish between enantiomeric anions. Following the procedure of Langlois *et al.*[118], a commercially available base, 3-quinuclidinol (**49**), was heated under reflux with acetic anhydride to give 3-acetoxyquinuclidine (**50**) as a colourless oil in 47% yield (Scheme 2.8).



49 **50**

Scheme 2.8

In 1947, Kaiser[119] reported a method of resolving 3-acetoxyquinuclidine (**50**) into its (R)- and (S)- isomers using tartaric acid. A 1:1 mixture of **50** and L-(+)-tartaric acid in an 80% ethanol solution was prepared and left for 3 days at room temperature. The precipitated solid was removed by filtration and recrystallised from 80% ethanol to give (R)-(+)-3-acetoxyquinuclidine tartrate as white needles which had a slightly higher optical rotation ($[\alpha]^{25}_D$ = +4.4° (c = 2.2, H_2O)) than the literature value ($[\alpha]^{25}_D$ = +3.6° (c = 2.2, H_2O))[118]. The resolved tartrate was then dissolved in water and the solution was made alkaline with potassium carbonate to give (R)-(+)-3-acetoxyquinuclidine (**51**) as a colourless oil which had a slightly lower optical rotation ($[\alpha]^{25}_D$ = +26.6° (c = 2.9, EtOH)) than that reported in the literature ($[\alpha]^{25}_D$ = +29.4° (c = 5.0, EtOH))[119]; ($[\alpha]^{25}_D$ = +28.5° (c = 2.2, EtOH))[118] (Scheme 2.9).

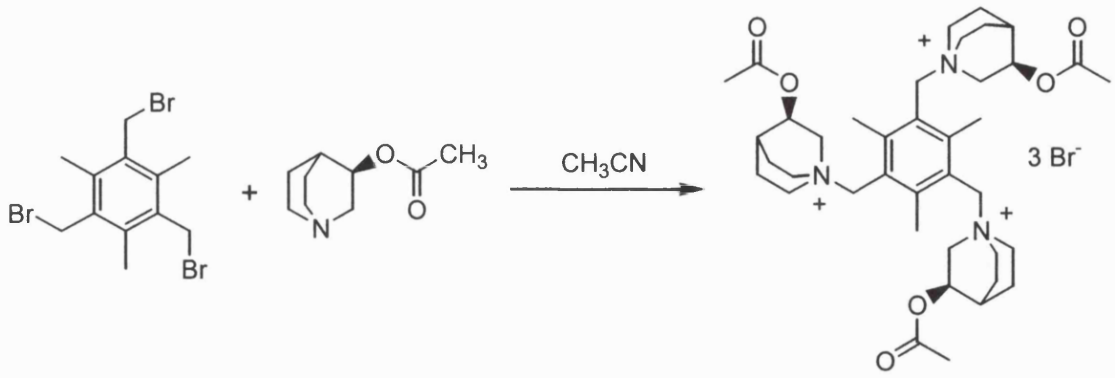


50 **51**

Scheme 2.9

The NMR and FAB mass spectra of compound **51** are identical to that of its racemate **50**.

Tricationic compound **46** was obtained in 92% yield by treating (R)-(+)-3-acetoxyquinuclidine **51** with 2,4,6-tris(bromomethyl)-1,3,5-trimethylbenzene **47** in acetonitrile (Scheme 2.10). Compound **46** showed an optical rotation of -14.2° but the enantiomeric purity was not determined.



47 **51** **46**

Scheme 2.10

The FAB mass spectra of compound **46** showed peaks corresponding to the loss of one bromide anion. Since none of the protons in the 3-acetoxyquinuclidine part of the molecule are equivalent, the ^{1}H NMR spectrum of compound **46** was extremely complicated . The ^{1}H NMR chemical shifts of compound **46** in deuterium oxide are illustrated in Figure 2.3. Broad multiplets are observed in the regions δ 4.88, 4.77, 3.60-3.48, 2.34-2.21 and 1.98-1.93. We can attribute this multiplicity as being due to the non-equivalence of the protons providing the signals. For example, the protons responsible for the signals at δ 3.60-3.48 are all non-equivalent with respect to the CH_3COO group.

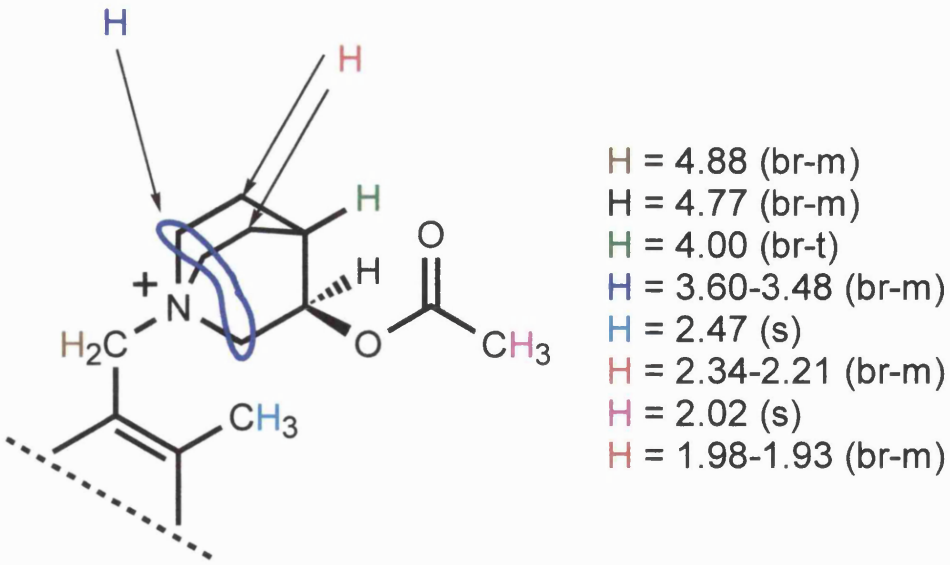
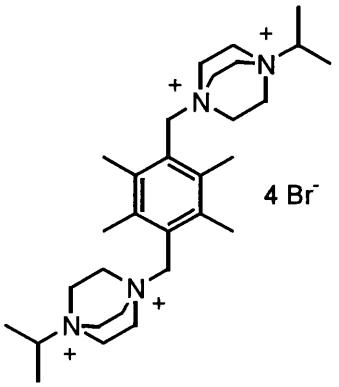


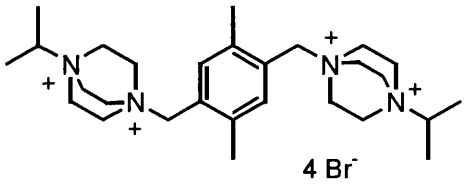
Figure 2.3 – ^{1}H Chemical shifts (δ) for compound 46 in deuterium oxide

2.3 Syntheses of Tetracationic Compounds

We have successfully synthesised a total of 5 structurally different tetracationic compounds, excluding tetracationic thiols, throughout our research. These compounds are illustrated below.



52



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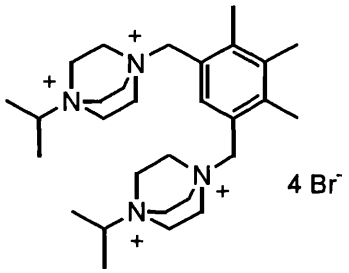

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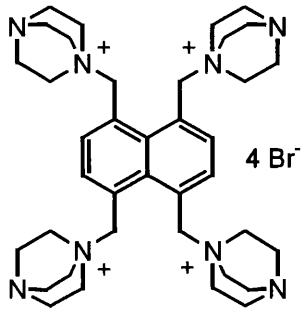

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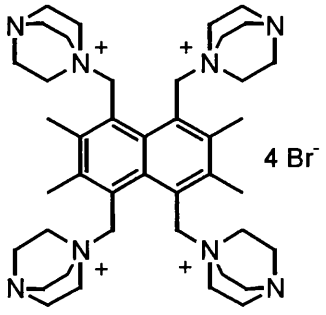
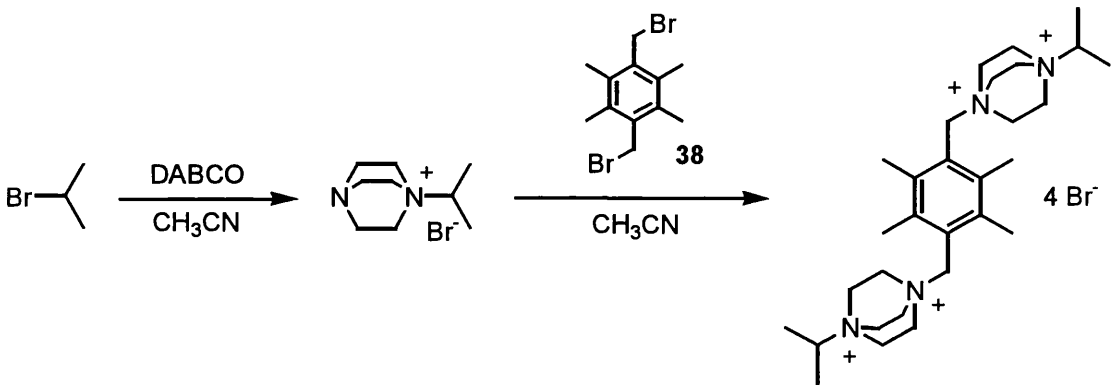


56

Compound **52**, **53** and **54** were derived from 3,6-bis(bromomethyl)-1,2,3,5-tetramethylbenzene (**38**), 2,6-bis(bromomethyl)-1,4-dimethylbenzene (**39**) and 4,6-bis(bromomethyl)-1,2,3-trimethylbenzene (**40**), respectively.

A monocationic DABCO derivative, N-isopropyl DABCO bromide (**57**)[116], was prepared by reacting DABCO with 2-bromopropane **58** in acetonitrile. The resulting white solid is extremely hygroscopic. Compound **52**, **53** and **54** were then obtained by reacting the bromomethyl substituted benzenes **38**, **39** and **40**, respectively with **57** in acetonitrile. Scheme 2.11 illustrates the reaction sequence for compound **52**.

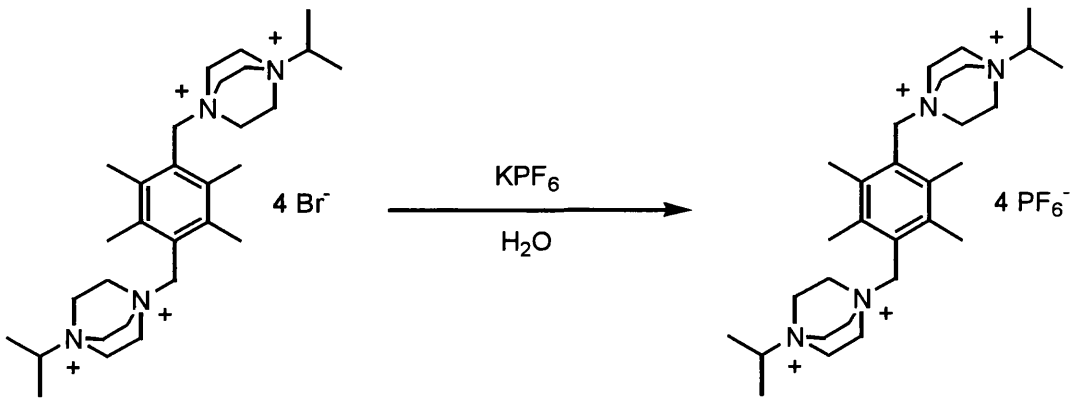


58 **57** **52**

Scheme 2.11

The ^{1}H NMR and ^{13}C NMR spectra of compound **52**, **53** and **54** were consistent with the assigned structures. The FAB mass spectrum for each compound showed an ion corresponding to the loss of one bromide anion. The integration of the ^{1}H NMR spectra showed the correct number of protons with the methylene signals in the region δ 5.25-4.93, DABCO and N^{+}-C**H**$(CH_3)_2$ signals in the region δ 4.14-3.87, and methyl signals in the region δ 2.52-2.36. The isopropyl methyl groups were observed as doublets in the region δ 1.49-1.46. The ^{13}C NMR spectra showed the correct number of non-identical carbon atoms.

The ^{1}H NMR spectrum of compound **52** shows multiple signals for the methylene groups, indicating that there is restricted rotation of the DABCO side arms on the NMR time scale. Again, due to the poor solubility of the compound **52** in organic solvents, an aqueous solution of **52** was converted into the hexafluorophosphate salt **59** by addition of a saturated, aqueous solution of potassium hexafluorophosphate (Scheme 2.12).

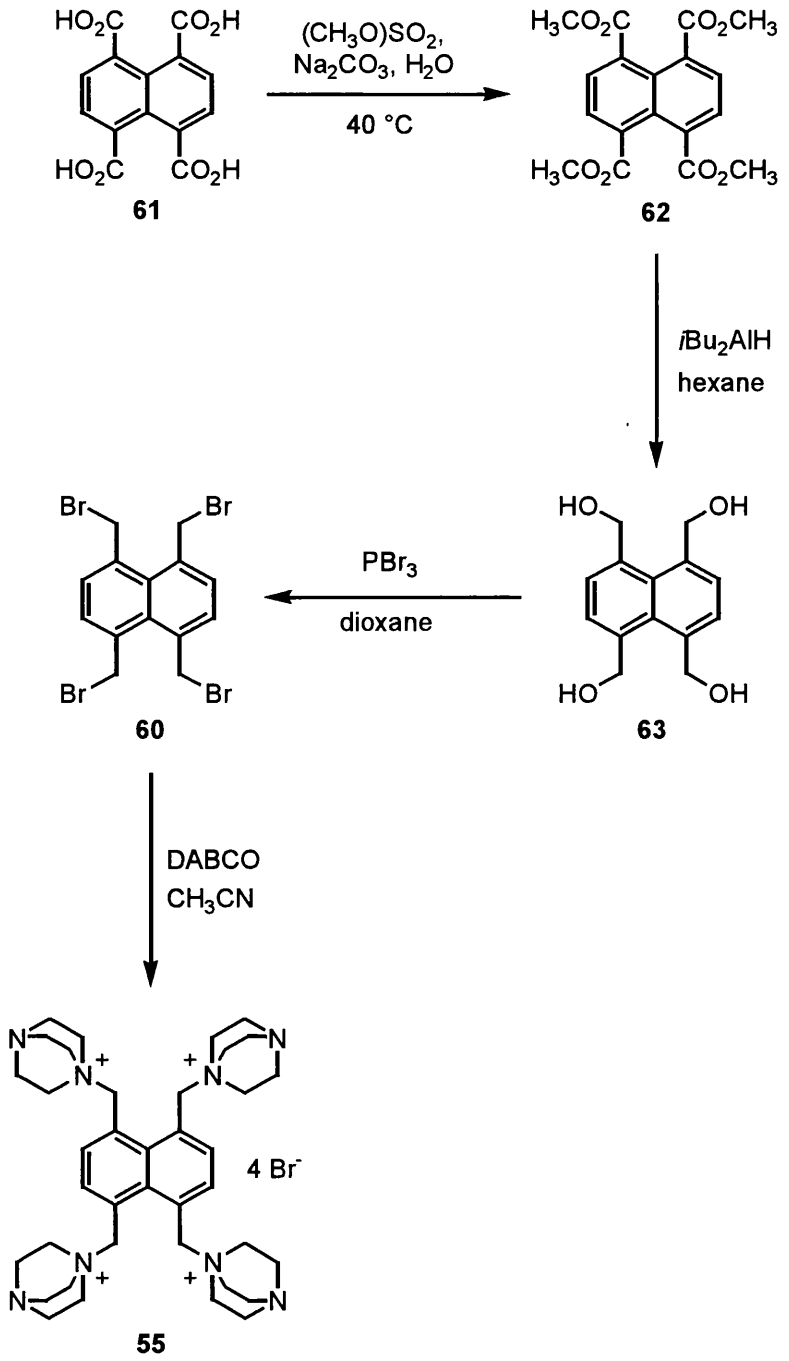


52 **59**

Scheme 2.12

A variable temperature NMR experiment was carried out on compound **59** in deuterated dimethyl sulfoxide, but the compound was found to decompose at 80 °C, and the coalescence temperature could not be determined.

The route to the tetracation **55** required the precursor 1,4,5,8-tetrakis(bromomethyl)naphthalene (**60**), which was synthesised by the method reported by Kamada and Wasada[120]. The commercially available 1,4,5,8-naphthalene-tetracarboxylate (**61**) was treated with dimethylsulfate in aqueous sodium carbonate solution to afford tetramethyl 1,4,5,8-naphthalene-tetracarboxylate (**62**) in 52% yield. It was found that tetramethyl ester **62** was unreactive towards lithium aluminium hydride[120], but it could be reduced by diisobutylaluminium hydride in hexane to give 1,4,5,8-tetrakis(hydroxymethyl)naphthalene (**63**) in 53% yield. Treatment of tetraol **63** with phosphorus tribromide gave **60** in 71% yield. The tetrabromide **60** was then treated with DABCO in the same manner as described before to give compound **55** as a white solid in 98% yield (Scheme 2.13). The overall yield from **61** to **55** was 19%.



Scheme 2.13

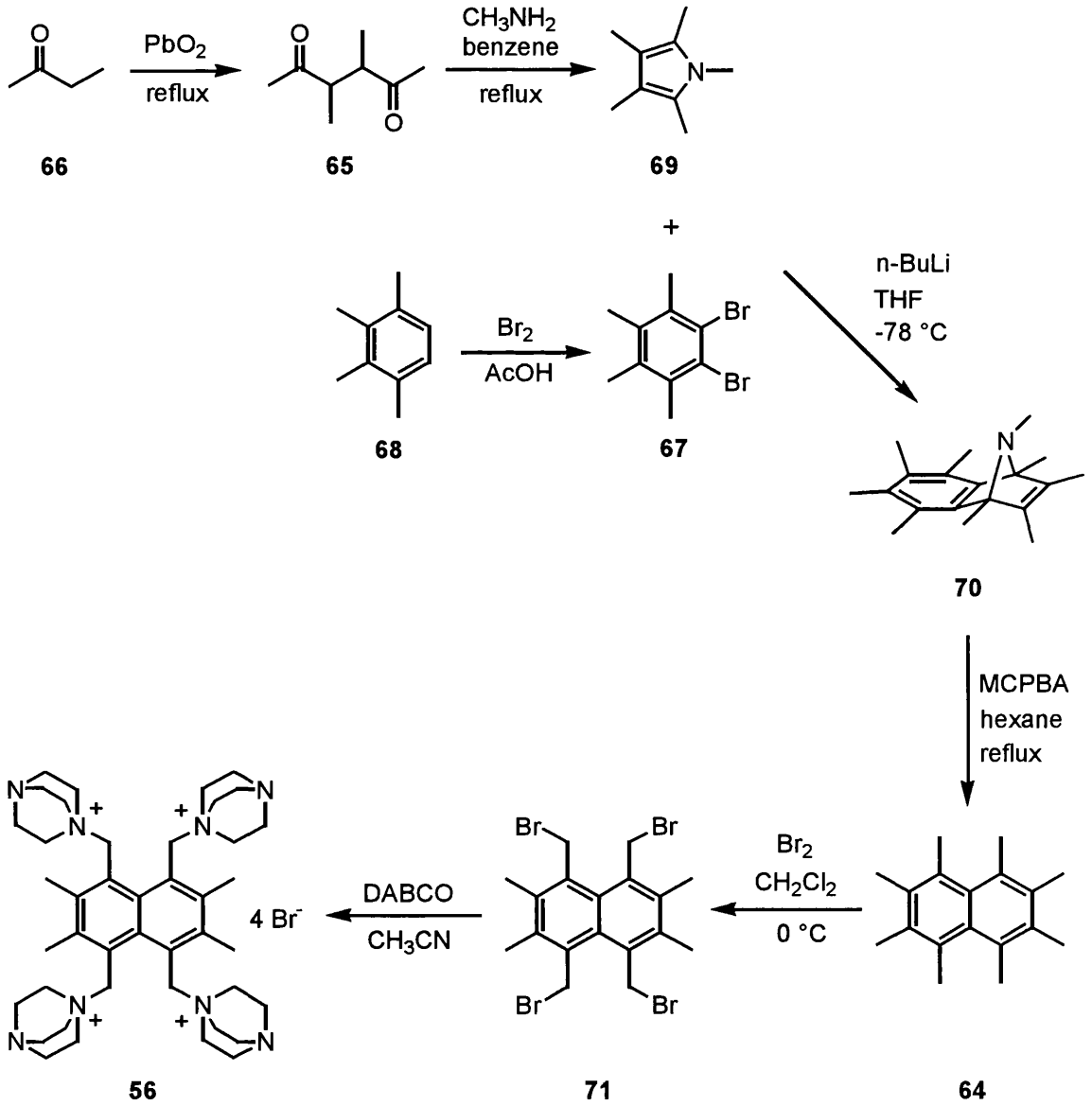
The integration of the ^{1}H NMR spectrum is in agreement with with that expected for compound **55**. The methylene signal was observed as a singlet at δ 5.21 and the DABCO signal was observed as two broad triplets in the region of δ 3.09-2.92. The ^{13}C NMR spectrum showed the correct number of non-identical carbon atoms and the FAB mass spectrum showed multiple ions, corresponding to the loss of one bromide ion, with the correct isotope pattern for three bromine atoms.

The route to the tetracation **56** required the precursor octamethylnaphthalene (**64**), which was synthesised by the method reported by Hart *et al.*[121]. 3,4-Dimethyl-2,5-hexanedione (**65**) was prepared by reacting 2-butanone (**66**) with lead (IV) oxide[122] and 5,6-dibromoprehnitene (**67**) was prepared from bromination of prehnitene (**68**) in acetic acid[123]. Treatment of Compound **65** with methylamine gave pentamethylpyrrole (**69**) which was found to be extremely unstable and needed to be used soon after it was made. *n*-Butyllithium solution in hexane was added to a mixture of compounds **67** and **69** to give nonamethyl-1,4-dihydronaphthalen-1,4-imine (**70**) as a yellow solid in 99% yield. Oxidation of compound **70** with *m*-chloroperbenzoic acid to the N-oxide and elimination of the nitrogen bridge as nitrosomethane led to octamethylnaphthalene **64** as white needles in 58% yield. In 1977, Hart *et al.*[124] reported the electrophilic halogenation of octamethylnaphthalene **64** by the addition of four equivalents of bromine in dichloromethane at 0 °C. This method gave 65% yield of the tetrabromo derivative **71** as white solid. Compound **71** was then treated with DABCO in acetonitrile with the usual method to give tetracationic compound **56** in overall yield of 12% from **68** (scheme 2.14). Possible mechanism for the elimination of the nitrogen bridge of compound **70** is shown in scheme 2.15 and the suggested mechanism for the bromination of **64** given by Hart[124] is outlined in scheme 2.16.

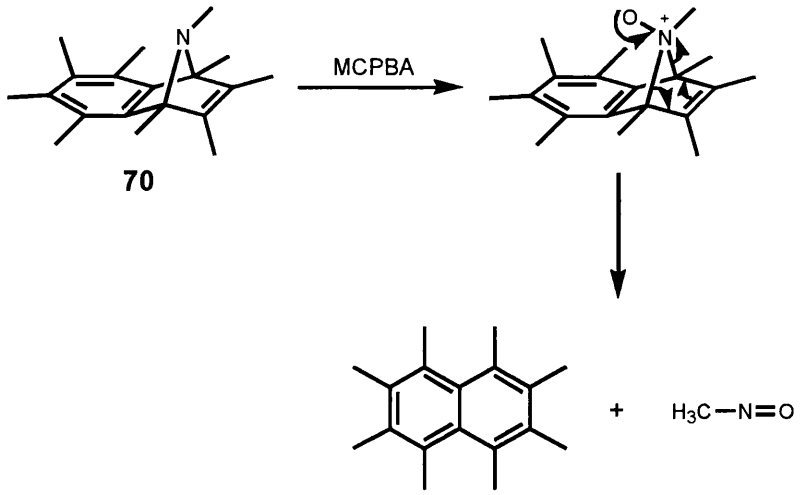
The regiospecificity of this bromination of octamethylnaphthalene is very interesting. Initial electrophilic attack occurs at C-1 position, followed by the loss of proton, to give the corresponding mono-brominated intermediate **73**. Because of the deactivating effect of the bromomethyl group of the mono-bromomethylated compound **74**, the second substitution occurs in the other ring. It was found by Hart[124] that the second attack takes place at the C-5 position instead of C-8, due to a consequence of steric hindrance to attack at C-8. Once the position of attack is determined and proton loss occurs, the 1,8-di-brominated structure **77** is formed. In this way, one can rationalise the formation of 1,8-bis(bromomethyl) compound, even though it is probably more strained than 1,5-di-brominated product which could be formed by the electrophilic attack at position C-8. If the initial attack occurs at C-2 position, the resulting positive charge would not have another contributing structure from the reacting ring. Initial attack on position C-1, by contrast, results in the positive charge being delocalised over two positions on the reacting ring, without loss of aromaticity of the second ring (Scheme 2.17).

The integration of the ^{1}H NMR spectrum of **56** showed the required number of protons in the molecule with the appropriate chemical shifts and the ^{13}C NMR spectrum showed the correct number of non-identical carbon atoms. The FAB mass spectrum showed multiple ions, corresponding to the loss of one bromide ion, with the correct isotope pattern for three bromine atoms.

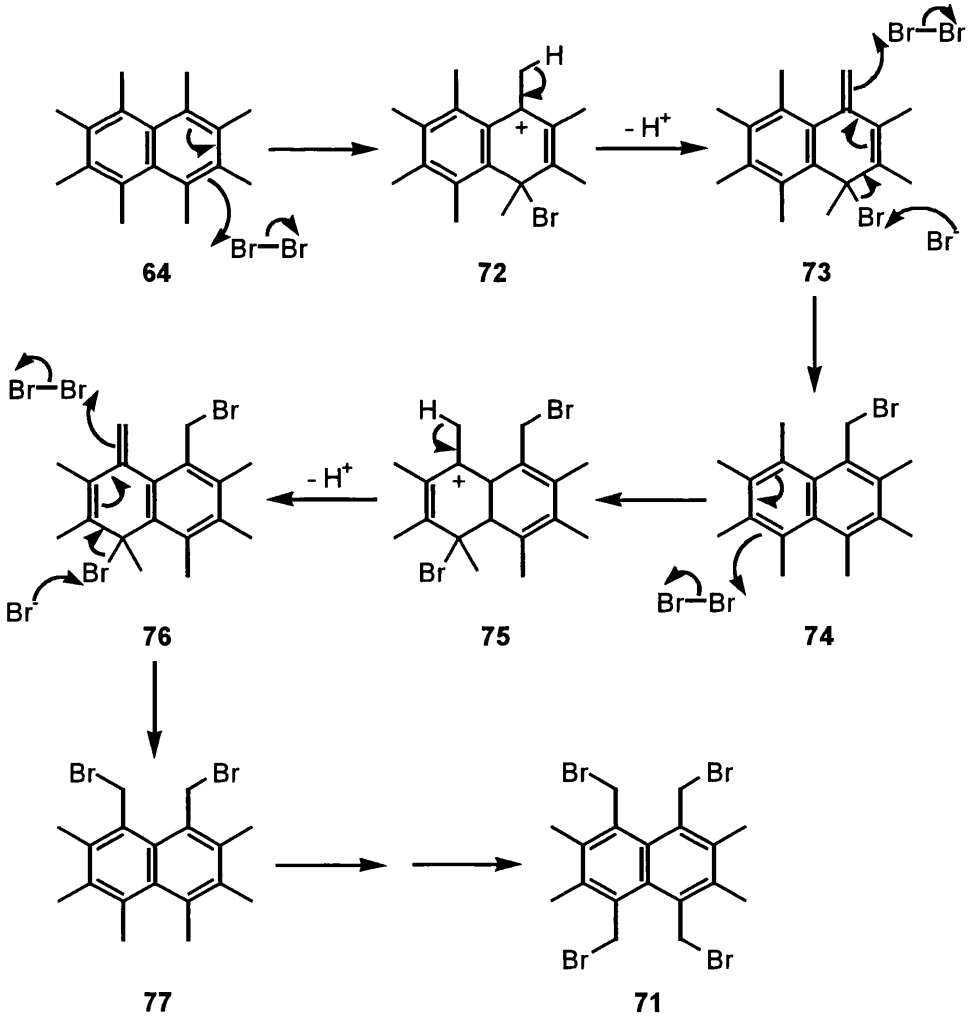
The ^{1}H NMR spectrum of the tetracation **56** shows multiple signals for the methylene groups indicating that there is restricted rotation on the NMR time scale. The bromide was, therefore, converted to the hexafluorophosphate using the same method as described before and a variable temperature NMR experiment was carried out up to 90 °C. Coalescence of the methylene signals was not, however, achieved at this temperature.



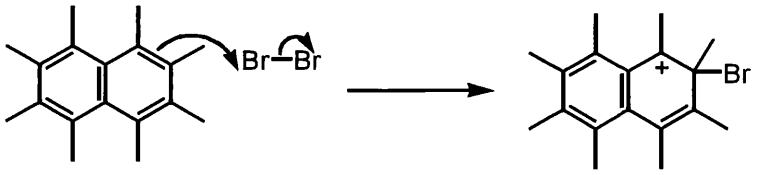
Scheme 2.14



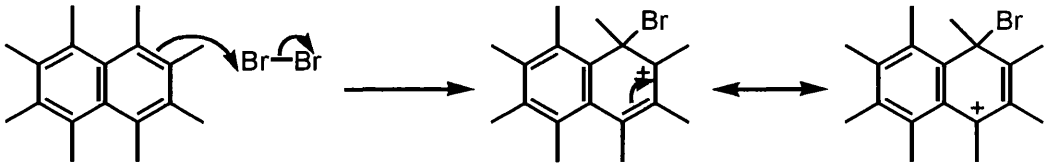
Scheme 2.15



Scheme 2.16



initial attack at C-2 position

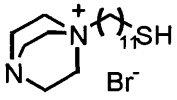


initial attack at C-1 position

Scheme 2.17

2.4 Syntheses of Tetracationic Thiols

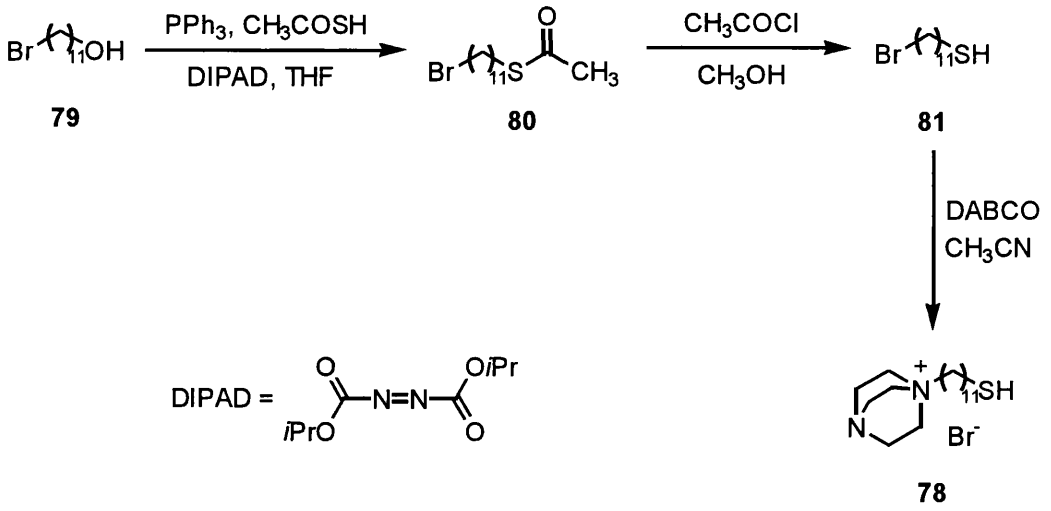
The most convenient way to attach compounds to a gold surface is via a sulfur-gold bond, and a series of cationic thiols were thus synthesised based on a monocationic DABCO derivative, N-(11-thioundecyl)-DABCO bromide (**78**).



N-(11-thioundecyl)-DABCO bromide

78

Following the procedure of Bain *et al.*[108], 11-bromo-1-undecanol (**79**) was treated with triphenylphosphine, diisopropyl azodicarboxylate and thioacetic acid in tetrahydrofuran at 0 °C to give 11-bromo-1-undecyl thioacetate (**80**) as a yellow oil in 65% yield. Compound **80** was then treated with acetyl chloride in methanol to give 11-bromo-1-undecanethiol (**81**) as a colourless oil in 91% yield. Using the same method as described in chapter 2.3, the monocationic DABCO derivative **78** was synthesised by treatment of **81** with DABCO in acetonitrile (Scheme 2.18).



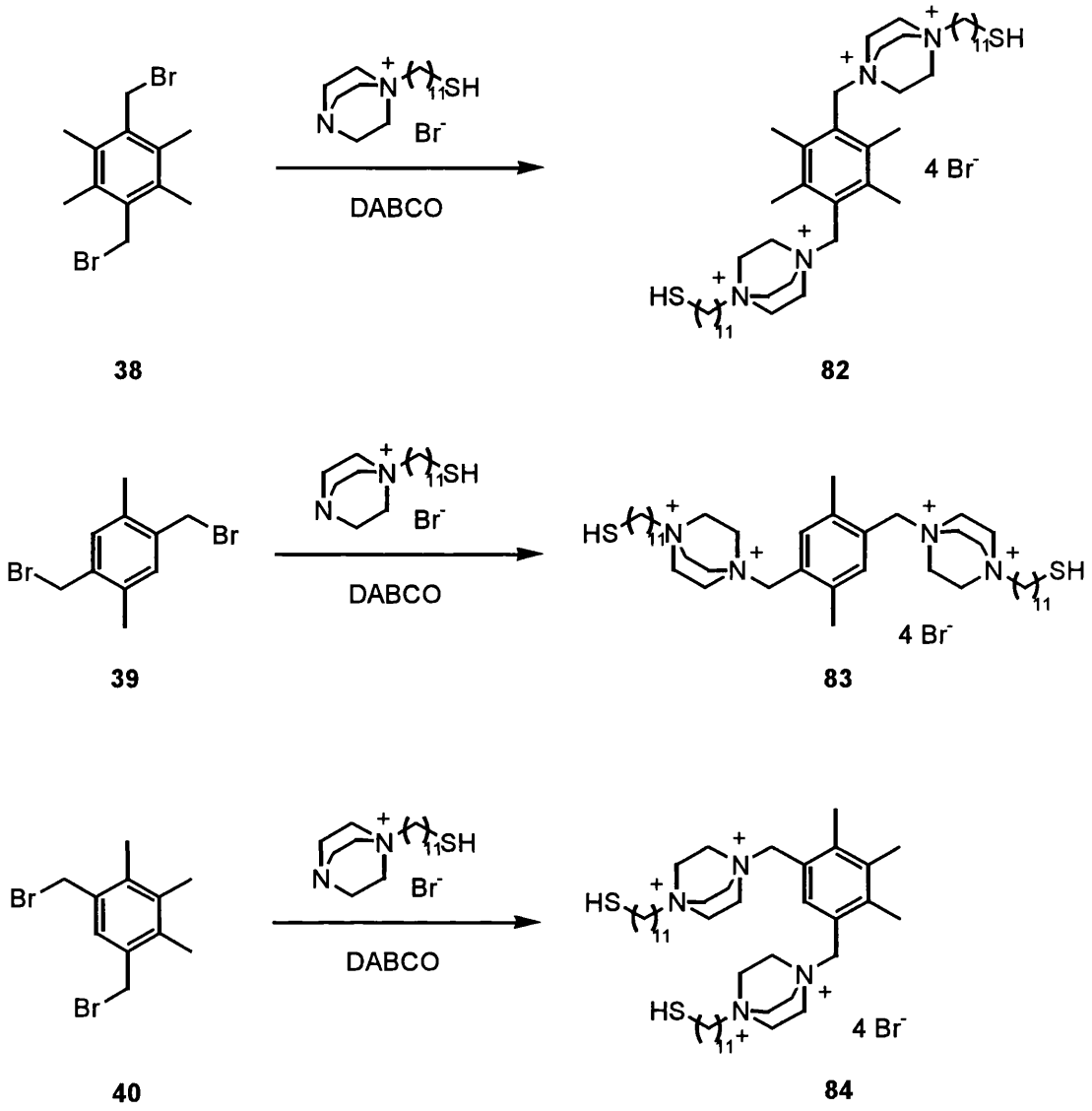
79 **80** **81** **78**

Scheme 2.18

The ^{1}H NMR spectrum of compound **78** was found to be complex due to the numerous protons in the long alkyl chain. The integration of the spectrum, however, showed the correct number of protons with the appropriate chemical shifts. The ^{13}C NMR spectrum showed signals corresponding to the expected number of non-identical carbon atoms. The FAB mass spectrum showed ion at *m/z* 299, corresponding to the loss of the bromide ion.

Treatment of compound **78** with the di-bromomethylated compound **38**, **39** and **40** in acetonitrile gave 3,6-bis(1-undecanethiol-N'-11-DABCO-N-methyl)-1,2,4,5-tetramethylbenzene tetrabromide (**82**), 2,5-bis(1-undecanethiol-N'-11-DABCO-N-methyl)-1,4-dimethylbenzene tetrabromide (**83**) and 4,6-bis(1-undecanethiol-N'-11-DABCO-N-methyl)-1,2,3-trimethylbenzene tetrabromide (**84**), respectively, in moderate yield (Scheme 2.19).

Unlike the previously described cationic compounds, these cationic thiols were found to be insoluble in water and deuterium oxide, but they were soluble in dimethyl sulfoxide. Deuterated dimethyl sulfoxide was, therefore, used as the solvent for NMR spectroscopy. The ^{1}H NMR and ^{13}C NMR spectra of these cationic thiols showed the correct number of protons at the appropriate chemical shifts and the correct number of non-identical carbon atoms. The FAB mass spectra showed ions corresponding to the loss of one bromide ion.

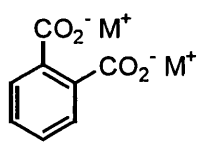


Scheme 2.19

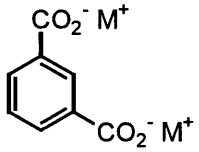
Compound **78** was also treated with 1,4,5,8-tetrakis(bromomethyl)-naphthalene (**60**) and 1,4,5,8-tetrakis(bromomethyl)-2,3,6,7-tetramethylnaphthalene (**71**), but no products were obtained. This is presumably caused by the poor solubilities of these naphthalene-based compounds in organic solvents.

2.5 Syntheses of Polyanionic Compounds

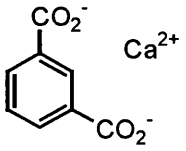
In order to study molecular recognition with electrostatic interaction, a total of 17 structurally different polyanionic compounds were used during the course of this research. These compounds are outlined Figure 2.4 below.



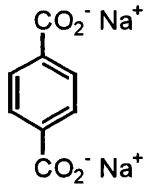
M = Li **85**
M = Na **86**
M = K **87**



M = Li **88**
M = Na **89**
M = K **90**



91



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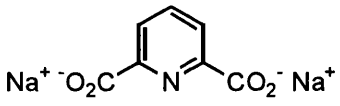

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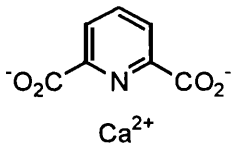

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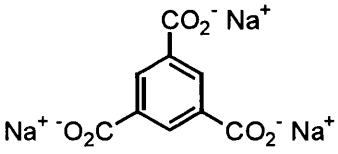

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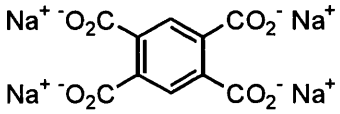

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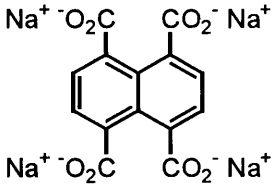

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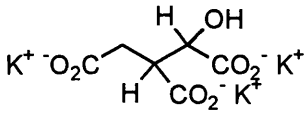

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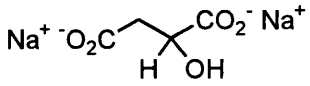

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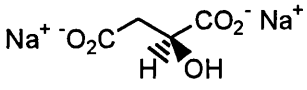

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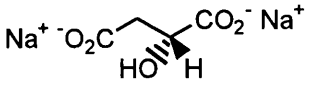


101

Figure 2.4 – Organic anions used in this project

Dipotassium 1,2-benzenedicarboxylate **87**, disodium 1,4-benzenedicarboxylate **92** and disodium L-malate **101** were commercially available and all other anions were made by simple procedures using the corresponding carboxylic acids. Compound **85**, for example, was prepared by mixing 1,2-benzenedicarboxylic acid (phthalic acid) with 2 equivalents of lithium hydroxide in water, followed by precipitation of the salt with acetone. All these organic anions were characterised by ^{1}H and ^{13}C NMR spectroscopy.

2.6 Nuclear Magnetic Resonance Techniques

2.6.1 Theory of NMR Titration[125]

There has recently been an increase in the number of groups that use NMR to study host-guest complexation. Of particular interest is the strength of the complexation reflected by the association constant *K*. Considering the cationic species to be host (H) and the anionic species to be guest (G), they are assumed to be in equilibrium with the complex (C).

$$H + G \rightleftharpoons C$$

$$K = \frac{[C]}{[H][G]} \tag{7}$$

Equation 7 can be rewritten in the form shown in equation 8.

$$K = \frac{[C]}{([H]_o - [C])([G]_o - [C])} \tag{8}$$

where $[H]_o$ and $[G]_o$ are the initial concentration of host and guest. Since $[C] = n_c[G]_o$, where n_c is the mole fraction of the complex, equation 8 can be rewritten as equation 9, where R is the ratio $[H]_o/[G]_o$.

$$K = \frac{n_c}{(1 - n_c)(R - n_c)[G]_o} \tag{9}$$

In order to use ^{1}H NMR spectroscopy to study such a complexation process, at least one site in the uncomplexed guest molecule must have a chemical shift δ_g that is significantly different from that of same site in the complexed host molecule δ_c. An assumption (equation 10) can be made for a fast exchange system.

$$\delta = n_g\delta_g + n_c\delta_c \tag{10}$$

where n_g represents the mole fraction of the guest and δ is the observed chemical shift.

Since the magnitude of difference in chemical shift is $\Delta\delta = \delta_g - \delta_c$ and $n_g = 1 - n_c$, equation 10 can be rearranged to the form shown in equations 11 and 12.

$$\delta = (1 - n_c)\delta_g + n_c\delta_c \tag{11}$$

Thus,

$$n_c = \frac{\delta_g - \delta}{\delta_g - \delta_c} = \frac{\delta_g - \delta}{\Delta\delta} \tag{12}$$

Equation 7 can be rewritten in the form shown in equations 13 and 14.

$$\begin{aligned} \frac{n_c}{K[G]_o} &= (1 - n_c)(R - n_c) \\ &= R - (R + 1)n_c + (n_c)^2 \end{aligned} \tag{13}$$

or

$$(n_c)^2 - \left(1 + R + \frac{1}{K[G]_o}\right)n_c + R = 0 \tag{14}$$

The real root of this quadratic equation is given by equation 15, where $b = 1 + R + \frac{1}{K[G]_o}$

$$n_c = \frac{b - \sqrt{b^2 - 4R}}{2} \tag{15}$$

Substituting equation 15 into equation 11 gives a complicated function of $[H]_o$, $[G]_o$, δ_g, δ_c and K.

$$\begin{aligned} \delta &= \left(1 - \frac{b - \sqrt{b^2 - 4R}}{2}\right)\delta_g + \left(\frac{b - \sqrt{b^2 - 4R}}{2}\right)\delta_c \\ &= \delta_g - (\delta_c - \delta_g)\left(\frac{b - \sqrt{b^2 - 4R}}{2}\right) \\ &= \delta_g - \frac{\Delta\delta}{2}\left(b - \sqrt{b^2 - 4R}\right) \end{aligned} \tag{16}$$

Assuming $B = b[G]_o = [H]_o + [G]_o + 1/K$, equation 16 can be rewritten in the form shown in equation 17.

$$\delta = \delta_g - \frac{\Delta\delta}{2[G]_o}\left(B - \sqrt{B^2 - 4[H]_o[G]_o}\right) \qquad (17)$$

Unfortunately, equation 16 requires that both δ_g, δ_c and K be known. Although δ_g can be easily determined from the chemical shift in the absence of host molecule, δ_c and K still remain unknown within one single equation. However, it is possible to use non-linear curve fitting to determine the values of K and δ_c by simulating an experimental data set of δ and R data. A program for doing this was written by Professor J H Ridd at University College London. The input includes the experimental values of δ, $[G]_o$ and $[H]_o$, together with the value of δ_g, the chemical shift in the unbound guest environment, and an estimate of the value of K. The program uses the initial estimate of K and equation 17 to calculate a value of δ_c. By using these values of δ_c and K, it calculates a value of δ for each experimental value of $[H]_o$ and $[G]_o$ from equation 17. It then compares the calculated value with the observed value for each point ($\delta_{obs} - \delta_{calc}$). If the differences are positive, the value of K is too large; if the differences are negative, the value of K is too small. This entire process is repeated until the change in K reaches < 1%. Thus, even when the estimated value of K is too large or too small, the program still converges on a best fit.

Deuterium oxide was chosen to be the medium for our titrations, since all of our polycationic (host) and polyanionic (guest) compounds were water soluble. Two standardised solutions were prepared, one containing an approximately 5:1 mixture of host and guest; and the other one containing guest only at the same concentration as guest in previous solution. These two solutions were combined to give a constant volume of solution, 0.8 mL, thus the concentration of guest remained constant throughout the experiment, while the ratio of [H]/[G] was varied from 5:1 to zero. The chemical shift δ_g was obtained when the ratio [H]/[G] was zero. ^{1}H NMR spectra at eight relative concentrations were recorded. The results of the NMR titration carried out with dicationic compound **41** (host) and disodium 1,3-benzenedicarboxylate **89** (guest), for example, are shown in Figure 2.6.

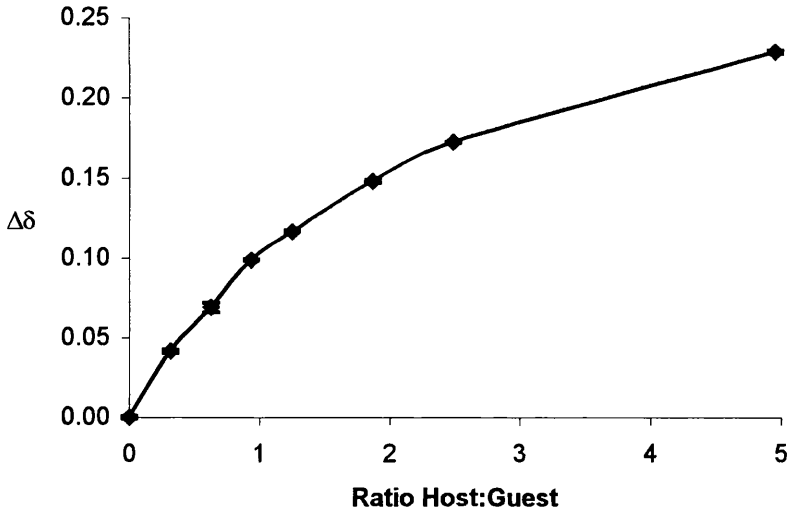


Figure 2.6 – a NMR titration curve (41 with 89)

2.6.2 Method of Continuous Variations[126]

NMR spectroscopy not only allows us to determine the strength of the binding between our polycationic and polyanionic compounds, it also can be used to study the nature of the binding, that is the stoichiometry of any complex formed. In order to determine stoichiometry, the so-called method of continuous variations, or Job's method, was used. For the study of a simple equilibrium

$$aH + bG \rightleftharpoons C \tag{16}$$

a series of solutions is prepared where the total concentration, [H] + [G], is kept constant while the ratio of $[H]_o/[G]_o$ varies in small steps. It can be shown that the concentration of the complex C, [C], has a maximum at for a H-to-G molar ratio equal to *a*/*b*.

$$x = \frac{[G]_o}{[H]_o + [G]_o} \tag{17}$$

$$x = \frac{b}{a+b} = \frac{1}{1+\frac{a}{b}} \tag{18}$$

Thus, a plot of [C] that is a linear function of [C], against mole fraction x (equation17) yields a curve having a maximum (equation 18) and zero values for x = 0 and x = 1.

$$[C] = [G]_o\left(\frac{\delta_{obs} - \delta_g}{\delta_c - \delta_g}\right) \quad (19)$$

By using the calculated value of δ_c from the equilibrium constant determination described previously, the concentration of complex can be obtained from equation 19. A plot of [C] against x can then be used to determine the stoichiometry of the complex. If the curve reaches maximum at x = 0.5, a 1:1 complex is authenticated.

This method is open to objections and has several limitations, and it currently suffers from poor repute[126]. There are several main reasons for the poor reputation of Job's method.

a) The existence of other equilibria concurrent with equation 16 can affect the determination of *a*/*b*. However, the concentration of complex [C] is still a maximum for the stoichiometric *a*/*b* ratio if the concentrations of the other concurrent complexes are much smaller for such a ratio.
b) The involvement of species other than H, G and C in the equilibrium may affect the value of *a*/*b* determined.
c) The individual values of *a* and *b* are not determined and only the ratio *a*/*b* is obtained. Thus, this method cannot distinguish between a 1:1 and a 2:2 complex.

However, most of the limitations to its direct use in a non-sophisticated analysis are common to other methods[126].

In order to determine the stoichiometry of the binding between our polycationic (host) and polyanionic (guest) compounds, two standardised solutions in deuterium oxide were prepared, one containing host at a known concentration and the other containing guest at the same concentration. The two solutions were combined to give a constant volume of 8 mL. This keeps the total concentration of ions constant while the mole fractions of host and guest can be varied. A Job's plot of dicationic compound **41** (host) and disodium 1,3-benzenedicarboxylate **89** (guest) is shown in Figure 2.7 as an example of the Job's method. The curve reaches the maximum at approximately mole fraction of 0.5 which corresponds to a 1:1 stoichiometry.

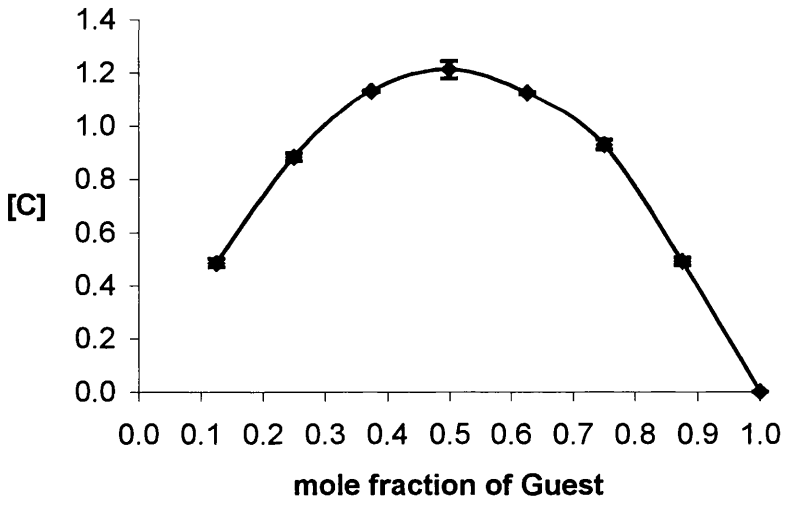
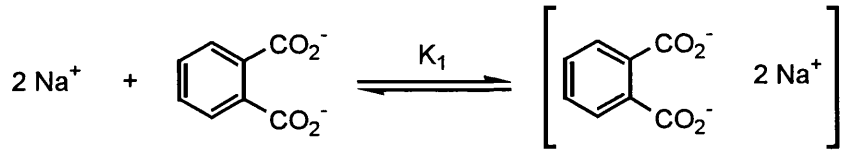


Figure 2.7 – A Job's plot (41 with 89)

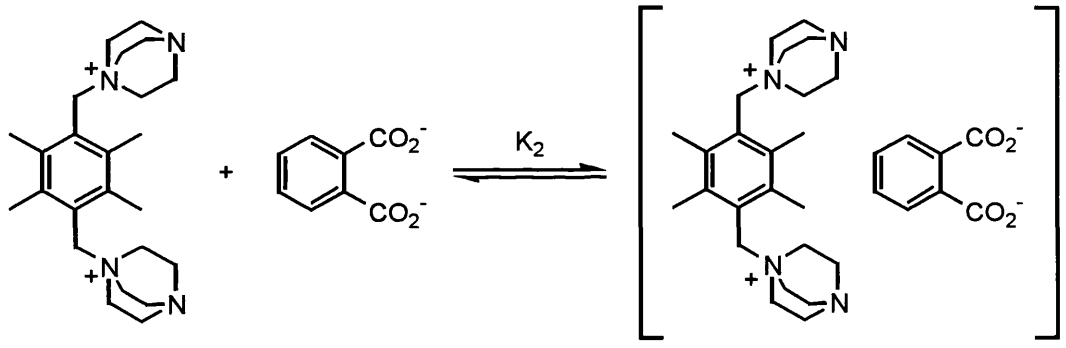
2.7 Results of Binding studies

Four different ions are involved in these mixture and four possible complexations take place. Two of these complexations are illustrated in Scheme 2.18, where K is the association constant.



2 A$^+$ **B^{2-}** **A$_2$B**

Equilibrium 1



C^{2+} **B^{2-}** **CB**

Equilibrium 2

These equilibria can be written as equations 20 and 21.

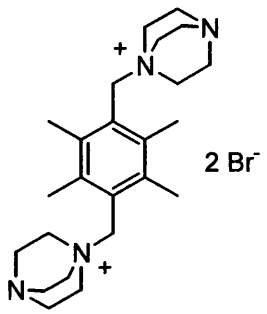
$$K_1 = \frac{[A_2B]}{[A^+]^2\,[B^{2-}]} \qquad (20)$$

$$K_2 = \frac{[CB]}{[C^{2+}]\,[B^{2-}]} \qquad (21)$$

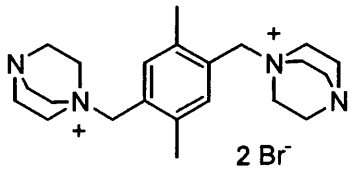
Dividing equation 20 by equation 21 gives equation 22.

$$K_2 = K_1 \frac{[A^+]^2\,[CB]}{[A_2B]\,[C^{2+}]} \qquad (22)$$

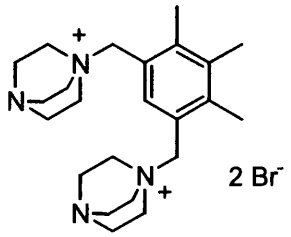
2.7.1 Dicationic Compounds



41



42



43

The results of the NMR titration and Job's experiment using these three dicationic compounds and 1,2-benzenedicarboxylate are outlined in Tables 2.1. Association constants (K_2) are shown in RED and the unit is M^{-1}; stoichiometries of the complexes are shown in BLUE, as Host : Guest; and GREEN question mark "**?**" represents non-satisfactory titration or Job's plot obtained which can possibly be caused by either the limitation of the program or Job's method, as described previously. Values given are good to 80%. See section 3.8 for experimental errors.

	1,2-benzenedicarboxylate		
	85 (Li^+)	**86 (Na^+)**	**87 (K^+)**
41	49	44	37
	1 : 1	1 : 1	1 : 1
42	27	22	23
	?	1 : 1	2 : 3
43	75	30	42
	1 : 1	**?**	**?**

Table 2.1

The smaller values of K_2 obtained for cation **42** indicated that the equilibrium 2 lies to the left and thus the interaction between cation and anion is weaker than that for cations **41** and **43**. The results obtained from titrations of **41** with **85**(Li^+), **86**(Na^+) and **87**(K^+) should be identical, if one assume that all of the 1,2-benzenedicarboxylate ions are not associated with the alkali metal ($K_1 \approx 0$). However, the results obtained show some differences but these differences are not sufficiently large to be significant. By comparing the results in the columns for **85**, **86** and

87, these show that they all have similar association constants and consequently suggested that the K_1 values for the dilithium, disodium and dipotassium 1,2-benzenedicarboxylates should be very similar. This is in the agreement with the literature association constants for these salts, which are 7.08 M^{-1} for dilithium 1,2-benzenedicarboxylate, 5.50 M^{-1} for disodium 1,2-benzenedicarboxylate and 6.92 M^{-1} for dipotassium 1,2-benzenedicarboxylate[127]. In most cases, the stoichiometries of these complexes were found to be 1:1 except for complex **42•87**. Due to the limitation of Job's method, only a stoichiometry of 1:1 is authenticated. If the stoichiometry obtained from Job's method is not 1:1, it means that the complex does not have a simple 1:1 stoichiometry but it does not provide the correct stoichiometry for a system that is more complex than 1:1.

The results of the NMR titration and Job's experiment using the same dicationic compounds and 1,3-benzenedicarboxylate and 1,4-benzenedicarboxylate are outlined in Tables 2.2.

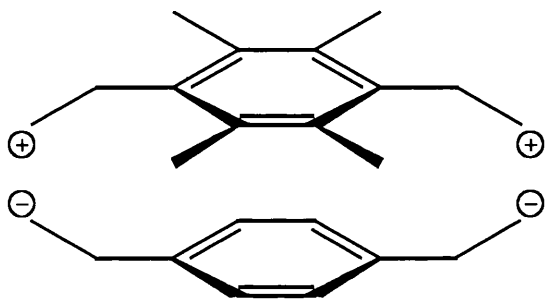
	1,3-benzenedicarboxylate				**1,4-benzene-dicarboxylate**
	88 (Li^+)	**89 (Na^+)**	**90 (K^+)**	**91 (Ca^{2+})**	**92 (Na^+)**
41	98	54	67	60	60
	1:1	1:1	1:1	1:1	1:1
42	89	91	66	75	78
	1:1	1:1	1:1	1:1	1:1
43	84	84	75	71	54
	1:1	1:1	1:1	1:1	1:1

Table 2.2

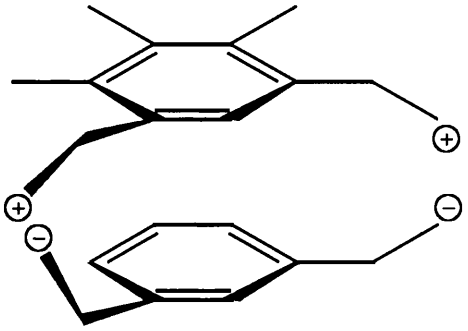
The results showed, as we had hoped, that all these complexes showed a 1:1 stoichiometry. The values of K_2 for these titrations are somewhat different but these differences are not sufficiently large to be significant, thus the K_1 values for these 1,3-benzenedicarboxylates are expected to be practically similar. However, in this case, no literature values were found to support these findings.

By comparing the results from Table 2.1 and 2.2, the smaller values of K_2 for dianion **86** suggested that 1,2-benzenedicarboxylate anion bind less strongly to the dicationic compounds **41**, **42** and **43** than 1,3- and 1,4-benzenedicarboxylate anions and this is in the agreement of the shape matching theory. The results for complexes **41•86**, **41•89** and **41•92** showed that

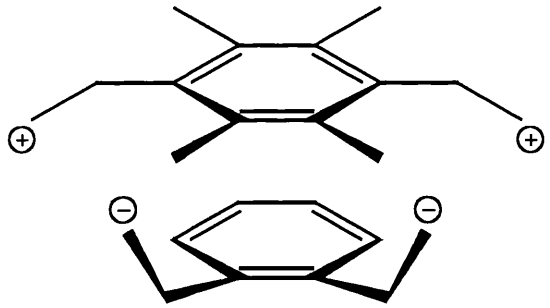
cation **41**, with positively charged arms at 1,4-position, binds with 1,4-dicarboxylate. However, the results for complexes **43•86**, **43•89** and **43•92** showed that cation **43**, with positively charged arms at 1,3-position, binds with 1,3-dicarboxylate. The low association constants obtained for 1,2-dicarboxylate indicated that the interaction between the dication and the 1,2-dicarboxylate is weak. This is possibly caused by the two negative charges at 1,2-position resulting in long distance interaction, thus weaker interaction. We believe that complexation occurs via a face-to-face orientation of the two species as illustrated in Figure 2.8.



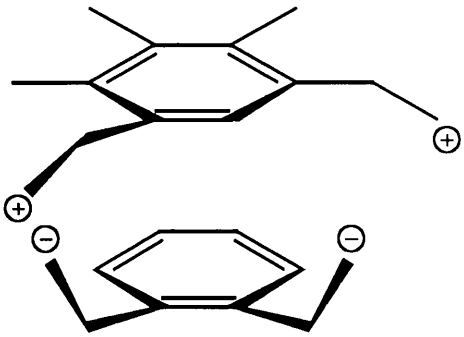
complexation **41·92**



complexation **43·89**



complexation **41·86**



complexation **43·86**

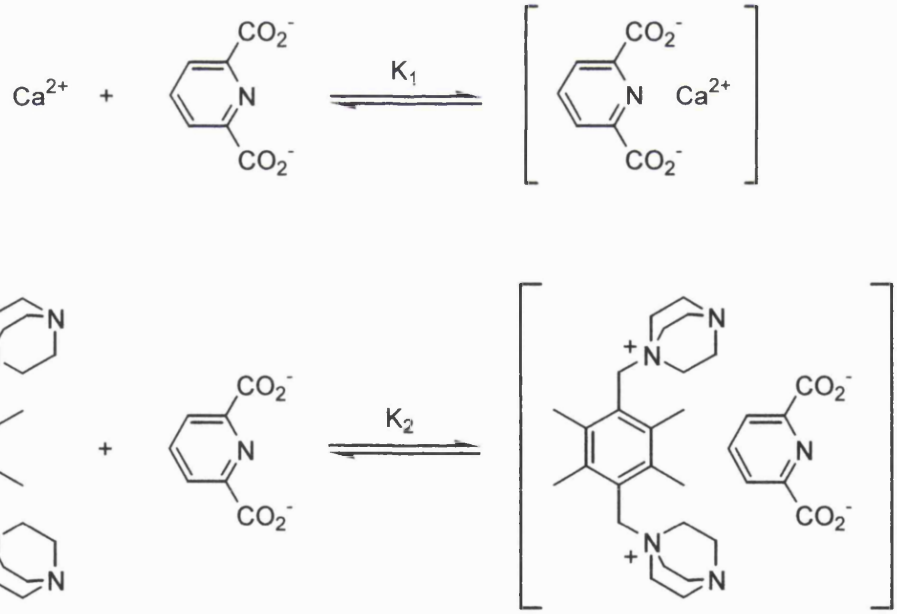
Figure 2.8 – possible modes of complexations

Dipicolinic acid was found to be an unique bacterial spore constituent the majority of which is associated in a chelated form with calcium[128]. In order to demonstrate the strength of binding between dipicolinic acid and calcium, NMR Titration and Job's experiment were also carried out for dipicolinates **93** and **94**, and the results using dication **41** are outlined in Table 2.3.

	dipicolinate	
	93 (Na^+)	94 (Ca^{2+})
41	46	15
	1:1	1:1

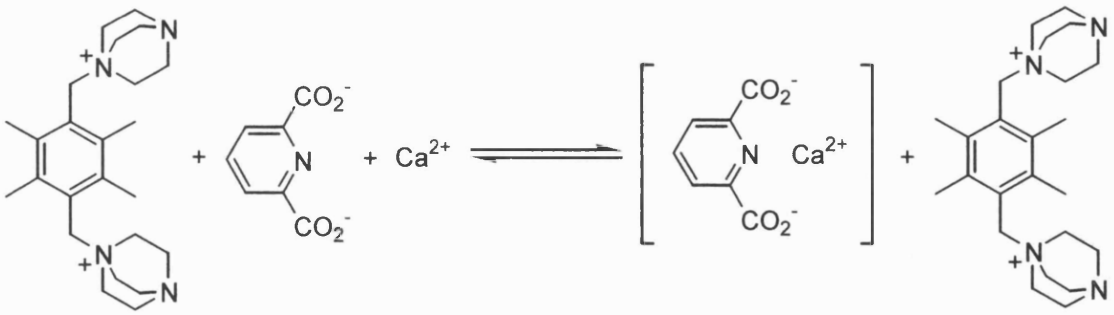
Table 2.3

The association constant K_2 for complex **41•93** was found very similar to that for complex **41•89**, and this suggested that **89** and **93** should have similar K_1 values. However, the K_2 value obtained for **41•94** was found much smaller than that for **41•91**. This consequently suggested that the K_1 value for **91** should be much smaller than that for **94**, and this is in the agreement with the literature values, that is 8.51 M^{-1} for **91** and 40738.00 M^{-1} for **94**[129]. The association constant K_2 determined for complex **41•94** is the smallest we observed and this can be attributed to the large association constant of calcium dipicolinate because the two equilibria compete against each other, as illustrated in Scheme 2.20.



Scheme 2.20

Since this association constant is much larger than that of the equilibrium between cation **41** and dipicolinate, it is more likely that dipicolinate form complex with calcium rather than complexing with dication **41**. Consequently, the concentration of free dipicolinate anion is greatly reduced as most of it is complexed to the calcium ions (Scheme 2.21), therefore the K_2 value obtained is believed to be incorrect.



$K_1 >> K_2$

Scheme 2.21

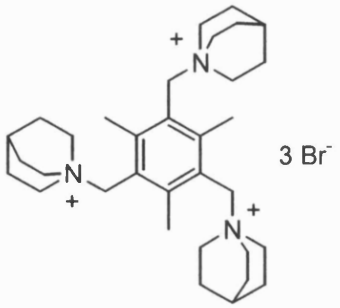
Dication **41** was also used for further NMR titration and Job's experiment using tri-anionic compound **95** and tetra-cationic compounds **96** and **97**. The results of these experiments are outlined in Table 2.4.

	tri-anion	tetra-anion	
	95 (Na^+)	**96 (Na^+)**	**97 (Na^+)**
41	115	224	151
	3:2	?	3:2

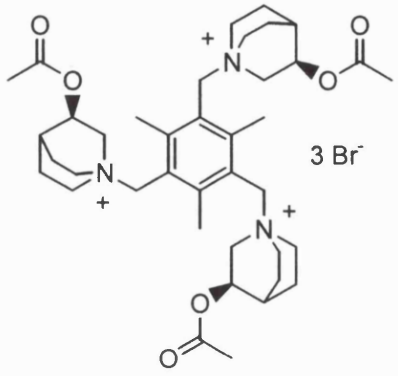
Table 2.4

By assuming K_1 to be small and equilibrium 1 lies to the left, complexes **41•96** has higher K_2 value indicating stronger interaction between dication **41** and benzene-based tetra-anion **96**. Since the naphthalene-based tetra-anion **97** is larger in size, compared to **96**, it cannot easily penetrate to the cavity created by the two DABCO arms of benzene-based dication **41** resulting in longer distance and weaker interaction, and consequently smaller K_2 value. However, benzene-based tetra-anion **96** is smaller, thus it can get closer to the cavity resulting in stronger interaction and larger value of K_2. The results obtained from Job's method suggested that all these three complexes do not have simple 1:1 stoichiometries.

2.7.2 Tricationic Compounds



45



46

In an attempt to demonstrate molecular recognition with the use of optically active cationic compound **46**, a structurally similar tricationic compound **45** was used to determine its association constants with racemic tripotassium isocitrate and disodium malate. The results are outlined in Table 2.5.

	DL-isocitrate	DL-malate
	98 (K^+)	**99 (Na^+)**
45	406	317
	?	?

Table 2.5

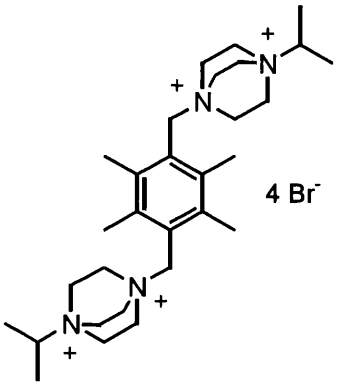
The association constant K_2 obtained are comparatively large, therefore it is believed that both isocitrate and malate bind strongly to trication **45**. In both cases, it was found that these complexes are more complex than a simple 1:1 system. Since the magnitudes of the association constants K_2 were found to be large, NMR titration and Job's experiment were carried out with optically active trication **46** and the anionic species were disodium D-malate **100** and disodium L-malate **101**. The results of these experiments are outlined in Table 2.6.

	D-malate	L-malate
	100 (Na^+)	**101 (Na^+)**
46	51	60
	?	?

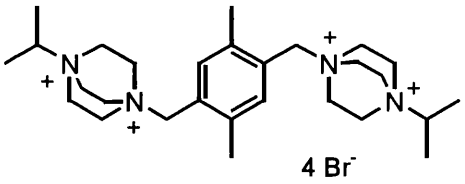
Table 2.6

With hydrogen bonding involved in these complexations as well as electrostatic interaction, we initially expected that these bindings would have larger association constants than the complexation between **45** and **99**. However, the attempt to demonstrate molecular recognition using optically active species was found to be unsuccessful, since the association constants found were small compared to complexes **45•98** and **45•99**, and complexes **46•100** and **46•101** have similar association constants which suggested that optically active trication **46** does not discriminate between them.

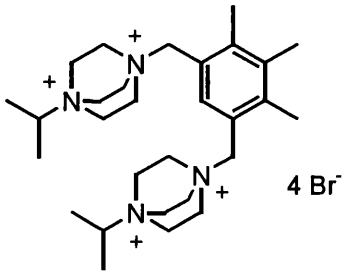
2.7.3 Tetracationic Compounds



52



53



54

NMR titration and Job's experiment were carried with these N-isopropyl DBACO based tetra-cationic compounds and tetra-anionic species **96** and **97** and the results are outlined in Table 2.7.

	Tetra-anion	
	96 (Na^+)	**97 (Na^+)**
52	?	?
	1:1	1:1
53	?	?
	1:1	1:1
54	?	?
	?	1:1

Table 2.7

It was found that it is impossible to determine the association constants for these complexes, this may be caused by an unusual phenomenon occurred during these experiments. The plot of the NMR titration shows that after rising to a maximum value, the magnitude of $\Delta\delta$ decreases with an increasing ratio of host:guest. The biggest decline in the magnitude of $\Delta\delta$ was observed with complex **52•96** which is shown in Figure 2.8.

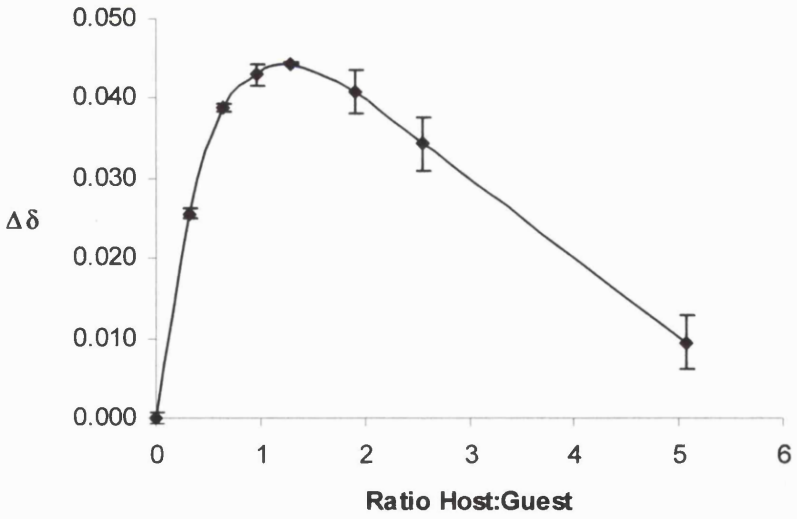


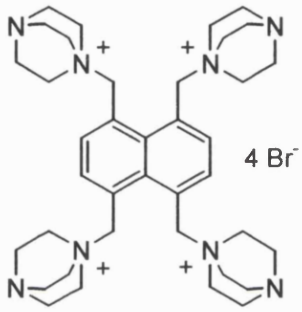
Figure 2.8 – NMR titration for complex 52•96

Dr Ashley Ibbett[130] attempted to investigate whether an excess of bromide ions had an effect on the chemical shift of the trisodium 1,3,5-benzenetricarboxylate **95**. An experiment was performed in which the chemical shift of a solution of tricarboxylate **95** in deuterium oxide was monitored in varying concentrations of sodium bromide. The results of this experiment showed that as the concentration of bromide anions increases, the chemical shift of the trianion moves downfield. Using corrected chemical shifts for the trianion, it was found that the decline in the

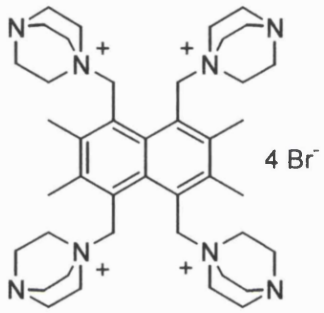
magnitude of $\Delta\delta$ was still present, but was somewhat reduced. Even using these data, however, an association constant could not be determined.

With estimated values of δ_c, it is still possible to determine the stoichiometries of these complexes which were found to be 1:1, except for complex **54•96** where a non-satisfactory Job's plot was obtained.

The naphthalene based tetracationic compounds were also used in a series of NMR titration and Job's experiment. The results are outlined in Table 2.8.



55



56

	tri-anion	tetra-anion	
	95 (Na^+)	**96 (Na^+)**	**97 (Na^+)**
55	374	612	459
	2:3	1:1	1:1
56	272	393	136
	2:3	1:1	1:1

Table 2.8

The larger values of K_2 obtained for **96** indicates that equilibrium 2 lies to the right. This suggests that tetracation **55** and **56** interact better with tetra-anion **96** than **97**, this is probably because of the smaller size of **96** which can slot into the cavity created by the four DABCO arms, whereas **97**, naphthalene-based tetra-anion, is larger in size and it possibly interact with the cations from a long distance resulting in weaker interaction and smaller K_2 values. It was found that tetracations **55** and **56** interact with tetra-anions **96** and **97** in a 1:1 manner, complexes **55•95** and **56•95**, however, do not have simple 1:1 stoichiometries. The K_2 values obtained for **55** with **96** and **97** are larger than those for **56**, this may be due to the fact that it is less likely to have all the positively charged DABCO groups on the same side with **56** than it is with **55** (see the X-ray crystal structure in Figure 2.21).

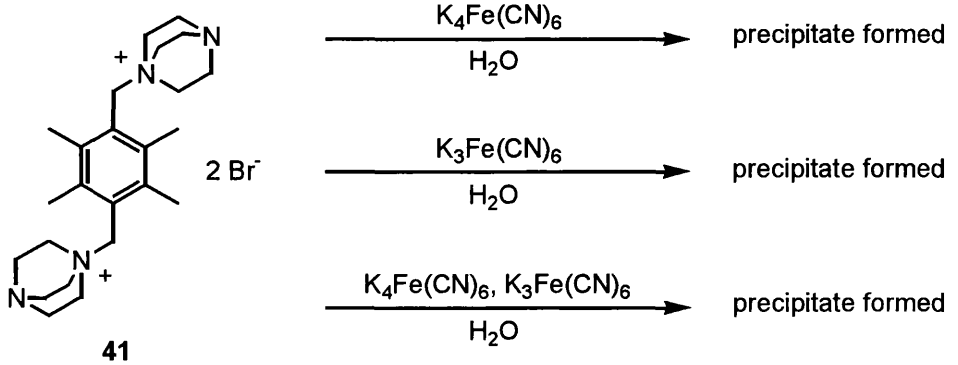
2.8 Selective Crystallisation – Simple Molecular Recognition Experiment

During the course of our research, a simple experiment was performed for most of the polycationic compounds synthesised to demonstrate their selectivities towards different anionic species. The ferrocyanide ($Fe(CN)_6^{4-}$) and ferricyanide ($Fe(CN)_6^{3-}$) ions were used which have the same shape but different charges.

Three similar experiments were carried out for each of the polycationic compounds and these are listed below.

(a) A half saturated solution of potassium ferrocyanide in water was added to a dilute solution of the polycationic compound (approximately 10 mg/mL), the precipitated solid was removed by filtration.
(b) A half saturated solution of potassium ferricyanide in water was added to a dilute solution of the polycationic compound (approximately 10 mg/mL), the precipitated solid was removed by filtration.
(c) An aqueous mixture was prepared by mixing same quantities of saturated solution potassium ferrocyanide and saturated solution of potassium ferricyanide. This mixture was then added to a dilute solution of the polycationic compound (approximately 10mg/mL), the precipitate solid was removed by filtration.

A schematic example of these experiments, using dicationic compound **41**, is shown in Scheme 2.22.



41

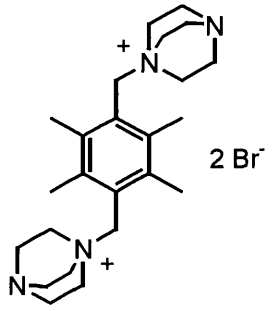
Scheme 2.22

In most cases, precipitates immediately appeared after the cyanide solutions were added to the solution of the cationic compounds. The resulting mixtures were then left at room temperature

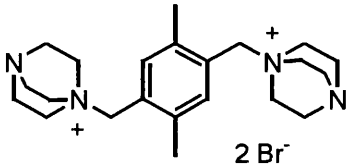
for 4-6 weeks after which time the precipitates were removed as powder-like solids. In some cases, crystals were obtained after prolonged standing.

Infra-red spectroscopy was used to determine the presence of ferrocyanide and ferricyanide anions which have absorption at approximately 2050 cm^{-1} and 2110 cm^{-1}, respectively.

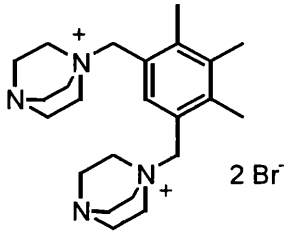
The results of these experiments are outlined in Tables 2.9 and 2.10, where an absorption value for the CN stretch indicates that precipitation occurred, and ✗ indicates no precipitate formed. The precipitates reported in this section are either powders or crystalline solids.



41



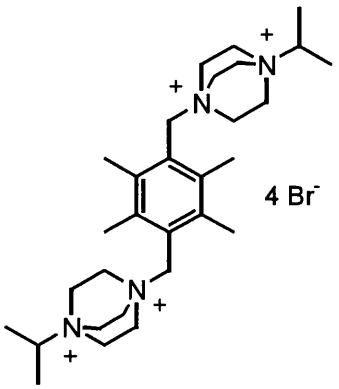
42



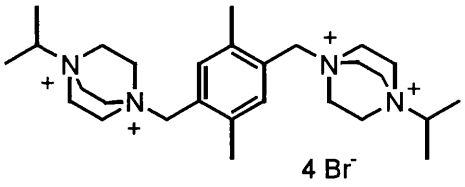
43

	dication		
	41	**42**	**43**
potassium ferrocyanide	2045 cm^{-1}	2053 cm^{-1}	✗
potassium ferricyanide	2108 cm^{-1}	✗	✗
mixture of ferro- and ferri-cyanide	2045 cm^{-1}, 2109 cm^{-1}	2056 cm^{-1}	✗

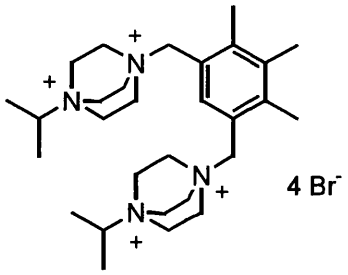
Table 2.9



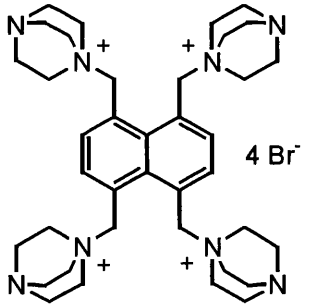
52



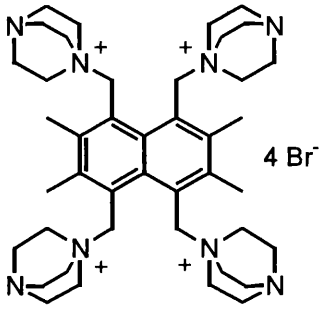
53



54



55



56

	tetracation				
	52	**53**	**54**	**55**	**56**
potassium ferrocyanide	2041 cm^{-1}	2054 cm^{-1}	✗	2047 cm^{-1}	✗
potassium ferricyanide	2108 cm^{-1}	crystals 2109 cm^{-1}	2109 cm^{-1}	crystals 2108 cm^{-1}	crystals 2109 cm^{-1}
mixture of ferro- and ferri-cyanide	2039 cm^{-1}, 2110 cm^{-1}	crystals 2111 cm^{-1}	2111 cm^{-1}	2048 cm^{-1}, 2110 cm^{-1}	2111 cm^{-1}

Table 2.10

There are two results of particular interest. First, dication **43** did not form a precipitate with either ferrocyanide or ferricyanide. Second, tetracation **53** forms a precipitate with the ferrocyanide solution and forms crystals with the ferricyanide solution, but only ferrocyanide crystals were formed when it was treated with the mixture. A possible explanation for the absence of a precipitate with **43** on either anion is that the DABCO arms in the 1,3-position make a smaller cavity than those with the dications **41** and **42**, and this cavity is too small to accommodate the ferrocyanide and ferricyanide anions and form a complex.

The results observed for tetracation **53** suggested that **53** binds much better with ferricyanide than ferrocyanide and that the association constant of the equilibrium between **53** and ferricyanide is much larger than the one between **53** and ferrocyanide (Scheme 2.23).

$$\mathbf{53} + Fe(CN)_6^{4-} \rightleftharpoons \mathbf{53}\cdot Fe(CN)_6^{4-} \qquad K_1$$

$$\mathbf{53} + Fe(CN)_6^{3-} \rightleftharpoons \mathbf{53}\cdot Fe(CN)_6^{3-} \qquad K_2$$

$$\mathbf{53} + Fe(CN)_6^{4-} + Fe(CN)_6^{3-} \rightleftharpoons \mathbf{53}\cdot Fe(CN)_6^{3-} + Fe(CN)_6^{4-} \qquad K_2 > K_1$$

Scheme 2.23

In both of these cases, however, that the process of nucleation does not occur effectively cannot be excluded.

X-ray crystallographic structural analysis was carried out for complexes **53•Fe(III)** and **56•Fe(III)** at –173 °C. The crystals of complex **55•Fe(III)**, however, were not of sufficiently high quality for such a study.

For complex **53•Fe(III)**, the molecular formula for the crystals was found to be $K(C_{28}H_{50}N_4)_2[Fe(CN)_6]_3.14H_2O$ which is comprised of two molecules of the cation **53**, three ferricyanide anions, one potassium ion and fourteen water molecules. The potassium ion was found to be disordered over two sites. One unit cell is shown in Figure 2.9 where the hydrogen atoms, water molecules and the potassium ion are omitted for clarity. Figure 2.10 shows the packing pattern of the crystals and the potassium ion is included.

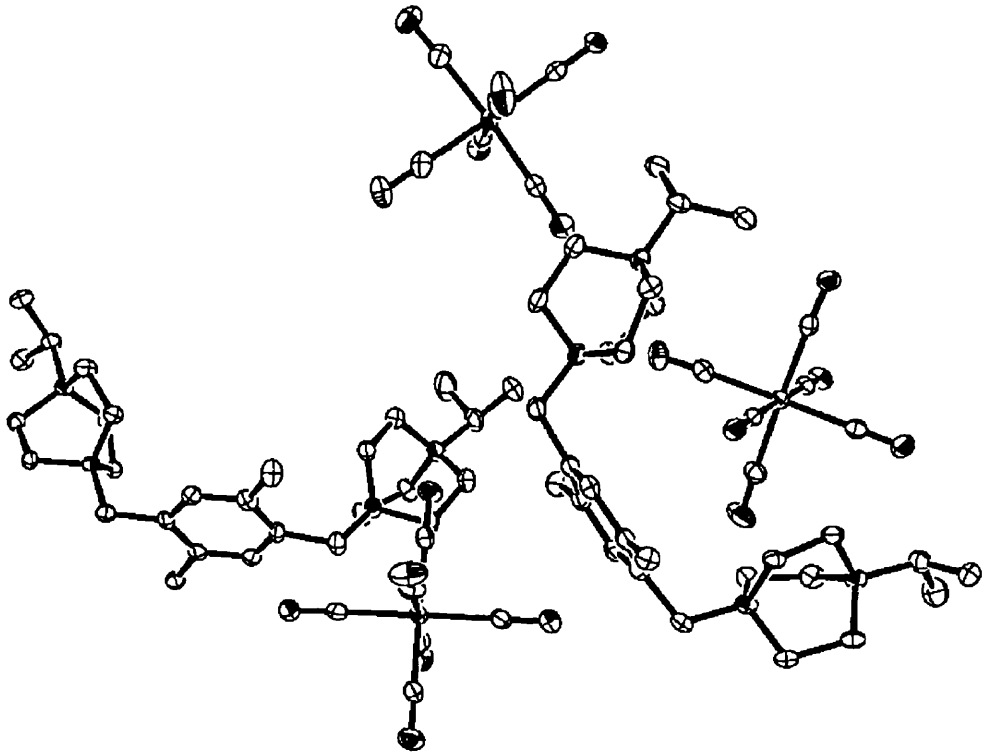


Figure 2.9 – A portion of the crystal structure of complex 53•Fe(III), $K(C_{28}H_{50}N_4)_2[Fe(CN)_6]_3.14H_2O$, showing 2 tetracation molecules and 3 ferricyanide ions.

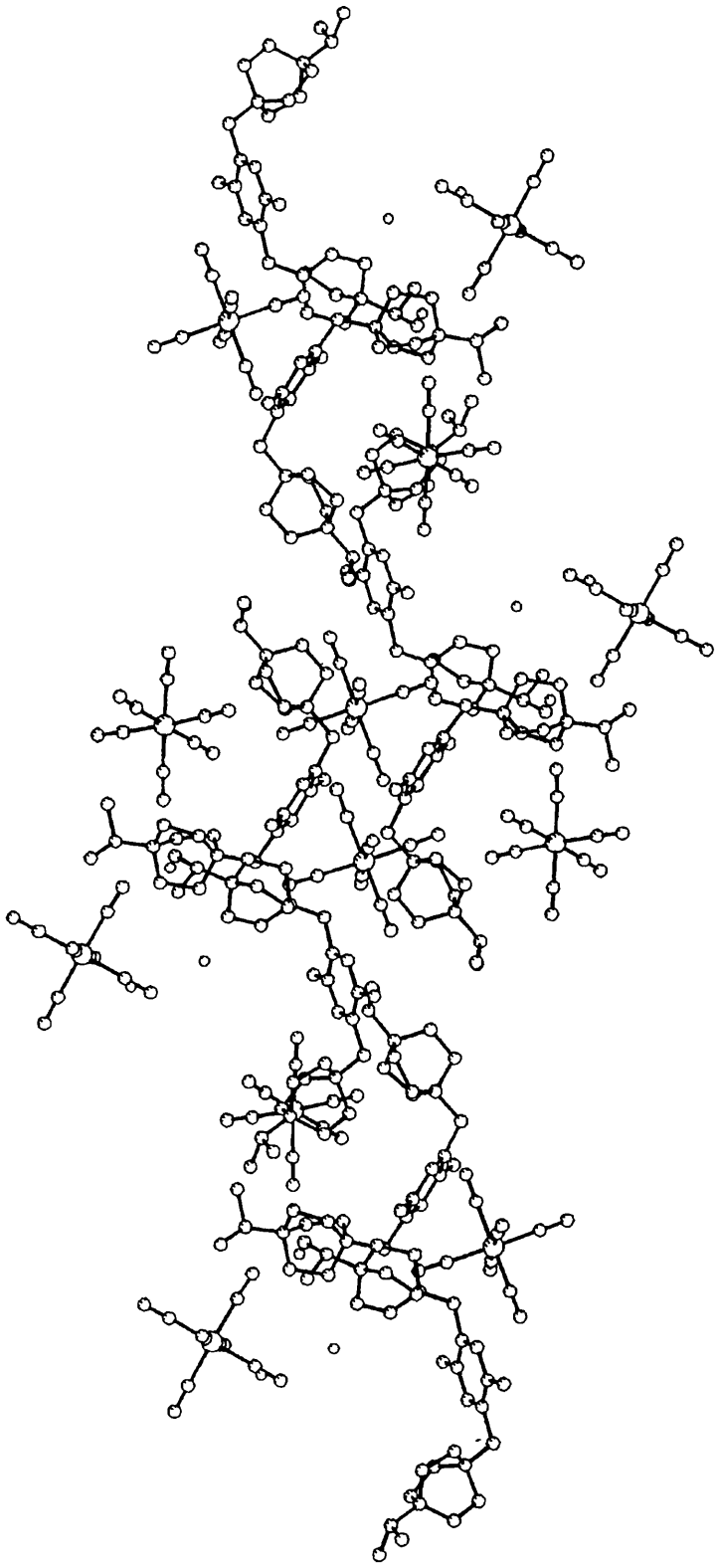


Figure 2.10 – Part of the crystal structure of complex 53•Fe(III), shows tetracation molecules, ferricyanide ions and potassium ions.

Figures 2.9 and 2.10 show the interaction of the dications in its all-cis conformation with the ferricyanide trianions. The crystal structure analysis also revealed that each asymmetric unit had 14 water molecules, which have been removed from the diagrams for clarity. It is probable that these water molecules are involved in some form of hydrogen bonding network which is possibly essential for the stabilisation of the crystal.

The empirical formula for complex **56•Fe(III)** was found to be $C_{51}H_{92}BrFe_3N_{17}O_{12}$ which is comprised of one molecule of the tetracation **56**, three halved ferricyanide ions, one bromide ion and twelve water molecules. The conformation of the DABCO arms was found to be alternate up and down (Figure 2.11). A diagram of the crystals is shown in Figure 2.12 which shows the positions of the ferricyanide, bromide and water molecules. It is believed that the isolated oxygen near one of the DABCO arms is oxonium ion (H_3O^+) having 1 positive charge; three halved ferricyanides carry 4.5 negative charges; one bromide, shared by two unit of cation **56**, carry 0.5 negative charge; and one cation **56** contains 4 positive charges. Figure 2.13 shows the crystal structure from a different angle.

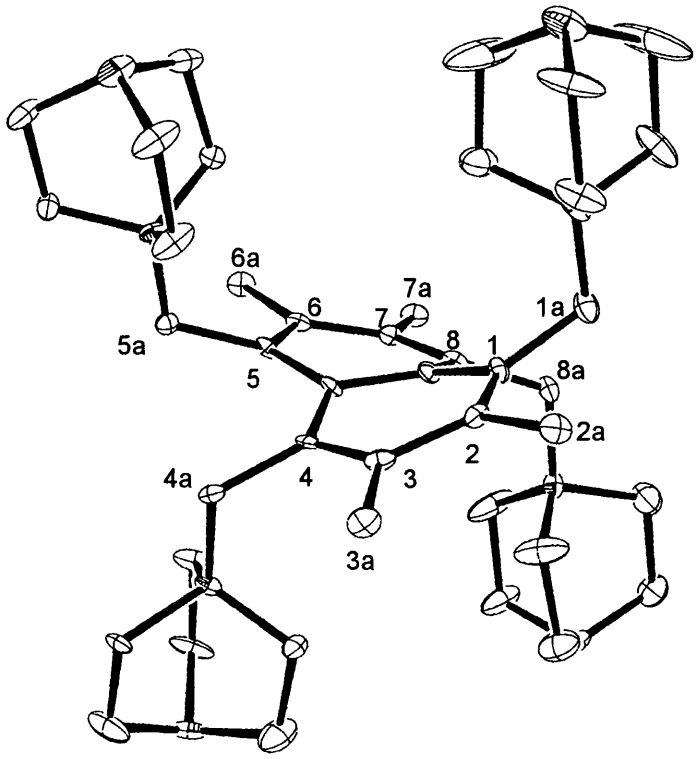


Figure 2.11 – Organic portion of crystal structure of complex 56•Fe(III)

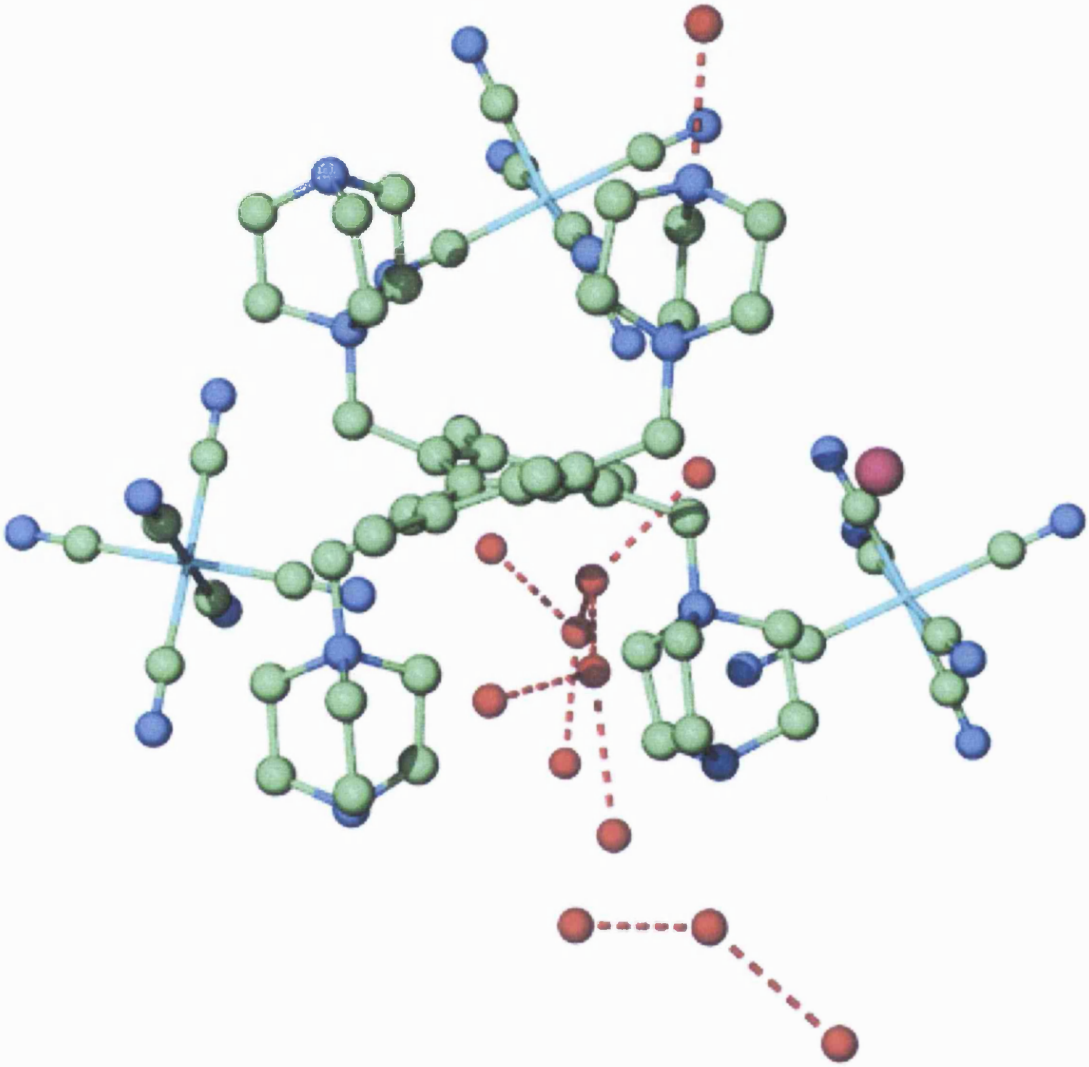


Figure 2.12 – Crystal structure of complex 56•Fe(III), $C_{51}H_{92}BrFe_3N_{17}O_{12}$, where carbon in GREEN, nitrogen in BLUE, bromide in PURPLE and oxygen in RED.

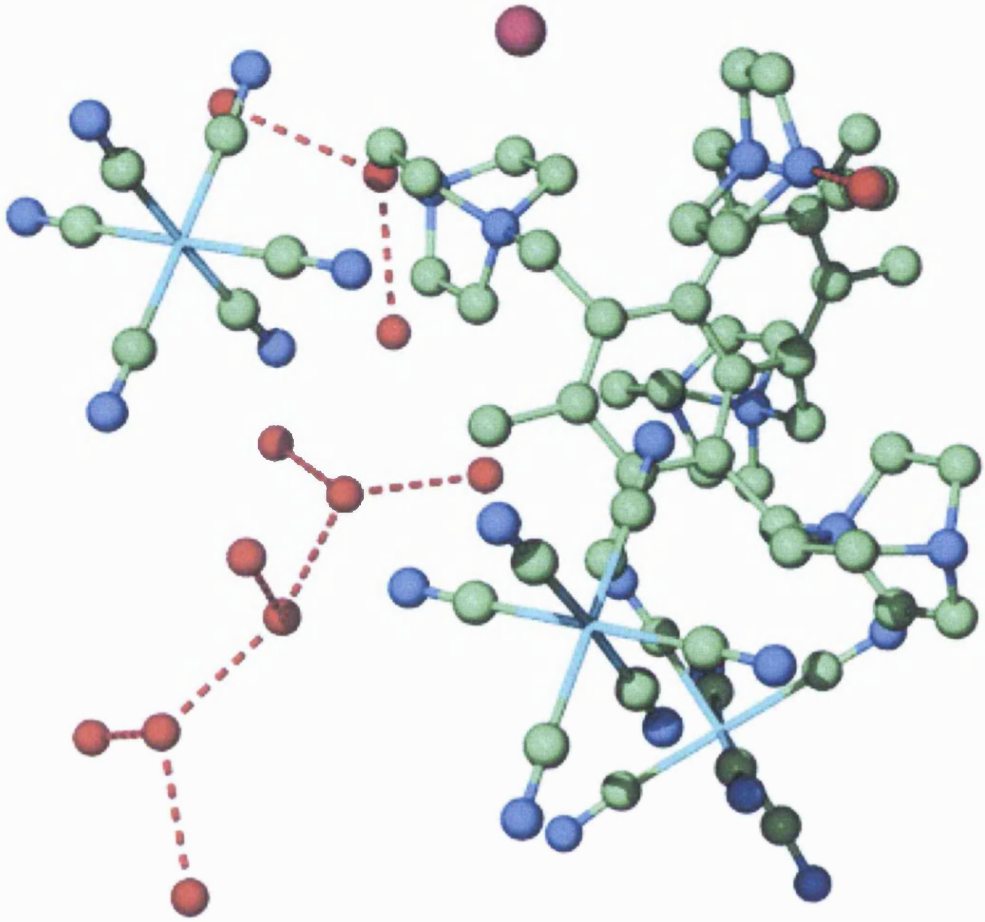
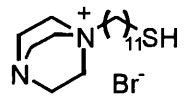


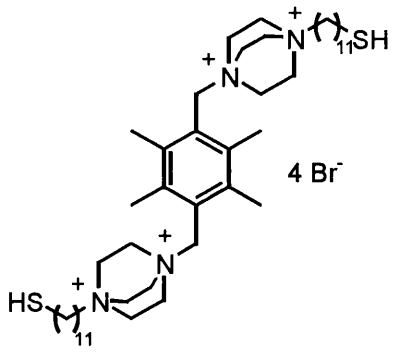
Figure 2.13 – Part of crystal structure of complex 56•Fe(III) from a different angle

Figure 2.11 shows distortion of the naphthalene rings which enables the positively charged DABCO arms to be as far away from each other as possible. Figures 2.12 and 2.13 show water-networks with the oxygen atoms in red spheres with dashed lines where hydrogen atoms have been removed from the diagrams for clarity. These water-networks are believed to be an important element for the stabilisation of the crystal as demonstrated by many previous publications[91-93].

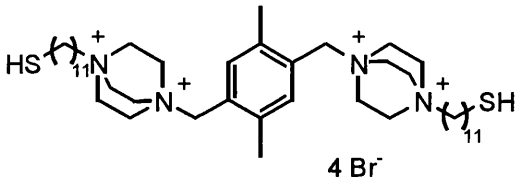
2.9 Electrochemistry



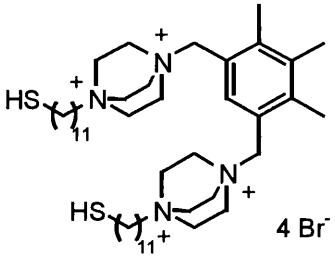
78



82

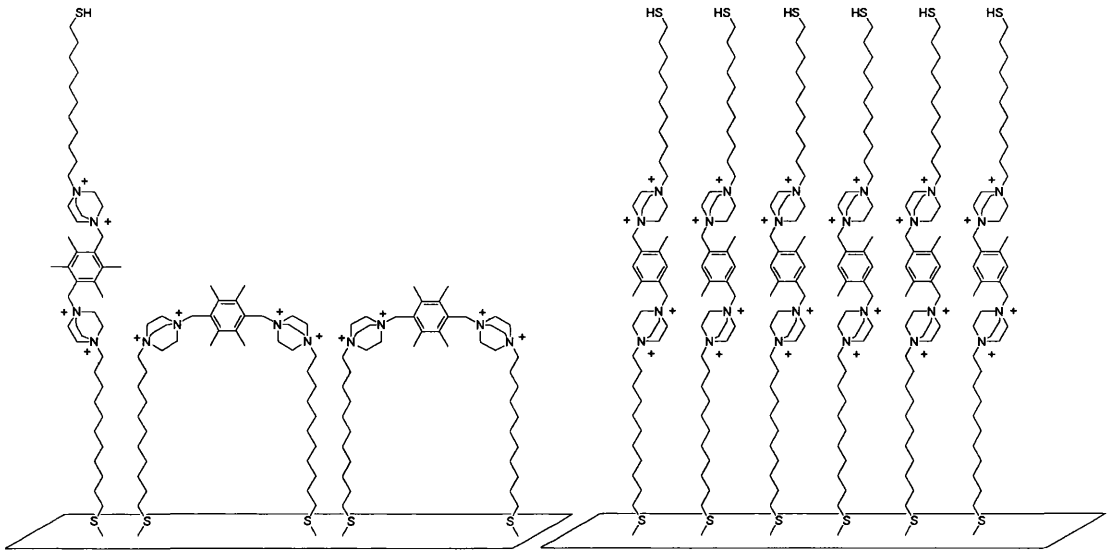


83



84

It has been shown by variable temperature NMR spectroscopy that polycations related to thiol **82** show restricted rotation around the positively charged side arms, and the related 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene shows a small preference for the syn over the anti conformer[130]. Thus, it is possible that thiol **82** forms a monolayer that contains molecules in which both of the thiol groups are attached to the gold surface, as shown in Figure 2.14a. Thiol **83** appears from the variable temperature NMR spectrum to have a lower barrier to rotation of the side arms and it thus seems likely that this molecule will mainly be bound to the gold surface by only one thiol group, as shown in Figure 2.14b, although binding of both thiols, as for **82**, remains a possibility. Thiol **84** also shows a low barrier to rotation in the variable temperature NMR spectrum and, from a comparison of the three structures, one might expect that the barrier is intermediate in magnitude between those of **82** and **83**.



(a) (b)

Figure 2.14 - Schematic drawings for possible modes of attachment of a) compound 82 and b) compound 83 to the gold surface.

2.9.1 Double-Layer Capacitance

Figure 2.15 shows the cyclic voltammograms obtained at the bare gold electrode and the electrode modified with thiol **83** in phosphate buffer under identical conditions. The behaviour of the charging current for the modified electrode is in marked contrast to that observed at electrodes covered by long-chain alkane thiols. SAMs of long alkane chains (9 or more methylene units) have a very low permeability for water and ions, resulting in a low total interfacial capacitance. The charging current for electrodes blocked by this type of SAMs is reduced by a factor of ca. 100 in comparison to the bare gold electrode[107]. The CVs shown in Figure 2.15 indicates that the SAM of **83** is either permeable to the electrolyte ions or/and the monolayers have a high dielectric constant. This is in agreement with the charging currents measured at gold electrodes modified with monolayers which contain polar or ionic groups such as -COOH, -OH, $-NH_2$ and NR_3^+ [131-133].

The CV of the bare gold electrode shows a gold oxidation and a reduction peak and these peaks are suppressed to some extent by all of the monolayers prepared from **78**, **82**, **83** and **84**, indicating inhibition of redox processes at the gold surface. Similar behaviour is reported for surfactants with $-CH_3$, $-CH_2OH$, -COOH as terminal groups and for fluorinated alkanes[111]. The slight enhancement in current at the anodic extreme of the scan made in phosphate buffer solution could be attributed to oxidation of bromide held within the layer.

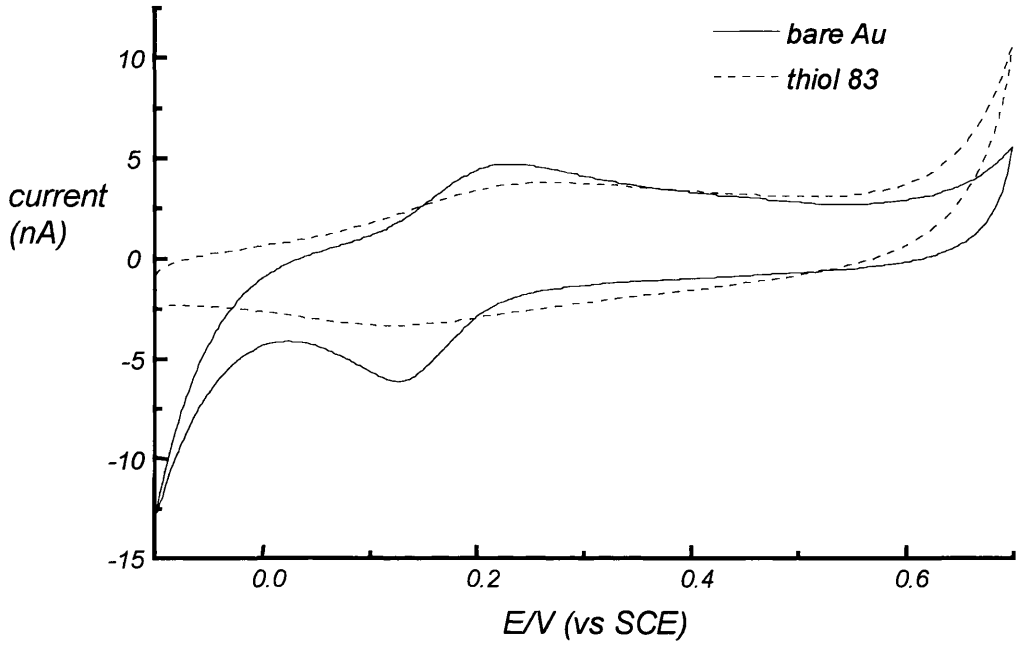


Figure 2.15 – Cyclic voltammograms of 50 mM KH_2PO_4 plus 29.1 mM NaOH aqueous solution (buffer solution) obtained with bare Au and Au|83 electrodes at pH 7.0. Scan rate 25 mV s^{-1}.

2.9.2 Oxidation of Ferrocyanide Ions

A cyclic voltammogram for the bare gold electrode is given in Figures 2.16, together with a calculated voltammogram for the bare gold electrode. The simulation was carried out by Dr. Jörg Strutwolf by solving the diffusion equation for the band electrode with the ADI finite difference method[134] and conformal mapping of the space variables[135]. Applying the same parameters as for the experiment (υ = 25 mV s^{-1}, concentration = 5 mM, electrode width and length are 11 μm and 5 mm respectively), and data taken from the literature (D = 0.65 x 10^{-9} m^2 s^{-1}, k^0 = 6.6 x 10^{-4} m s^{-1}, α = 0.49[136]) a fairly good agreement is achieved. This indicates the correctness of the geometry of the band. Simulations with the Nernst equation as boundary condition are not distinguishable from the one using the Butler-Volmer equation with the kinetic values given above. The redox reaction of $Fe(CN)_6^{4-}$ is, therefore, reversible in the time window of our experiments.

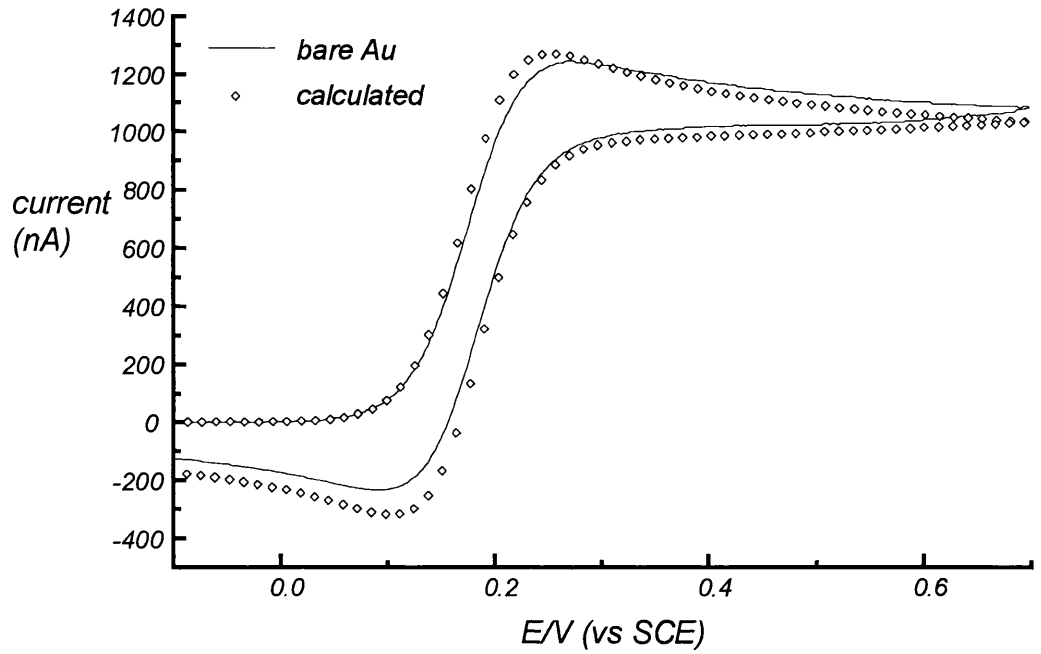


Figure 2.16 – Cyclic voltammogram of 5 mM $K_4Fe(CN)_6$ plus buffer solution obtained with bare Au electrode. Scan rate 25 mV s^{-1}. Calculated values ◊ for the bare Au electrode. The simulation was done by solving the diffusion equation for the band electrode with the ADI finite difference method[134] and conformal mapping of the space variables[135].

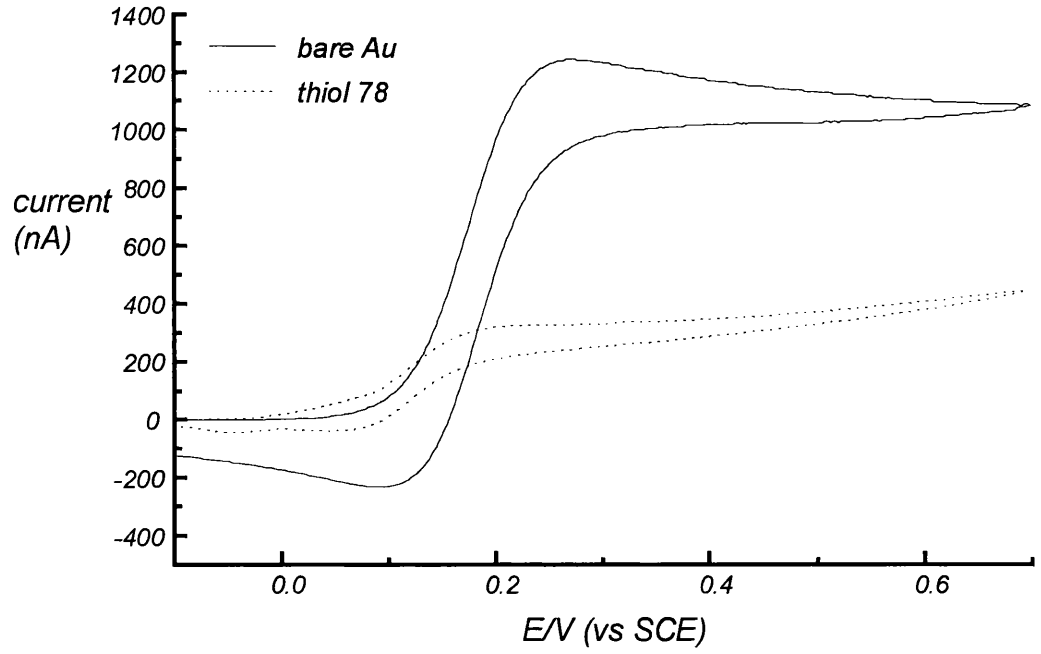


Figure 2.17 – Cyclic voltammograms of 5 mM $K_4Fe(CN)_6$ plus buffer solution obtained with bare Au and Au|78 electrodes. Scan rate 25 mV s^{-1}.

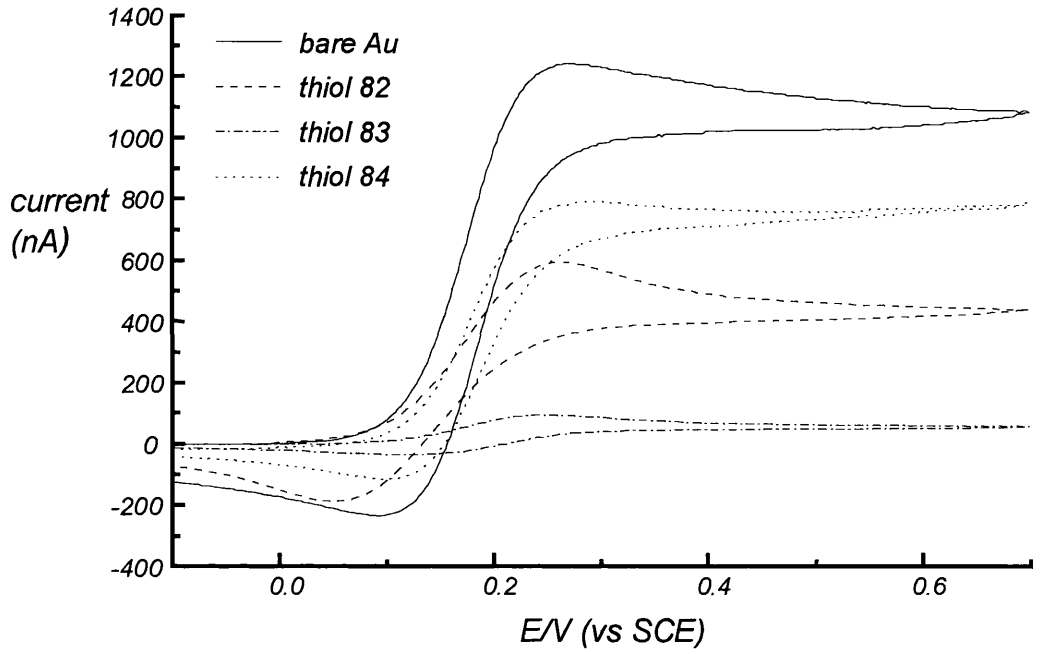


Figure 2.18 – Cyclic voltammograms of 5 mM $K_4Fe(CN)_6$ plus buffer solution obtained with bare Au, Au|82, Au|83 and Au|84 electrodes. Scan rate 25 mV s^{-1}.

Figures 2.17 and 2.18 show cyclic voltammograms for the Au|**78**, Au|**82**, Au|**83** and Au|**84** electrodes. All absorbed molecules are to some extent blocking the surface, as can be seen from the lowering of the currents. A complete blockage of the reaction, $Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^-$, is not, however, observed. The oxidation of ferrocyanide is most efficiently blocked by the thiol **83**. Since **82** and **83** are, in terms of the 1,4-connection to the benzene ring, very similar, this supports the idea that many more molecules of thiol **82** are bound by both thiol groups to the gold surface than are those of thiol **83**. In **83** the chains are presumably extended out from the surface in parallel arrays held apart by charge repulsion, and the extended long chains then form an efficient barrier to approach of the $Fe(CN)_6^{4-}$ ions to the electrode surface (Figure 2.19).

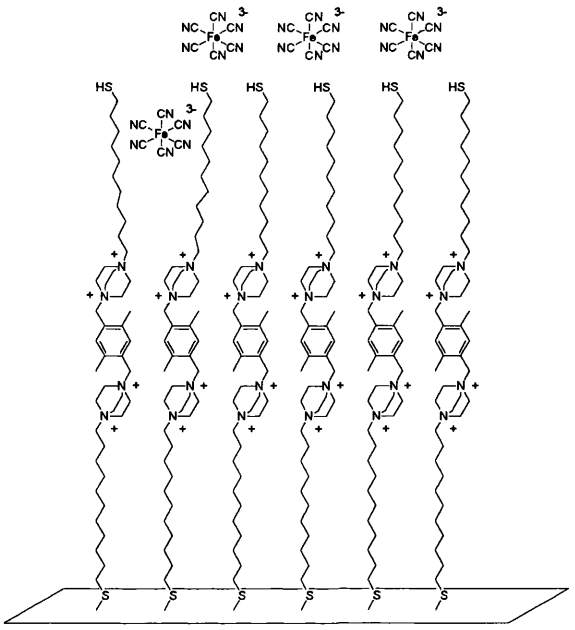


Figure 2.19 - Schematic drawings for possible modes of attachment of compound 83 blocking the oxidation of ferrocyanide. Potassium ions omitted for clarity.

The 1,3-attachment of the groups in **84** hinders the extension of the non-attached side chain and thus produces a less efficient layer for intercepting the ferrocyanide ions. Defect sites are more likely to occur in this case. As a consequence of the molecular geometry or the multiple nature of the binding (Figures 2.20 and 2.21), the currents for **82** and **84** are higher than that for **83**.

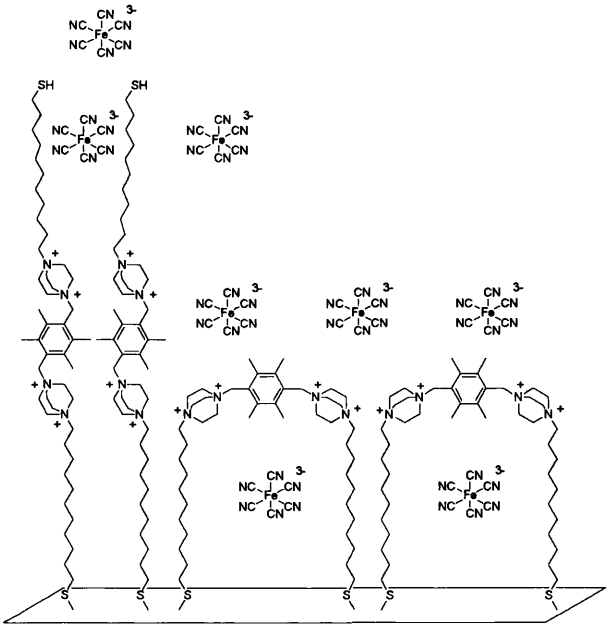


Figure 2.20 - Schematic drawings for possible modes of attachment of compound 82 blocking the oxidation of ferrocyanide. Potassium ions omitted for clarity.

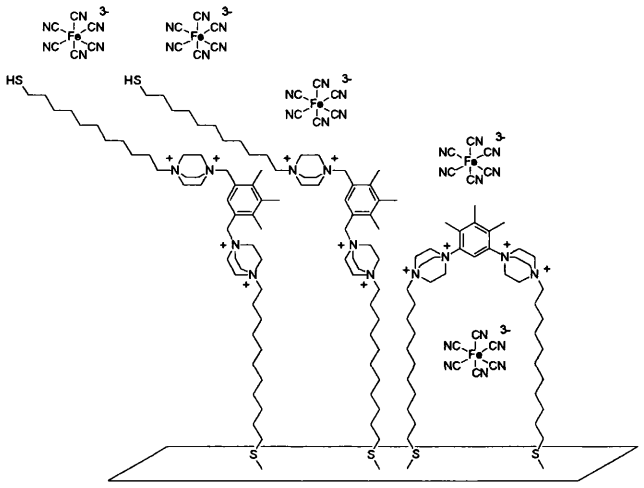


Figure 2.21 - Schematic drawings for possible modes of attachment of compound 84 blocking the oxidation of ferrocyanide. Potassium ions omitted for clarity.

A slight shift (≈ 6 mV) of the half peak potential in the negative direction relative to the half peak potential of the bare gold electrode is observed for all the species **82**, **83** and **84**. The half wave potential for **78**, the simple DABCO N-alkyl thiol, is shifted 60 mV in the negative direction. The direction of the shifts are in agreement with theoretical results of Smith and White[137] concerning interfacial potential distribution of electrodes coated with electroactive films and the effect on the reversible voltammetric response. According to their findings, a negative shift is observed for enhanced surface concentrations of electroactive redox centres and for a high dielectric constant of the electroactive film. In our systems the surface concentration of ferrocyanide can be enhanced by attraction to positively charged groups of the monolayer. Furthermore, charged layers have high dielectric constants and the presence of charged groups effects the potential distribution in the assembled monolayer. For thiol **78**, the positive charge would be on the outside of the SAM (Figure 2.22).

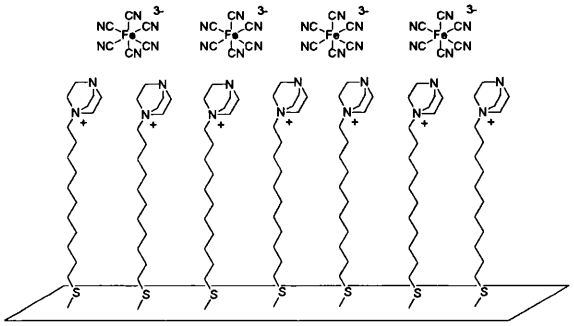


Figure 2.22 - Schematic drawings for possible modes of attachment of compound 78 blocking the oxidation of ferrocyanide. Potassium ions omitted for clarity.

For thiol **83**, which is assumed to be mainly bound to the gold surface by only one thiol group, the positive charges would be buried in the centre of the film as shown in Figure 2.19. For thiol

82 and **84**, the positive charges would be either buried or exposed, as shown in Figures 2.20 and 2.21, according to conformation adopted.

2.9.3 Oxidation of Bromide Ions

Whereas compound **78** is single positively charged, compounds **82**, **83** and **84** posses four positive charges when attached to the gold electrode in buffer solution. A charged layer will affect the distribution of ions in the vicinity of the electrode. The positively charged monolayer will attract anions and ion pairs are possibly formed. To investigate this effect and for comparison with $Fe(CN)_6^{4-}$, we added 5 mM NaBr to the buffer solution. Figure 2.23 shows CVs recorded in the buffer/NaBr electrolyte.

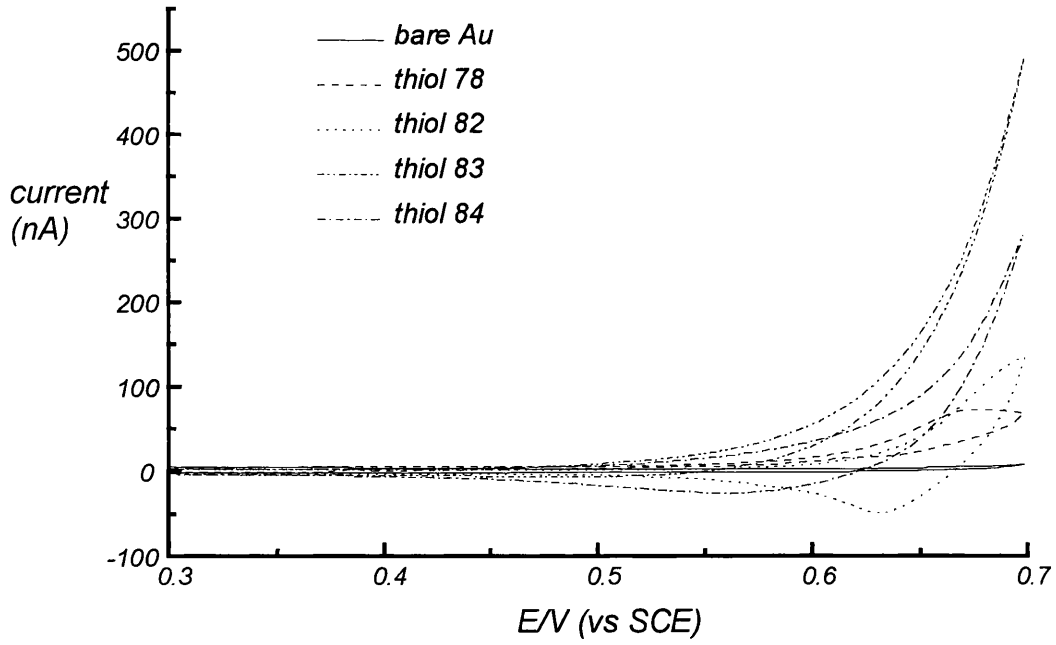


Figure 2.23 – Cyclic voltammograms of 5 mM NaBr plus buffer solution obtained with bare Au, Au|78, Au|82, Au|83 and Au|84 electrodes. Scan rate 25 mV s^{-1}.

For the modified electrodes, that is the voltammograms for **82**, **83** and **84**, a sharp rise of the current at the positive potential limit is observed which can be attributed to the enhanced oxidation of bromide. For the Au|**78** electrode, the enhancement is lower than that for the other modified electrodes. This can be attributed to the difference in charge per molecule absorbed for **78** compared to the tetracations. If simple ion pairing is, however, responsible for the higher surface concentration of bromide, the oxidation current for **82**, **83** and **84** should be the same and four times greater than that for **78**. This is clearly not the case and presumably arises from

the difference in structure of **82**, **83** and **84.** The packing of these monolayers would be expected to be different and it is, therefore, likely that the charged surface presented to the anions will be different in each case.

Since these thiols carry positively charged units, repulsion is to be expected between the molecules already bound and new molecules arriving at the gold electrode and it is thus likely to be less completely covered than it would be with an uncharged alkanethiol. One can envisage the bromide molecules fitting into the interstitial spaces between the charged molecules and therefore being available for oxidation. This process may occur as the molecules are laid down as charge neutrality is presumably retained and the cation being attached to the gold electrode is accompanied by counter ions. Since thiol **78** is mono-charged the repulsions between molecules, particularly with their associated counter ions, is likely to be low with the surface thus being well covered and the interstitial spaces between molecules small, so that the surface is not readily accessible to the bromide ions (Figure 2.24).

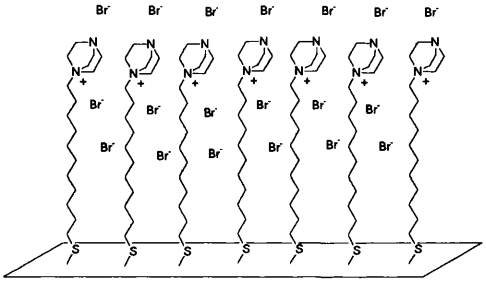


Figure 2.24 - Schematic drawings for possible modes of attachment of compound 78 showing the penetration of bromide ions into the monolayer. Sodium ions omitted for clarity.

With the tetra-cations the repulsions would be expected to be greater and the gold surface less covered and these surfaces should afford greater accessibility for the bromide ions to approach the surface and be oxidised. Of the three tetra-cations, the electrode with compound **82** shows the smallest increase in oxidising power. This can be attributed to a greater number of these molecules being attached by both thiol groups to the gold surface (Figure 2.25) than those of compounds **83** or **84**.

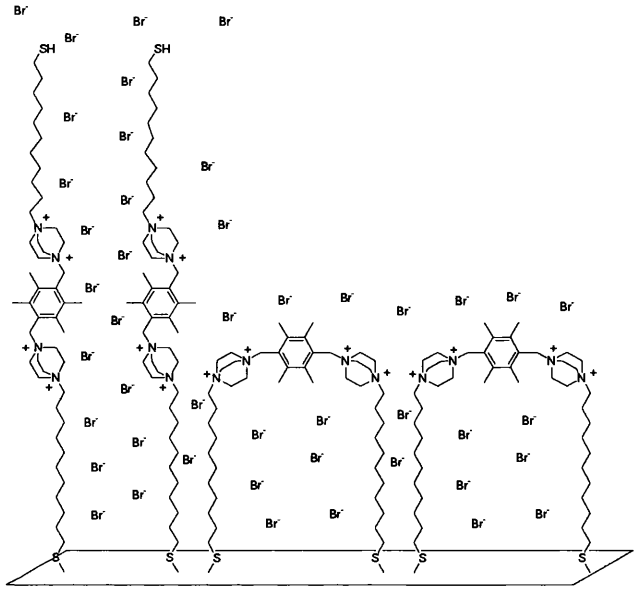


Figure 2.25 - Schematic drawings for possible modes of attachment of compound 82 showing the penetration of bromide ions into the monolayer. Sodium ions omitted for clarity.

Double attachment would provide an alkane-like environment at the gold surface with the cation layer held away and the bromide ions thus retained away from the gold surface. For thiols **83** and **84** double attachment appears less likely and the intermolecular repulsion between the tetra-cations leads to larger spacing between molecules and easier access to the gold surface (Figure 2.26). In all cases, however, the positive charge attracts bromide ions to the vicinity of the gold, leading to the observed increase in oxidation.

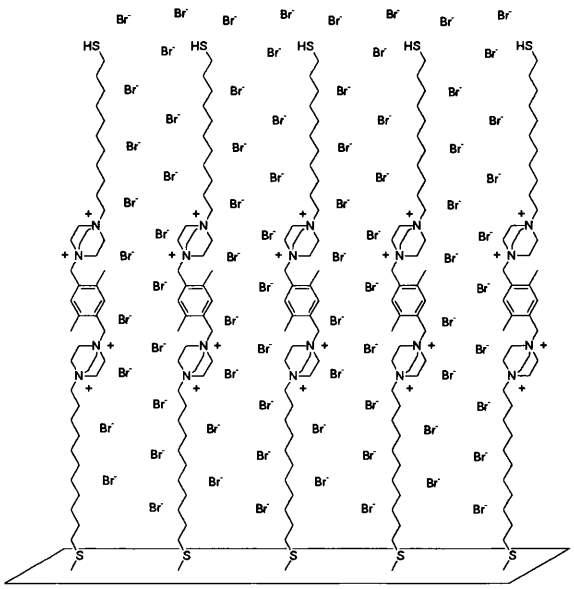


Figure 2.26 - Schematic drawings for possible modes of attachment of compound 83 showing the penetration of bromide ions into the monolayer. Sodium ions omitted for clarity.

As may be seen from the results displayed in Figure 2.23, the oxidation of bromide is enhanced more by forming a monolayer of the thiol **83** than it is by forming monolayers with thiols **78**, **82** or **84**. On the other hand, the oxidation of $Fe(CN)_6^{4-}$ is inhibited more by the formation of the monolayer with **83** than it is with monolayers of the other cations. This difference in behaviour of the anion and the polyanion we attribute to the different sizes of the solvated anions, with the larger ferrocyanide ion unable to penetrate efficiently into the monolayers. The lower blocking effect of thiol **82** to the oxidation of ferrocyanide may arise from such ions being trapped in the "hoop" formed by the double attachment of some of the molecules and thus being presented to the electrode surface.

3 Experimental

3.1 Synthesis

Melting points were determined on a Reichert melting point apparatus and are uncorrected. Unless otherwise stated, infra-red (I.R.) spectra were recorded on a Perkin-Elmer 1605 FT-IR spectrophotometer using potassium bromide pellets; absorptions are recorded in terms of frequency (ν_{max} in cm^{-1}). Optical rotations were measured on an Optical Activity Ltd Polar 2000 automatic polarimeter. Mass spectra were recorded either on a VG-ZAB SE fast atom bombardment (FAB) mass spectrometer with Finnigan Incos II data system at University College London or on the same machine at School of Pharmacy, London. Peaks corresponding to parent ions are reported, together with three or more biggest peaks. For the cationic compounds, parent ion peaks were not observed, thus only the peaks corresponding to the loss of bromine ions are reported, except when peaks were too small to identify.

^{1}H NMR spectra were recorded at 400 MHz and 300 MHz on a Varian VXR-400 and a Bruker AC300 instrument, respectively. ^{13}C NMR spectra were recorded at 100 MHz and 75 MHz on the same machines, respectively. Residual protic solvent was used 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 insertion of the sample to be examined. Spectra were recorded in the solvent specified, with chemical shifts expressed in parts per million (δ) relative to the internal standard, and coupling constants J measured in Hertz (Hz).

X-ray Crystallography was carried out by Dr Jonathan Steed at King's College, London. Crystals were mounted on a thin glass fibre using a fast setting epoxy resin and cooled on the diffractometer to the temperature stated using an Oxford Cryostream low temperature attachment. Measurement was recorded using a Nonius KappaCCD diffractometer with a detector to crystal distance of 25 - 35 mm.

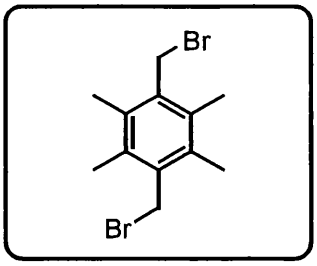
Elemental analyses were carried out by the microanalytical section of the Chemistry Department, University College London. Since bromide reading is recorded separately from carbon, hydrogen and nitrogen, it is difficult to observe accurate bromide readings for the hygroscopic cationic compounds, thus only carbon, hydrogen and nitrogen readings are reported here.

Chemical reagents were purchased from Aldrich Chemical Co., Lancaster Synthesis, ACROS and BDH. Tetrahydrofuran was distilled over sodium and benzophenone 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 (tlc) was performed on pre-coated aluminium backed plates (Merck Kieselgel 60 F_{254}) and visualised using ultraviolet light (254 nm), iodine or potassium permanganate solution as appropriate.

3.2 Starting Materials for Synthesising Cationic Compounds

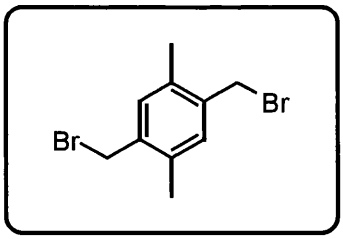
3.2.1 3,6-Bis(bromomethyl)-1,2,4,5-tetramethylbenzene (38)[117]



A solution of hydrogen bromide in acetic acid (49% w/v, 50 mL) was added rapidly to a mixture of durene (15.04 g, 110.0 mmol), paraformaldehyde (13.60 g, 450.0 mmol) and glacial acetic acid (120 mL). The mixture was stirred for 5 h at 110 °C and then poured into water (1000 mL). The precipitate formed was removed by filtration and washed exhaustively with water. The crude solid was then dissolved in acetone and a white precipitate was formed upon addition of water. The solid was removed by filtration and dried under vacuum. Recrystallisation from ethyl acetate gave **38** as white crystals (24.31 g, 70.0 mmol, 68 %).

Mp	217-219 °C, lit.[117] 212 °C
^{1}H 400 MHz NMR ($CDCl_3$)	4.58 (s, 4H, CH_2Br), 2.31 (s, 12H, $ArCH_3$)
^{13}C 100 MHz NMR ($CDCl_3$)	134.6, 134.1, 31.0, 15.9
IR (cm^{-1})	1437, 1388, 1258, 1193
MS (m/z %)	322 (33) (M^+), 242 (100), 161 (100), 77 (24)

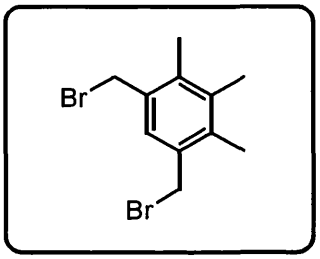
3.2.2 2,5-Bis(bromomethyl)-1,4-dimethylbenzene (39)[117]



A solution of hydrogen bromide in acetic acid (49% w/v, 60 mL) was rapidly added to a solution of paraformaldehyde (6.00 g, 200.0 mmol) and 1,4-xylene (6 mL, 5.20 g, 49.0 mmol) in glacial acetic acid (250 mL). The mixture was stirred at 100 °C for 6 h and then poured into water (500 mL). The precipitate formed was removed by filtration and washed exhaustively with water. The crude solid was then dissolved in acetone and re-precipitated by addition of water. The solid was removed by filtration and recrystallised from petroleum spirit 60-80 °C to give **39** as a yellow solid (6.60 g, 22.6 mmol, 46 %).

Mp	145-148 °C, lit.[117] 160 °C
^{1}H 400 MHz NMR ($CDCl_3$)	7.11 (s, 2H, Ar**H**), 4.44 (s, 4H, CH_2Br), 2.34 (s, 6H, $ArCH_3$)
^{13}C 100 MHz NMR ($CDCl_3$)	136.3, 135.2, 132.4, 31.7, 18.2
IR (cm^{-1})	1504, 1447, 1398, 1207
MS (m/z %)	291 (14) (M^+), 211 (92), 132 (100), 77 (7)

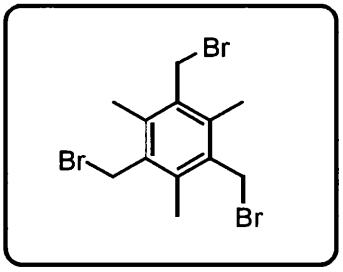
3.2.3 4,6-Bis(bromomethyl)-1,2,3-trimethylbenzene (40)



A solution of hydrogen bromide in acetic acid (49% w/v, 11.5 mL) was added in one portion to a solution of paraformaldehyde (3.00 g, 100.0 mmol) and hemellitol (5 mL, 4.47 g, 40.0 mmol) in glacial acetic acid (250 mL). The resulting mixture was stirred at 100-110 °C for 6 h and was then poured into water. A brown precipitate formed which was removed by filtration and washed exhaustively with water. The solid was then dissolved in acetone and re-precipitated by the addition of water. The mixture was then stirred for 2 h, and the solid was removed by filtration and dried under vacuum to give **40** as a white solid (4.38 g, 14.3 mmol, 36%).

Mp	147-149 °C, lit.[138] 153-154 °C
^{1}H 400 MHz NMR ($CDCl_3$)	7.15 (s, 1H, Ar**H**), 4.51 (s, 4H, CH_2Br), 2.32 (s, 6H, $ArCH_3$ [1,3]), 2.23 (s, 3H, $ArCH_3$ [2])
^{13}C 100 MHz NMR ($CDCl_3$)	136.3, 135.2, 132.4, 31.7, 18.2
IR (cm^{-1})	1437, 1384, 1292, 1239
MS (m/z %)	306 (100) (M^+), 226 (39), 145 (36), 77 (16)

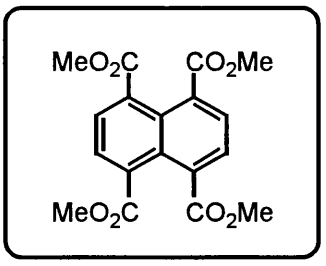
3.2.4 2,4,6-Tris(bromomethyl)-1,3,5-trimethylbenzene (47)[117]



A solution of hydrogen bromide in acetic acid (49% w/v, 17.5 mL) was added in one portion to a solution of paraformaldehyde (2.51 g, 83.6 mmol) and mesitylene (3.00 g, 25.0 mmol) in glacial acetic acid (50 mL). The resulting mixture was stirred at 100 °C for 6 h and was then poured into water (300 mL). A white precipitate formed which was removed by filtration and washed exhaustively with water. The solid was then dissolved in acetone and re-precipitated by the addition of water. Recrystallisation from chloroform/petroleum spirit 60-80 °C gave **47** as a white solid (5.78 g, 14.5 mmol, 58%).

Mp	178-180 °C, lit.[117] 186 °C
^{1}H 400 MHz NMR ($CDCl_3$)	4.58 (s, 6H, CH_2Br), 2.17 (s, 9H, $ArCH_3$)
^{13}C 100 MHz NMR ($CDCl_3$)	137.9, 133.3, 29.9, 15.4
IR (cm^{-1})	2916, 1564, 1445, 1378, 1192
MS (m/z %)	398 (6) (M^+), 319 (100), 237 (15), 77 (22)

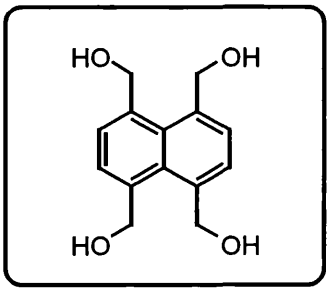
3.2.5 Tetramethyl 1,4,5,8-naphthalene-tetracarboxylate (62)[120]



To a stirred solution of sodium carbonate (38.67 g, 364.8 mmol) in water (500 mL) at 40 °C was added, portionwise, 1,4,5,8-naphthalene-tetracarboxylic acid (37.00 g, 121.6 mmol) followed by dimethyl sulfate (46 mL, 61.33 g, 486.3 mmol). The resulting mixture was stirred at 40 °C for 1 hour. Sodium carbonate (38.67 g, 364.8 mmol) and dimethyl sulfate (70 mL, 93.33 g, 740.0 mmol) were added successively and stirring was continued for 1 hour. The precipitated solid was removed by filtration and washed with water. Recrystallisation from dioxane gave **62** as a white solid (22.67 g, 62.9 mmol, 52%).

Mp	195-197 °C, lit.[120] 198-199 °C
^{1}H 400 MHz NMR ($CDCl_3$)	8.06 (s, 4H, Ar**H**), 3.93 (s, 12H, CO_2CH_3)
^{13}C 100 MHz NMR ($CDCl_3$)	168.3, 133.3, 129.3, 128.9, 52.5
IR (cm^{-1})	3003, 2951, 2852,1919, 1730
MS (m/z %)	360 (26) (M^+), 329 (59), 301 (100), 255 (40)

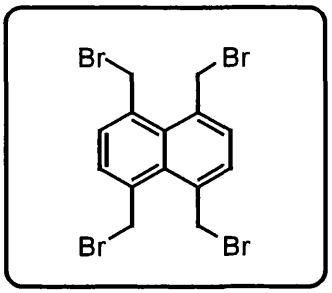
3.2.6 1,4,5,8-Tetrakis(hydroxymethyl)naphthalene (63)[120]



To a solution of diisobutylaluminum hydride (1.0 M solution in hexane) (365 mL, 365.0 mmol) under nitrogen, tetramethyl 1,4,5,8-naphthalene-tetracarboxylate **62** (9.00 g, 25.0 mmol) was added in portions, keeping the temperature below 30 °C. The resulting clear solution was stirred at room temperature for 30 hours. Methanol (120 mL) was added cautiously, followed by hydrochloric acid (6 M, 275 mL). The precipitated solid was removed by filtration and recrystallised from dimethyl sulfoxide/chloroform to give **63** as a white solid (3.30 g, 13.3 mmol, 53%).

Mp	237-240 °C, lit.[120] 231-233 °C
^{1}H 300 MHz NMR (d_6-DMSO)	7.58 (s, 4H, Ar**H**), 5.25 (br s, 4H, O**H**), 5.07 (s, 8H, CH_2OH)
^{13}C 75 MHz NMR (d_6-DMSO)	138.6, 132.1, 127.2, 64.2
IR (cm^{-1})	3449, 2958, 2897, 1749, 1724
MS (m/z %)	230 (8) (M^+), 212 (100), 154 (38)

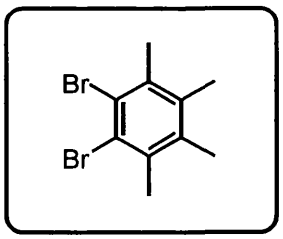
3.2.7 1,4,5,8-Tetrakis(bromomethyl)naphthalene (60)[120]



Phosphorus tribromide (5.2 mL, 14.82 g, 54.7 mmol) was added dropwise, over a period of 5 minutes, to a suspension of 1,4,5,8-tetrakis(hydroxymethyl)naphthalene **63** (1.23 g, 5.0 mmol) in anhydrous dioxane (40 mL) under nitrogen. The resulting mixture was stirred for 1 hour. More phosphorus tribromide (5.2 mL, 14.82 g, 54.7 mmol) was then added to the mixture which was stirred at room temperature for 20 hours. Water (50 mL) was added to the mixture with ice cooling and stirring was continued for 30 minutes. The precipitated solid was removed by filtration and recrystallised from dioxane to give **60** as a white solid (1.76 g, 3.5 mmol, 71%).

Mp	248-250 °C (dec.), lit.[120] > 220 °C (dec.)
IR (cm^{-1})	3448, 3056, 2363, 1918, 1654, 613
MS (m/z %)	500 (3) (M^+), 419 (32) ($[M-Br]^+$), 340 (28) ($[M-2Br]^+$), 259 (74) ($[M-3Br]^+$), 180 (100) ($[M-4Br]^+$), 165 (73)

3.2.8 5,6-Dibromoprehnitene (67)[123]

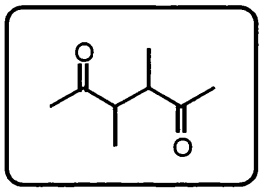


Prehnitene (22 mL, 19.80 g, 147.5 mmol) was added to glacial acetic acid (60 mL) with a crystal of iodine. To the resulting mixture, a solution of bromine (16 mL, 49.92 g, 312.4 mmol) in glacial acetic acid (40 mL) was added over a period of 20 minutes, after which the mixture was left to stand for 2 hours. The resulting mass of liquid and solid was diluted with water and the liquid was decanted. The residual solid was then washed with sodium carbonate solution followed by water, after which it was removed by filtration and dried under vacuum. Recrystallisation from chloroform/methanol gave **67** as a white solid (15.73 g, 53.9 mmol, 37%)

Mp	201-203 °C, lit.[123] 208 °C

^{1}H 300 MHz NMR ($CDCl_3$)	2.52 (s, 6H, ArCH_3 [1,4]), 2.27 (s, 6H, ArCH_3 [2,3])
^{13}C 75 MHz NMR ($CDCl_3$)	167.0, 135.6, 125.5, 22.7, 17.8
IR (cm^{-1})	2920, 1654, 1375, 1194, 890, 771
MS (m/z %)	292 (100) (M^+)

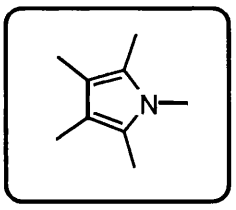
3.2.9 3,4-Dimethyl-2,5-hexanedione (65)[122]



Lead (IV) oxide (100.00 g, 418.1 mmol) was added to 2-butanone (372 mL, 300.00 g, 4160.3 mmol) and the resulting mixture was refluxed for 15 h. Lead (IV) oxide was removed by filtration and unreacted 2-butanone was removed by rotary evaporation. The resulting liquid was then distilled at 92-120 °C at 13 mmHg to give **65** as a yellow liquid (47.32 g, 332.8 mmol, 8%).

Bp	92-120 °C (13 mmHg), lit.[122] 90-105 °C (18 mmHg)
^{1}H 300 MHz NMR ($CDCl_3$)	2.76 (m, 2H, $CH(CH_3)_3$), 2.10 (d, 6H, $COCH_3$), 1.00 (d, 6H, J_{H-H} = 7.2 Hz, $CH(CH_3)_3$)
IR (cm^{-1})	3508, 1716, 2975, 1456, 1259, 1279

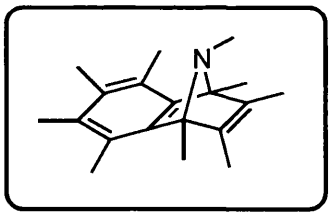
3.2.10 Pentamethylpyrrole (69)[121]



A mixture of 3,4-dimethyl-2,5-hexanedione **65** (20.00 g, 140.6 mmol), methylamine (40% aqueous, 75 mL, 27.18 g, 875.1 mmol) and benzene (300 mL) was refluxed for 6 h, the water being removed continuously with a Dean and Stark trap. The solution was dried with Magnesium sulfate and evaporated under reduced pressure. The solid residue was dried under vacuum to give **69** as yellow solid (16.98 g, 123.7 mmol, 88%).

^{1}H 300 MHz NMR ($CDCl_3$)	3.37 (s, 3H, CH_3-N), 2.14 (s, 6H, N-C(CH_3)-C), 1.96 (s, 6H, N-C(CH_3)-C(CH_3))

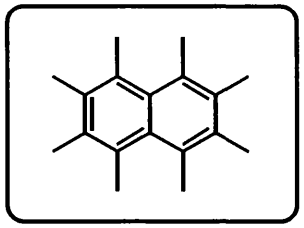
3.2.11 Nonamethyl-1,4-dihydronaphthalen-1,4-imine (70)[121]



N-butyllithium (1.6 M solution in hexane) (30 mL, 48 mmol) was added dropwise over a period of 1 h to a suspension of 5,6-dibromoprehnitene **67** (10.64 g, 36.4 mmol) and pentamethylpyrrole **69** (5.00 g, 36.4 mmol) in anhydrous tetrahydrofuran (170 mL) at –78 °C under nitrogen. After addition, the resulting mixture was kept at this temperature for an additional hour and left for 20 h at room temperature. Water (10 mL) and diethyl ether (20 mL) were added slowly, the layers were separated, and the aqueous layer was extracted with diethyl ether (20 mL). Combined organic layers were dried with magnesium sulfate and evaporated under vacuum. Petroleum ether 40-60 °C (40 mL) was added to the residue, the solution was filtered, and the solvent was removed by rotary evaporation to give **70** as a yellow solid (9.66 g, 35.9 mmol, 99 %).

Mp	90-92 °C, lit.[121] 94-96 °C
^{1}H 300 MHz NMR ($CDCl_3$)	2.25 (s, 3H, N-C-C(CH_3), 2.14 (s, 6H, N-C(CH_3)), 1.95 (s, 3H, N-CH_3), 1.70, 1.68 (2s, 12H, ArCH_3)
^{13}C 75 MHz NMR ($CDCl_3$)	143.6, 143.1, 143.1, 129.9, 127.1, 73.9, 28.5, 14.1, 13.6, 9.1
IR (cm^{-1})	2967, 2849, 1654, 1636
MS (m/z %)	269 (21) (M^+), 254 (12), 215 (100)

3.2.12 Octamethylnaphthalene (64)[121]

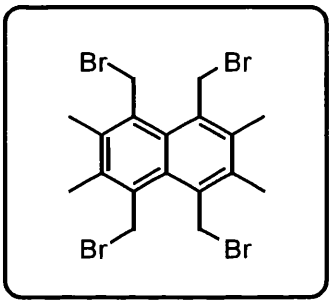


A mixture of nonamethyl-1,4-dihydronaphthalen-1,4-imine **70** (9.00 g, 33.4 mmol), anhydrous sodium carbonate (3.60 g, 34.0 mmol), *m*-chloroperbenzoic acid (57-86%, 11.22 g, 37.1 mmol) and benzene (200 mL) was heated under reflux for 15 h. Water (100 mL) was added, the layers were separated, and the aqueous layers was extracted with chloroform (50 mL). The combined organic layers were dried with magnesium sulfate and evaporated under reduced pressure.

The solid residue was triturated with methanol (55 mL) and filtered to give **64** as white needles (4.67 g, 19.4 mmol, 58%).

Mp	180-182 °C, lit.[121] 181-182 °C
^{1}H 300 MHz NMR ($CDCl_3$)	2.53 (s, 12H), 2.36 (s, 12H)
^{13}C 75 MHz NMR ($CDCl_3$)	134.9, 134.4, 128.3, 21.8, 16.7
IR (cm^{-1})	2997, 2896, 1654, 1637
MS (m/z %)	240 (86) (M^+), 225 (13), 133 (100)

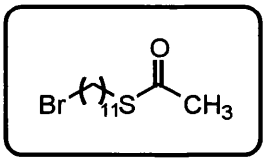
3.2.13 1,4,5,8-Tetrakis(bromomethyl)-2,3,6,7-tetramethylnaphthalene (71)[124]



A solution of bromine (3.84 mL, 11.98 g, 75.0 mmol) in dichloromethane (190 mL) was added dropwise to a solution of octamethylnaphthalene **64** (4.50 g, 18.7 mmol) in dichloromethane (560 mL) at 0 °C. The resulting solution was left at room temperature for 2 h, then was washed with saturated aqueous sodium carbonate (3 x 600 mL) and dried with magnesium sulfate. The solvent was removed by rotary evaporation and the solid residue was recrystallised from tetrahydrofuran to give **71** as a white solid (6.79 g, 12.2 mmol, 65%).

Mp	178-181 °C (dec.), lit.[124] 180 °C (dec.)
^{1}H 300 MHz NMR ($CDCl_3$)	5.31, 4.72 (2d, 8H, CH_2Br), 2.53 (s, 12H, $ArCH_3$)
^{13}C 75 MHz NMR ($CDCl_3$)	167.4, 139.0, 130.4, 34.9, 17.0
IR (cm^{-1})	3037, 2919, 1654, 1458, 1206, 1165, 838, 588
MS (m/z %)	556 (6) (M^+), 475 (52) ($[M-Br]^+$), 397 (55), 395 (28), 316 (15), 236 (27), 235 (100), 221 (63), 206 (22)

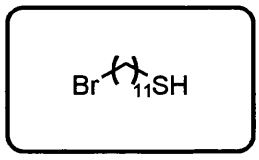
3.2.14 11-Bromo-1-undecyl thioacetate (80)[108]



Triphenylphosphine (8.50 g, 32.4 mmol) was added to anhydrous tetrahydrofuran (120 mL) at 0 °C under nitrogen. Upon addition of diisopropyl azodicarboxylate (6.5 mL, 33.0 mmol), a white precipitate was formed. After stirring at 0 °C for 30 min, 11-bromo-1-undecanol (7.53 g, 30.0 mmol) was added as a 1M solution in tetrahydrofuran. A 1 M solution of thioacetic acid in tetrahydrofuran (20 mL) was added to the resulting mixture over a period of 10 min and produced a clear solution. The solution was then stirred at 0 °C for 15 min and allowed to warm to room temperature. Two drops of water were added and the solvent was removed by rotary evaporation. The residue was extracted into ether and triphenylphosphine oxide was removed by filtration. Kugelrohr distillation and column chromatography using 3:2 hexane/dichloromethane gave **80** as a yellow oil (6.0 g, 19.4 mmol, 65%).

^{1}H 300 MHz NMR ($CDCl_3$)	3.35 (t, 2H, $J_{H\text{-}H}$ = 6.9 Hz, CH_2Br), 2.80 (t, 2H, $J_{H\text{-}H}$ = 7.3 Hz, CH_2CO), 2.26 (s, 3H, SCH_3), 1.80 (m, 2H, $J_{H\text{-}H}$ = 7.1 Hz), 1.51 (m, 2H, $J_{H\text{-}H}$ = 7.3 Hz), 1.37 (m, 2H), 1.22 (br s, 12H)
IR (cm^{-1})	3037, 2919, 1654, 1458, 1206, 1165, 838, 588
MS (m/z %)	309 (35) (M^+), 279 (37), 247 (18), 43 (100)

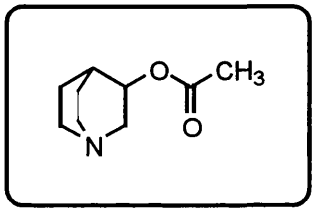
3.2.15 11-Bromo-1-undecanethiol (81)[108]



A solution of dry hydrochloride in methanol was prepared by careful addition of acetyl chloride (24 mL) to degassed methanol (240 mL) at 0 °C. 11-Bromo-1-undecyl thioacetate **80** (2.39 g, 7.7 mmol) was added and the solution was stirred at room temperature for 3 h under nitrogen. The resulting mixture was then poured into water (240 mL) and the organic layer was extracted into hexane (150 mL). The aqueous layer was extracted with hexane (2 x 100 mL) and the combined organic layers were washed with water (2 x 250 mL). The hexane solution was dried with magnesium sulfate, reduced to a volume of 15 mL on a rotary evaporator. Column chromatography using 2:1 hexane/dichloromethane gave **81** as a colourless oil (1.87 g, 7.0 mmol, 91%).

^{1}H 400 MHz NMR ($CDCl_3$)	3.34 (t, 2H, $J_{H\text{-}H}$ = 6.9 Hz, CH_2Br), 2.45 (q, 2H, $J_{H\text{-}H}$ = 7.4 Hz, SCH_2), 1.79 (m, $J_{H\text{-}H}$ = 7.4 Hz, 2H), 1.54 (m, $J_{H\text{-}H}$ = 7.4 Hz, 2H), 1.38-1.22 (br-m & br-s, 15H)
^{13}C 100 MHz NMR ($CDCl_3$)	34.0, 33.9, 32.8, 29.4, 29.3, 29.2, 29.0, 28.7, 28.3, 28.1, 24.6
MS (m/z %)	267 (38) (M^+), 187 (100), 154 (27)

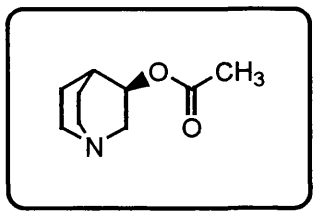
3.2.16 3-Acetoxyquinuclidine (50)[118]



Racemic 3-quinuclidinol (9.00 g, 70.8 mmol) and acetic anhydride (80 mL) were heated under reflux for 4 h. The solution was concentrated under reduced pressure, neutralised with saturated sodium hydrogen carbonate solution (200 mL) and extracted with chloroform (3 x 300 mL). The combined organic extracts were dried with magnesium sulfate and the solvent was removed by rotary evaporation. The residue was distilled at 77 °C at 1.5 mmHg to give **50** as a colourless oil (5.67 g, 33.5 mmol, 47%).

^{1}H 300 MHz NMR ($CDCl_3$)	4.80-4.74 (m, 1H, **H**OAc), 3.25-3.17 (m, 1H, NCH_2CH_2CH), 2.90-2.62 (m, 5H), 2.05 (s, 3H, CH_3), 1.99-1.96 (m, 1H), 1.84-1.81 (m, 1H), 1.68-1.63 (m, 1H), 1.56-1.53 (m, 1H), 1.42-1.33 (m, 1H)
^{13}C 75 MHz NMR ($CDCl_3$)	170.9, 71.2, 55.3, 47.2, 46.3, 25.1, 24.4, 21.1, 19.4
MS (m/z %)	170 (100) (MH^+)

3.2.17 (R)-(+)-3-Acetoxyquinuclidine (51)[118]



To a solution of L-(+)-Tartaric acid (0.89 g, 5.9 mmol) in 80% ethanol (15 mL), racemic 3-acetoxyquinuclidine **50** (1.00 g, 5.9 mmol) was added. The resulting solution was left for 72 h at

room temperature. The precipitated solid was removed by filtration and recrystallised from 80% ethanol to give (R)-(+)-3-acetoxyquinuclidine tartrate as white needles (0.67 g, 4.0 mmol, 68%).

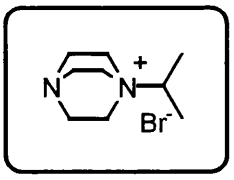
Mp	87-89 °C, lit.[118] 94-95
$[\alpha]^{25}_D$	+4.4° (c = 2.2, H_2O), lit.[8] +3.6° (c = 2.2, H_2O)

The resolved tartrate was dissolved in water and the solution was made alkaline with potassium carbonate. The ester was extracted with chloroform (3 x 50 mL). The extracts were dried over magnesium sulfate, filtered and concentrated to provide **51** as a colourless oil.

$[\alpha]^{25}_D$	+26.6° (c = 2.9, EtOH), lit.[118] +28.5° (c = 2.2, EtOH)
^{1}H 300 MHz NMR ($CDCl_3$)	4.80-4.74 (m, 1H, **H**OAc), 3.26-3.18 (m, 1H, NCH_2CH_2CH), 2.89-2.63 (m, 5H), 2.06 (s, 3H, CH_3), 2.00-1.96 (m, 1H), 1.84-1.81 (m, 1H), 1.68-1.63 (m, 1H), 1.56-1.53 (m, 1H), 1.42-1.33 (m, 1H)
^{13}C 75 MHz NMR ($CDCl_3$)	170.9, 71.3, 55.4, 47.3, 46.4, 25.1, 24.5, 21.2, 19.4
MS (m/z %)	170 (100) (MH^+)

3.3 Syntheses of Monocationic Compounds

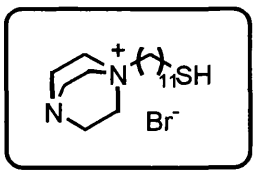
3.3.1 N-Isopropyl DABCO bromide (57)[116]



2-Bromopropane (5 mL, 6.04 g, 49.1 mmol) was added to a solution of DABCO (6.61 g, 58.9 mmol) in acetonitrile (200 mL). The resulting mixture was stirred for 48 h, after which time the solution was poured into diethyl ether (400 mL) and stirred for 30 min. The white solid formed was removed by filtration, washed with diethyl ether, and finally dried under vacuum to give **57** as a white hygroscopic solid (9.16 g, 39.0 mmol, 79%).

Mp	218-219 °C, lit.[116] 228 °C
^{1}H 400 MHz NMR (D_2O)	3.57 (m, 1H, J_{H-H} = 6.6 Hz), 3.40 (t, 6H, J_{H-H} = 7.4 Hz), 3.19 (t, 6H, J_{H-H} = 7.3 Hz), 1.38 (d, 6H, J_{H-H} = 6.6 Hz)
^{13}C 100 MHz NMR (D_2O)	69.0, 51.6, 46.8, 17.9
IR (cm^{-1})	2969, 2893, 2099, 1624, 1467, 1396, 1121, 1058, 852
MS (m/z %)	711 (8) ($[M-Br]^+$), 155 (100), 112 (3)

3.3.2 N-(11-thioundecacyl)-DABCO bromide (78)

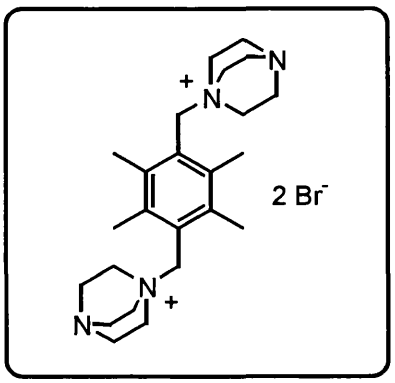


11-Bromo-1-undecanethiol **81** (3.87 g, 14.5 mmol) was added to a solution of DABCO (2.91 g, 25.9 mmol) in acetonitrile (50 mL). The resulting mixture was stirred for 72 h, after which time the solution was poured into diethyl ether (600 mL) and stirred for 30 min. The white precipitate was removed by filtration, washed with diethyl ether, and dried under vacuum to give **78** as a white solid (5.23 g, 13.8 mmol, 95%).

Mp		260-262 °C (dec.)						
^{1}H 300 MHz NMR (D_2O)		3.31 (t, 6H, $J_{H\text{-}H}$ = 7.4 Hz, N-CH_2CH_2-N^+), 3.16 (overlap-t, 2H, $(CH_2)_{10}CH_2$-N^+), 3.10 (t, 6H, $J_{H\text{-}H}$ = 7.5 Hz, N-CH_2CH_2-N^+), 2.45 (t, 2H, $J_{H\text{-}H}$ = 7.1 Hz), 1.70-1.62 (br-m, 2H), 1.51 (m, 2H, $J_{H\text{-}H}$ = 7.3 Hz), 1.26, 1.21 (2 br-s, 15H)						
^{13}C 75 MHz NMR (D_2O)		97.7, 65.4, 52.9, 45.0, 34.0, 29.5, 29.4, 29.3, 29.1, 28.4, 26.5, 24.7, 22.0						
IR (cm^{-1})		2918, 2850, 2450, 2346, 1466, 1317, 1099, 1057						
MS (m/z %)		299 (100) ([M-Br]$^+$), 266 (5)						
$C_{17}H_{35}BrN_2S$	(365.43)	requires	C	55.88	H	9.65	N	7.67	Br	21.87
+ $1H_2O$	(379.44)	requires		53.81		9.83		7.38		21.06
		found		52.45		9.24		7.11		20.95

3.4 Syntheses of Dicationic Compounds

3.4.1 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide (41)

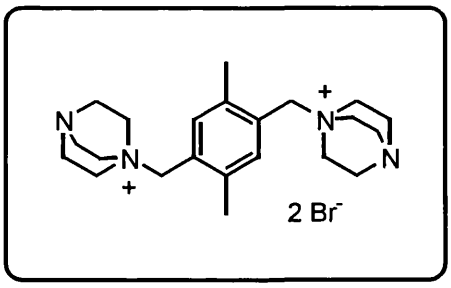


A solution of 3,6-bis(bromomethyl)-1,2,4,5-tetramethylbenzene **38** (1.45 g, 4.5 mmol) was added to a solution of DABCO (1.55 g, 13.8 mmol) in acetonitrile (100 ml). The mixture was

then stirred for 48 hours. The mixture was then poured into diethyl ether (300 mL) and stirred for 30 min . The precipitate formed was removed by filtration, washed with diethyl ether, and dried under vacuum to give **41** a white solid (2.12 g, 3.9 mmol, 86%).

Mp		256-259 (dec.)			
^{1}H 400 MHz NMR (D_2O)		4.93 (s, 4H, Ar**CH$_2$**N$^+$), 3.48 (t, 12H, J = 7.3 Hz, N-**CH$_2$**CH$_2$-N$^+$), 3.16 (t, 12H, J = 7.8 Hz, N-**CH$_2$**CH$_2$-N$^+$), 2.42 (s, 12H, **CH$_3$**)			
^{13}C 100 MHz NMR (D_2O)		140.8, 128.6, 65.1, 54.4, 47.1, 21.4			
IR (cm^{-1})		3010, 2961, 2889, 1653, 1497			
MS (m/z %)		463 (100) ([M-Br]$^+$), 383 (7) ([M-2Br]$^+$), 271 (33), 160 (29), 112 (71)			
$C_{24}H_{40}Br_2N_4$	(544.41)	requires C	52.95	H 7.35	N 10.29
		found	52.76	7.14	10.18

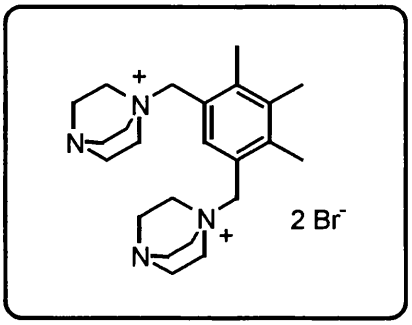
3.4.2 2,5-Bis(DABCO-N-methyl)-1,4-dimethylbenzene dibromide (42)



2,5-bis(bromomethyl)-1,4-dimethylbenzene **39** (1.00 g, 3.4 mmol) was added to a solution of DABCO (0.88 g, 7.8 mmol) in acetonitrile (100 ml). The resulting mixture was stirred for 48 hours. After stirring, the mixture was poured into diethyl ether (300 mL) and stirred for 30 min. The precipitate formed was removed by filtration, washed with diethyl ether, and dried under vacuum to give **42** as a white solid (0.96 g, 1.8 mmol, 53%).

Mp		238-240 °C (dec.)			
^{1}H 400 MHz NMR (D_2O)		7.48 (s, 2H, Ar**H**), 4.59 (s, 4H, Ar**CH$_2$**N$^+$), 3.53 (t, 12H, J = 7.4 Hz, N-**CH$_2$**CH$_2$-N$^+$), 3.20 (t, 12H, J = 7.2 Hz, N-**CH$_2$**CH$_2$-N$^+$), 2.46 (s, 6H, **CH$_3$**)			
^{13}C 100 MHz NMR (D_2O)		140.9, 140.2, 130.3, 67.9, 55.0, 47.2, 21.7			
IR (cm^{-1})		2957, 2892, 1646, 1611			
MS (m/z %)		435 (100) ([M-Br]$^+$), 355 (7) ([M-2Br]$^+$), 243 (26), 132 (20)			
$C_{22}H_{36}Br_2N_4$	(516.36)	requires C	51.17	H 7.03	N 10.85
+ 1H_2O	(534.38)	requires	49.45	7.17	10.48
		found	50.03	7.12	10.63

3.4.3 4,6-Bis(DABCO-N-methyl)-1,2,3-trimethylbenzene dibromide (43)

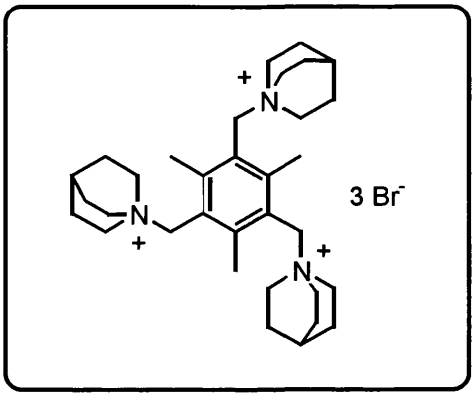


4,6-Bis(bromomethyl)-1,2,3-trimethylbenzene **40** (1.34 g, 4.4 mmol) was added to a solution of DABCO (1.23 g, 11.0 mmol) in acetonitrile (180 ml), and the resulting mixture was stirred for 48 hours. After stirring, the mixture was poured into diethyl ether (400 mL) and stirred for 30 minutes. The precipitate was removed by filtration and dried under vacuum to give **43** as a white solid (1.61 g, 2.8 mmol, 64%).

Mp		245-247 °C (dec.)			
^{1}H 400 MHz NMR (D_2O)		7.36 (s, 1H, Ar**H**), 4.66 (s, 4H, Ar**CH$_2$**N$^+$), 3.45 (t, 12H, J = 6.7 Hz, N-CH$_2$**CH$_2$**-N$^+$), 3.16 (t, 12H, J = 6.7 Hz, N-**CH$_2$**CH$_2$-N$^+$), 2.41 (s, 6H, **CH$_3$** [1,3]), 2.32 (s, 3H, **CH$_3$** [2])			
^{13}C 100 MHz NMR (D_2O)		144.3, 143.1, 140.1, 125.5, 68.9, 54.8, 47.2, 20.3, 19.3			
IR (cm^{-1})		2987, 2961, 2947, 2886, 1459, 1363			
MS (m/z %)		449 (100) ([M-Br]$^+$), 369 (16) ([M-2Br]$^+$), 258 (61), 146 (56), 112 (49)			
$C_{23}H_{38}Br_2N_4$	(530.39)	requires C	52.09	H 7.22	N 10.56
+ 2H_2O	(566.42)	requires	48.77	7.47	9.89
		found	49.16	7.18	10.02

3.5 Syntheses of Tricationic Compounds

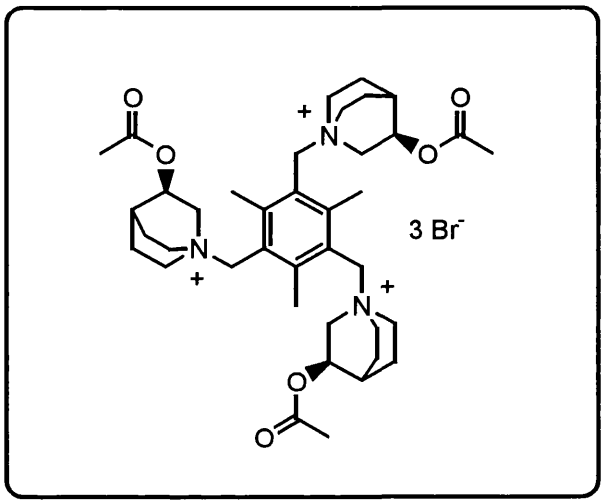
3.5.1 2,4,6-Tris(quinuclidine-N-methyl)-1,3,5-trimethylbenzene tribromide (45)[139]



Quinuclidine (0.92 g, 8.3 mmol) was added to a solution of 2,4,6-tris(bromomethyl)-1,3,5-trimethylbenzene **47** (0.90 g, 2.3 mmol) in acetonitrile (80 mL). The resulting mixture was stirred for 48 h and poured into diethyl ether (300 mL). After stirring for 30 min, the precipitated solid was removed by filtration, washed with diethyl ether, and dried under vacuum to give **45** as a white solid (1.47 g, 2.0 mmol, 89%).

Mp	253-255 °C (dec.), lit.[139] 267-270 °C (dec.)
^{1}H 300 MHz NMR (D_2O)	4.62 (s, 6H, Ar**C**H_2), 3.52-3.32 (br, 18H, CH_2**C**H_2-N^+), 2.52 (s, 9H, Ar**C**H_3), 2.04 (br-m, 3H, **C**H(CH_2)$_3$), 1.86 ((br-s, 18H, **C**$H_2$$CH_2$-$N^+$)
^{13}C 75 MHz NMR (D_2O)	147.2, 128.1, 64.0, 55.4, 24.6, 21.8, 19.5
IR (cm^{-1})	2968, 2951, 1659, 1463, 1053, 998
MS (m/z %)	652 (7) ([M-Br]$^+$), 112 (100)

3.5.2 2,4,6-Tris((R)-(+)-3-acetoxyquinuclidine-N-methyl)-1,3,5-trimethylbenzene tribromide (46)[139]

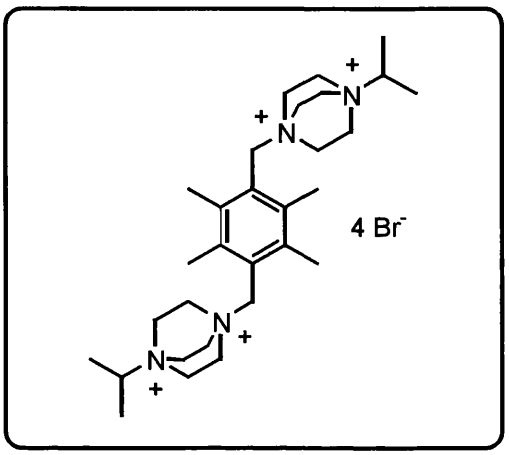


(R)-(+)-3-Acetoxyquinuclidine **51** (1.46 g, 8.6 mmol) was added to a solution of 2,4,6-tris(bromomethyl)-1,3,5-trimethylbenzene **47** (0.81 g, 2.0 mmol) in acetonitrile (150 mL). The resulting mixture was stirred for 48 h after which time the mixture was poured into diethyl ether (300 mL) and stirred for 30 min. The precipitated solid formed was removed by filtration, washed with diethyl ether, and dried under vacuum to give **46** as a white solid (1.70 g, 1.9 mmol, 92%).

Mp	250-252 °C (dec.), lit.[139] 249-252 °C (dec.)
$[\alpha]^{25}_D$	-14.2° (c = 1.0, H_2O), lit.[10] –14.7° (c = 1.0, H_2O)
^{1}H 300 MHz NMR (D_2O)	4.88 (br-m, 6H, $ArCH_2$), 4.77 (br-m, 3H, $HCOCOCH_3$), 4.00 (br-t, 3H, N^+-CH_2CH_2CH), 3.60-3.48 (2 br-m, 18H, N^+-$(CH_2)_3$), 2.47 (br-s, 9H, $ArCH_3$), 2.34-2.21 (br-m, 6H), 2.02 (br-s, 9H, $COCH_3$), 1.98-1.93 (br-m, 6H)
^{13}C 75 MHz NMR (D_2O)	174.4, 147.5, 127.8, 69.3, 63.9, 60.4, 56.2, 53.5, 24.1, 21.8, 21.7, 21.3, 19.0
IR (cm^{-1})	2953, 1709, 1653, 1489, 1254, 1037, 928
MS (m/z %)	826 (13) ($[M-Br]^+$), 170 (100)

3.6 Syntheses of Tetracationic Compounds

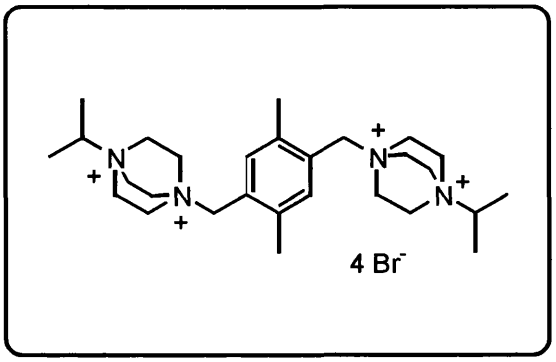
3.6.1 3,6-Bis(N'-isopropyl-DABCO-N-methyl)-1,2,4,5-tetramethylbenzene tetrabromide (52)



Isopropyl-DABCO bromide **57** (4.00 g, 17.0 mmol) was added to a solution of 3,6-bis(bromomethyl)-1,2,4,5-tetramethylbenzene **38** (2.00 g, 6.2 mmol) in acetonitrile (200 mL). The mixture was stirred for 72 hours. The solid formed was removed by filtration, washed with acetonitrile and dried under vacuum to give **52** as a white solid (4.15 g, 5.0 mmol, 81%).

Mp		249-251 °C (dec.)				
^{1}H 400 MHz NMR (D_2O)		5.25 (s, 4H, Ar**CH**$_2$), 4.06 (br-t, 12H, Ar**CH**$_2$-N$^+$-**CH**$_2$), 3.93-3.87 (br-t, 14H, *i*Pr-N$^+$-**CH**$_2$ & **CH**(CH$_3$)$_2$), 2.46 (s, 12H, Ar**CH**$_3$), 1.46 (d, 12H, J = 6.5 Hz, N$^+$-CH(**CH**$_3$)$_2$)				
^{13}C 100 MHz NMR (D_2O)		141.6, 128.5, 71.3, 65.8, 53.7, 51.4, 21.6, 18.2				
IR (cm^{-1})		2995, 2074, 1636, 1496, 1475				
MS (m/z %)		711 (8) ([M-Br]$^+$), 155 (100), 112 (3)				
$C_{30}H_{54}Br_4N_4$	(790.40)	requires	C	45.59	H 6.89	N 7.09
+ 2H_2O	(826.43)	requires		43.60	7.07	6.78
		found		43.96	7.11	6.84

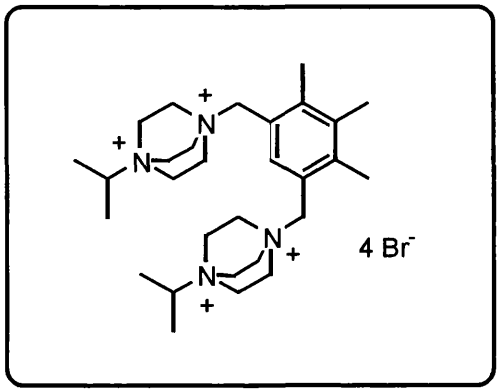
3.6.2 2,5-Bis(N'-isopropyl-DABCO-N-methyl)-1,4-dimethylbenzene tetrabromide (53)



Isopropyl-DABCO bromide **57** (2.00 g, 8.5 mmol) was added to a solution 2,5-bis(bromomethyl)-1,4-dimethylbenzene **39** (1.00 g, 3.4 mmol) in acetonitrile (150 mL). The mixture was stirred for 48 hours. The solid formed was removed by filtration, washed with acetonitrile and dried under vacuum to give **53** as a white solid (2.51 g, 3.1 mmol, 91%).

Mp		232-235 °C (dec.)				
^{1}H 400 MHz NMR (D_2O)		7.58 (s, 2H, Ar**H**), 4.93 (s, 4H, Ar**CH$_2$**), 4.14 (br-t, 12H, Ar**CH$_2$**-N$^+$-**CH$_2$**), 3.98 (br-t, 14H, *i*Pr-N$^+$-**CH$_2$** & **CH**(CH$_3$)$_2$), 2.52 (s, 12H, Ar**CH$_3$**), 1.49 (d, 12H, J = 6.5 Hz, N$^+$-CH(**CH$_3$**)$_2$)				
^{13}C 100 MHz NMR (D_2O)		141.5, 140.3, 130.0, 71.4, 68.2, 53.9, 51.4, 21.6, 18.2				
IR (cm^{-1})		3022, 2053, 1625, 1488, 1473, 1122, 839				
MS (m/z %)		683 (26) ([M-Br]$^+$), 603 (4) ([M-2Br]$^+$), 155 (100), 112 (4)				
$C_{28}H_{50}Br_4N_4$	(762.35)	requires	C	44.11	H 6.61	N 7.35
+ $3H_2O$	(816.39)	found		41.19	6.91	6.86
		found		41.09	7.16	6.69

3.6.3 4,6-Bis(N'-isopropyl-DABCO-N-methyl)-1,2,3-trimethylbenzene tetrabromide (54)

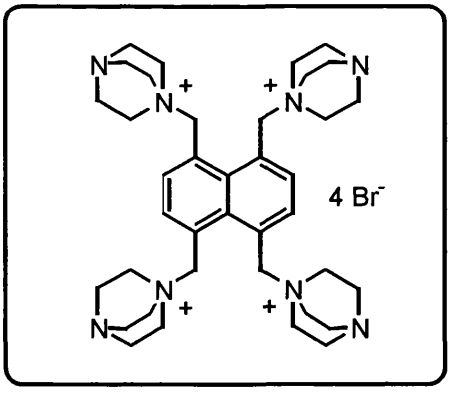


Isopropyl-DABCO bromide **57** (1.56 g, 6.6 mmol) was added to a solution 4,6-bis(bromomethyl)-1,2,3-trimethylbenzene **40** (0.50 g, 1.6 mmol) in acetonitrile (150 mL). The

mixture was stirred for 48 hours. The solid formed was removed by filtration, washed with acetonitrile and dried under vacuum to give **54** as a white solid (1.22 g, 1.5 mmol, 94%).

Mp	240-242 °C (dec.)
^{1}H 400 MHz NMR (D_2O)	7.52 (s, 1H, ArH), 5.00 (s, 4H, $ArCH_2$), 4.06 (br-t, 12H, $ArCH_2$-N^+-CH_2), 3.94 (br-t, 14H, *i*Pr-N^+-CH_2 & $CH(CH_3)_2$), 2.47 (s, 6H, $ArCH_3$ [1,3]), 2.36 (s, 3H, $ArCH_3$ [2]), 1.47 (d, 12H, J = 6.2 Hz, N^+-$CH(CH_3)_2$)
^{13}C 100 MHz NMR (D_2O)	145.4, 144.2, 139.4, 125.0, 71.3, 69.1, 53.8, 51.4, 20.3, 19.5, 18.2
IR (cm^{-1})	2991, 2903, 2050, 1635, 1476, 1443
MS (m/z %)	697 (13) ($[M-Br]^+$), 616 (3) ($[M-2Br]^+$), 155 (100), 112 (3)
$C_{29}H_{52}Br_4N_4$ (776.37)	requires C 44.86 H 6.75 N 7.22
+ $3H_2O$ (830.42)	requires 41.95 7.04 6.75
	found 42.23 6.95 6.62

3.6.4 1,4,5,8-Tetrakis(DABCO-N-methyl)naphthalene tetrabromide (55)

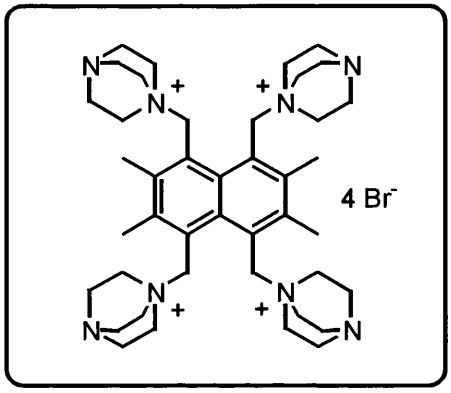


1,4,5,8-tetrakis(bromomethyl)naphthalene **60** (0.42 g, 0.8 mmol) was added to a solution of DABCO (0.57 g, 5.1 mmol) in acetonitrile (100 mL). The resulting mixture was stirred for 72 h. The solid formed was removed by filtration, washed with acetonitrile, and dried under vacuum to give **55** as a white solid (0.79 g, 0.8 mmol, 98%).

Mp	281-285 °C (dec.)
^{1}H 300 MHz NMR (D_2O)	8.00 (s, 4H, ArH), 5.21 (s, 8H, $ArCH_2$), 3.09 (br-t, 24H, $ArCH_2$-N-CH_2CH_2-N^+), 2.92 (br-t, 24H, N-CH_2CH_2-N^+)
^{13}C 75 MHz NMR (D_2O)	139.6, 128.0, 98.2, 71.2, 55.2, 46.8
IR (cm^{-1})	2962, 2891, 2371, 1648, 1459, 1363
MS (m/z %)	869 (13) ($[M-Br]^+$), 755 (3), 675 (8), 483 (45), 371 (52), 259 (23), 179 (52), 112 (100)

$C_{38}H_{60}Br_4N_8$	(948.56)	requires	C	48.12	H	6.38	N 11.81
+ $3H_2O$	(1002.61)	requires		45.52		6.63	11.18
		found		45.39		6.58	11.07

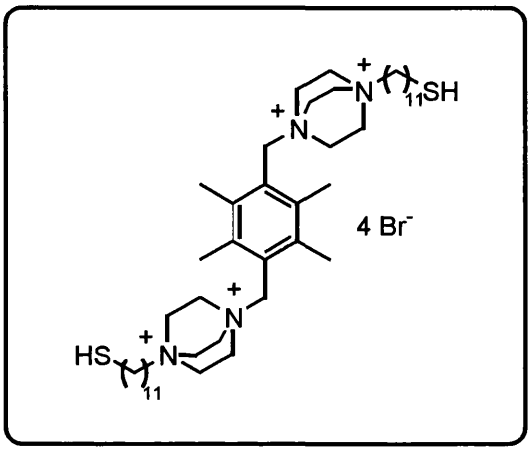
3.6.5 1,4,5,8-Tetrakis(DABCO-N-methyl)-2,3,6,7-tetramethylnaphthalene tetrabromide (56)



1,4,5,8-Tetrakis(bromomethyl)-2,3,6,7-tetramethylnaphthalene **71** (2.40 g, 4.3 mmol) was added to a solution of DABCO (2.45 g, 21.8 mmol) in acetonitrile (200 mL). The mixture was stirred for 72 h. The solid formed was removed by filtration, washed with acetonitrile, and dried under vacuum to give **56** as a white solid (3.98 g, 3.6 mmol, 85%).

Mp		268-270 °C (dec.)					
^{1}H 300 MHz NMR (D_2O)		5.48, 4.93 (2d, 8H, ArC**H**$_2$), 3.00 (br-t, 12H), 2.85 (br-m, 36H), 2.57 (s, 12H, ArC**H**$_3$)					
^{13}C 100 MHz NMR (D_2O)		147.5, 136.7, 123.8, 67.5, 55.3, 47.2, 22.6					
IR (cm^{-1})		2960, 2884, 2074, 1636, 1459, 1358, 1191					
MS (m/z %)		923 (5) ([M-Br]$^+$), 813 (2), 731 (7), 619 (13), 539 (28), 427 (37), 315 (17), 235 (38), 112 (100)					
$C_{42}H_{68}Br_4N_8$	(1004.67)	requires	C	50.21	H	6.82	N 11.15
+ $5H_2O$	(1094.74)	requires		46.08		7.18	10.24
		found		45.97		7.08	10.43

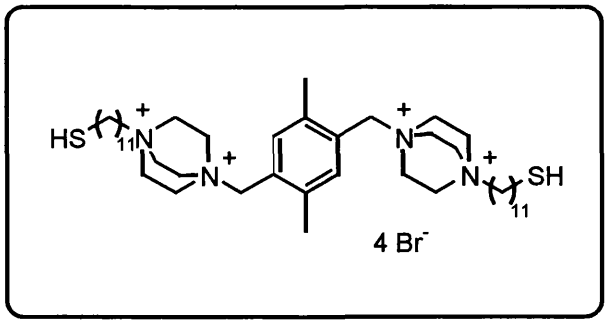
3.6.6 3,6-Bis(1-undecanethiol-N'-11-DABCO-N-methyl)-1,2,4,5-tetramethylbenzene tetrabromide (82)



3,6-Bis(bromomethyl)-1,2,4,5-tetramethylbenzene **38** (0.25 g, 0.8 mmol) was added to a solution of N-(11-thioundecacyl)-DABCO bromide **78** (0.72 g, 1.9 mmol) in acetonitrile (100 mL). The resulting mixture was stirred for 48 h. The solid formed was removed by filtration, washed with acetonitrile, and dried under vacuum to give **82** as a white solid (0.50 g, 0.5 mmol, 57%).

Mp	265-269 °C (dec.)					
^{1}H 300 MHz NMR (d_6-DMSO)	5.19 (s, 4H, ArCH_2), 3.92 (br-m, 28H), 3.49 (br-m, 4H), 2.41 (s, 12H, ArCH_3), 1.62 (br-m, 4H), 1.51 (br-m, 4H), 1.24 (br-s, 30H)					
^{13}C 75 MHz NMR (d_6-DMSO)	138.2, 126.1, 50.5, 49.8, 33.3, 28.9, 28.8, 28.7, 28.5, 28.3, 27.7, 25.5, 23.7, 21.3, 19.0					
IR (cm^{-1})	2923, 2852, 2473, 2369, 1466, 1390, 1105, 1059					
MS (m/z %)	998 (< 1) ([M-Br]$^+$), 917 (< 1) ([M-2Br]$^+$), 299 (100), 112 (17)					
$C_{46}H_{86}Br_4N_4S_2$ (1078.95)	requires	C	51.21	H	8.03	N 5.19
+ $1H_2O$ (1096.96)	found		50.37		8.09	5.11
	found		50.46		8.16	4.93

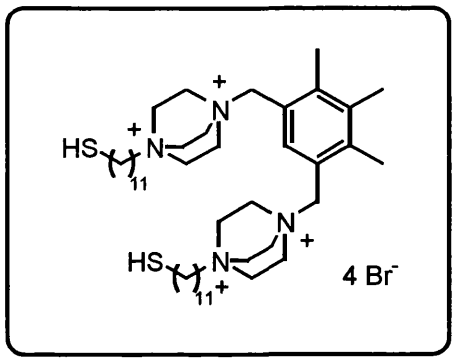
3.6.7 2,5-Bis(1-undecanethiol-N'-11-DABCO-N-methyl)-1,4-dimethylbenzene tetrabromide (83)



2,5-Bis(bromomethyl)-1,4-dimethylbenzene **39** (0.20 g, 0.7 mmol) was added to a solution of of N-(11-thioundecacyl)-DABCO bromide **78** (0.77 g, 2.0 mmol) in acetonitrile (100 mL). The resulting mixture was stirred for 48 h. The solid formed was removed by filtration, washed with acetonitrile, and dried under vacuum to give **83** as a white solid (0.38 g, 0.3 mmol, 50%).

Mp	243-247 °C (dec.)				
^{1}H 300 MHz NMR (d_6-DMSO)	7.53 (s, 2H, Ar**H**), 4.96 (s, 4H, ArC**H**$_2$), 4.07, 3.91 (2 br-s, 28H), 3.51 (br-m, 4H), 2.44 (s, 6H, ArC**H**$_3$), 1.63 (br-m, 4H), 1.51 (br-m, 4H), 1.25 (br-s, 30H)				
^{13}C 75 MHz NMR (d_6-DMSO)	137.7, 127.7, 63.4, 50.5, 50.0, 33.3, 28.9, 28.8, 28.7, 28.5, 28.4, 27.7, 25.5, 23.7, 19.3				
IR (cm^{-1})	2994, 2924, 2852, 2372, 1466, 1389, 1107				
MS (m/z %)	972 (4) ([M-Br]$^+$), 677 (6), 591 (10), 299 (85), 154 (100), 112 (57)				
$C_{44}H_{82}Br_4N_4S_2$ (1050.89)	requires	C	50.29	H 7.86	N 5.33
+ $2H_2O$ (1086.93)	found		48.62	7.97	5.15
	found		48.39	8.06	5.15

3.6.8 4,6-Bis(1-undecanethiol-N'-11-DABCO-N-methyl)-1,2,3-trimethylbenzene tetrabromide (84)



4,6-Bis(bromomethyl)-1,2,3-trimethylbenzene **40** (0.18 g, 0.6 mmol) was added to a of N-(11-thioundecacyl)-DABCO bromide **78** (0.56 g, 1.5 mmol) in acetonitrile (70 mL). The resulting mixture was stirred for 48 h. The solid formed was removed by filtration, washed with acetonitrile, and dried under vacuum to give **84** as a white solid (0.52 g, 0.5 mmol, 77%).

Mp	253-256 °C (dec.)							
^{1}H 300 MHz NMR (d_6-DMSO)	7.55 (s, 1H, Ar**H**), 5.02 (s, 4H, ArC**H**$_2$), 3.99, 3.95 (2 br-s, 28H), 3.52 (br-m, 4H), 2.45 (s, 6H, ArC**H**$_3$ [1,3]) 2.28 (s, 3H, ArC**H**$_3$ [2]), 1.67 (br-m, 4H), 1.53 (br-m, 4H), 1.27 (br-s, 30H)							
^{13}C 75 MHz NMR (d_6-DMSO)	141.7, 139.2, 50.5, 50.2, 33.3, 28.9, 28.8, 28.7, 28.5, 27.7, 23.7, 17.6							
IR (cm^{-1})	3000, 2924, 2853, 2365, 1466, 1390, 1107, 1062							
MS (m/z %)	983 (29) ([M-Br]$^+$), 903 (18) ([M-2Br]$^+$), 605 (95), 523 (100)							
$C_{45}H_{84}Br_4N_4S_2$ (1064.92)	requires	C	50.75	H	7.95	N	5.26	S	6.02
+ $3H_2O$ (1118.97)	found		48.30		8.11		5.01		5.73
	found		48.25		8.25		4.91		5.75

3.7 Syntheses of Polyanionic Compounds

3.7.1 General Procedure

A solution of a hydroxide in water was added to a solution of a carboxylic acid in water. The resulting solution was stirred for 30 min, after which time acetone was added. The precipitated solid formed was removed by filtration and dried under vacuum.

A series of polyanions synthesised is outlined in Table 3.1, 3.2 and 3.3 , including starting materials for making these polyanions and their percentage yields.

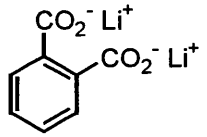
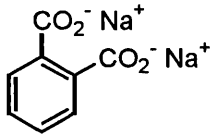
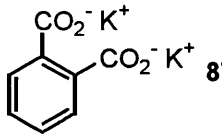
	Starting materials / Sources	yield
 **85** dilithium 1,2-benzenedicarboxylate	phthalic acid (1.98 g, 11.9 mmol) lithium hydroxide (0.57 g, 23.8 mmol)	1.98 g, 11.1 mmol, 93%
 **86** disodium 1,2-benzenedicarboxylate	phthalic acid (2.01 g, 12.1 mmol) sodium hydroxide (0.97 g, 24.3 mmol)	2.50 g, 11.9 mmol, 98%
 **87** dipotassium 1,2-benzenedicarboxylate	commercially available from Aldrich	---

Table 3.1

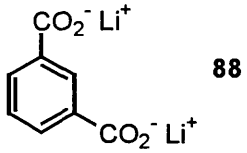
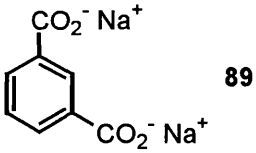
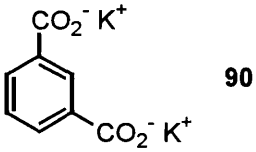
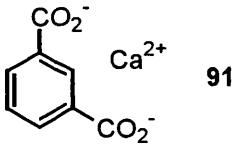
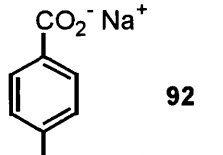
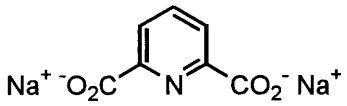
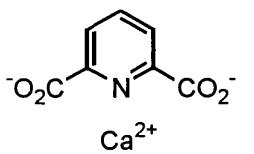
	Starting materials / Sources	yield
 **88** dilithium 1,3-benzenedicarboxylate	isophthalic acid (2.00 g, 12.0 mmol) lithium hydroxide (0.58 g, 24.2 mmol)	2.04 g, 11.5 mmol, 95%
 **89** disodium 1,3-benzenedicarboxylate	isophthalic acid (2.00 g, 12.0 mmol) sodium hydroxide (0.96 g, 24.0 mmol)	2.46 g, 11.7 mmol, 97%
 **90** dipotassium 1,3-benzenedicarboxylate	isophthalic acid (2.01 g, 12.1 mmol) potassium hydroxide (1.36 g, 24.2 mmol)	2.73 g, 11.3 mmol, 93%
 **91** calcium 1,3-benzenedicarboxylate	isophthalic acid (1.12 g, 6.7 mmol) calcium hydroxide (0.50 g, 6.7 mmol)	1.17 g, 5.7 mmol, 85%
 **92** disodium 1,4-benzenedicarboxylate	commercially available from Aldrich	----------
 **93** disodium dipicolinate	dipicolinic acid (2.00 g, 12.0 mmol) sodium hydroxide (0.96 g, 24.0 mmol)	2.31 g, 10.9 mmol, 91%
 **94** calcium dipicolinate	dipicolinic acid (1.25 g, 7.5 mmol) calcium hydroxide (0.56 g, 7.6 mmol)	1.24 g, 6.0 mmol, 81%

Table 3.2

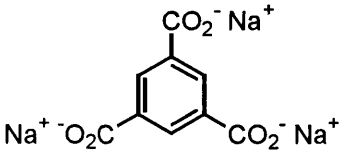
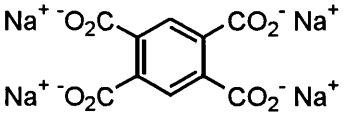
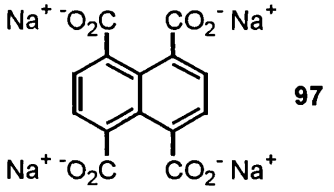
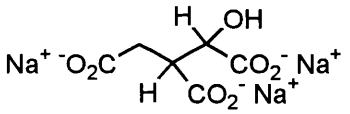
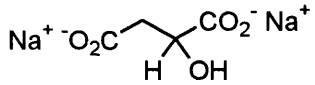
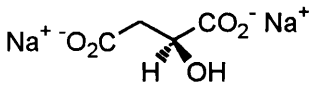
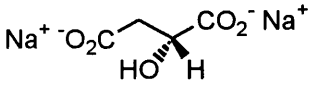
	Starting materials / Sources	yield
 **95** trisodium 1,3,5-benzenetricarboxylate	trimesic acid (1.80 g, 8.6 mmol) sodium hydroxide (1.03 g, 25.8 mmol)	2.12 g, 7.7 mmol, 90%
 **96** tetrasodium 1,2,4,5-benzenetetracarboxylate	pyromellitic acid (1.50 g, 5.9 mmol) sodium hydroxide (0.95 g, 23.8 mmol)	1.67 g, 4.9 mmol, 83%
 **97** tetrasodium 1,4,5,8-naphthalene-tetracarboxylate	1,4,5,8-naphthalene-tetracarboxylic acid hydrate (1.53 g, 5.0 mmol) sodium hydroxide solution was added until the pH of the mixture became neutral	1.51 g, 3.9 mmol, 77%
 **98** tripotassium DL-isocitrate	DL-isocitric acid, monopotassium salt (10.00 g, 43.4 mmol) potassium hydroxide (4.87 g, 86.8 mmol)	11.92 g, 38.9 mmol, 90%
 **99** disodium DL-malate	DL-malic acid (10.00 g, 74.6 mmol) sodium hydroxide (5.97 g, 149.2 mmol)	13.21 g, 74.2 mmol, 99%
 **100** disodium D-malate	D-malic acid (0.70 g, 5.2 mmol) sodium hydroxide (0.42 g, 10.5 mmol)	0.89 g, 5.0 mmol, 96%
 **101** disodium L-malate	commercially available from Aldrich	----------

Table 3.3

3.8 NMR Titrations and Job Plots

This section consists of a series of tables summarising results obtained from NMR titrations using dications **41-43**, trications **45-46** and tetracations **52-56** with a variety of polyanions synthesised. For anions where more than one chemical shift was observed, only the simplest and clearest signal was used for calculations, as all the chemical shifts moved equally and in the same direction as each other. The anionic signal used for each titration is indicated in bold later in this section. For the polycations, the benzyl and methyl signals were used for calculations, as they are usually the simplest and clearest. Where more than one titration was performed, the results shown are the average over all experiments.

3.8.1 General Procedure – NMR Titration

Two standardised solutions **X** and **Y** were prepared in deuterium oxide at known concentration. Solution **X** contains polycation and polyanion, whereas solution **Y** contains polyanion only. These solutions were then combined to give a constant volume of 0.8 mL and the ratio host:guest was varied stepwise from 5:1 to zero unless otherwise stated using 1.0 mL syringes. The accuracy of this syringe is ± 0.01 mL. ^{1}H NMR spectra were taken at 8 relative concentrations. Spectra were recorded at 300 MHz on a Bruker 300 instrument. Chemical shifts at different concentrations were observed and the changes in chemical shifts were plotted against host:guest ratio. This affords association constants of the complexes.

Experiment errors in chemical shifts were determined as follows:

$$\delta_{\varepsilon set1} = \delta_{ave} - \delta_{set1}$$
$$\delta_{\varepsilon set2} = \delta_{ave} - \delta_{set2}$$
$$\delta_{\varepsilon set3} = \delta_{ave} - \delta_{set3}$$

where δ_ε is the error in chemical shift, δ_{ave} is the average chemical shift of three sets of titrations and $\delta_{set n}$ is the chemical shift of one one titration for one specific concentration. The largest of the three δ_ε values was then used as the experimental error.

3.8.2 General Procedure – Job Plot

Standardised solutions of polycation and polyanion were prepared in deuterium oxide at same concentration. Solutions of different relative concentrations were prepared and the total concentration of host and guest remained constant using 1.0 mL syringes. The accuracy of this syringe is ± 0.01 mL. ^{1}H NMR spectra were taken at 9 relative concentrations. Spectra were recorded at 300 MHz on a Bruker AC300 instrument. The changes in chemical shifts of both cationic and anionic protons were recorded. The concentrations of the complex at different concentrations were estimated as follows:

$$[AC] = \frac{[A]_{tot}\,(\delta_{obs}-\delta_A)}{\delta_{AC}-\delta_A}$$

where: [AC] = concentration of the complex

$[A]_{tot}$ = total concentration of A in solution

δ_{obs} = observed chemical shift

δ_A = chemical shift in the environment of A only

δ_{AC} = chemical shift in the complex (obtained from NMR titration data)

The same equation was used to determine the concentration of complex from measurements of the chemical shifts in the polycations. The concentration of complex was plotted against mole fraction. This leads to preferred stoichiometries of the complexes.

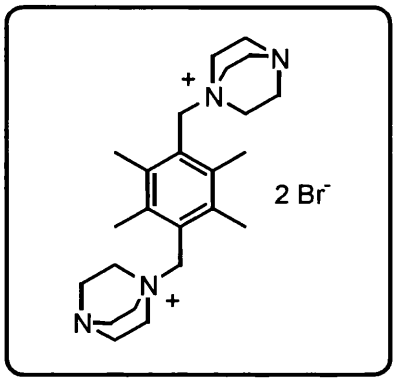
Experimental errors in the concentrations of the complex were calculated using the following equation:

$$[AC]_\varepsilon = \left(\frac{[A]_{tot}\,((\delta_{obs} + \delta_{\varepsilon obs})-(\delta_A + \delta_{\varepsilon A}))}{\delta_{AC} - (\delta_A + \delta_{\varepsilon A})}\right) - [AC]$$

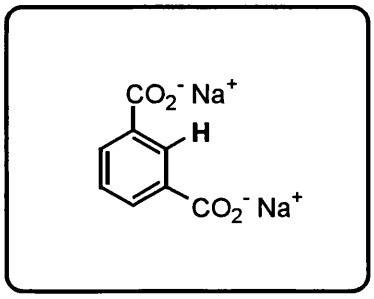
where $[AC]_\varepsilon$ is the error in concentration of the complex, $\delta_{\varepsilon A}$ is the error in the chemical shift in the environment of A only and $\delta_{\varepsilon obs}$ is the error in the observed chemical shift. Both $\delta_{\varepsilon A}$ and $\delta_{\varepsilon obs}$ were determined by using the same method of calculating errors in chemical shifts described in section 3.8.1.

Results of these experiments are available in separate appendix and one example is given below.

3.8.3 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and disodium 1,3-benzenedicarboxylate



41



89

NMR Titration

	37 / g	79 / g	D_2O / mL	[4] / mM	[39] / mM
Solution X	0.2722	0.0212	10	50.00	10.09
Solution Y	0	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[89] / mM	Ratio (41:89)	δ	Δδ	Error
0.80	0.00	50.00	10.09	4.96	7.90543	0.22864	0.00115
0.40	0.40	25.00	10.04	2.49	7.96177	0.17230	0.00020
0.30	0.50	18.75	10.03	1.87	7.98608	0.14799	0.00081
0.20	0.60	12.50	10.02	1.25	8.01763	0.11643	0.00060
0.15	0.65	9.37	10.01	0.94	8.03516	0.09891	0.00044
0.10	0.70	6.25	10.01	0.62	8.06504	0.06902	0.00313
0.05	0.75	3.12	10.00	0.31	8.09266	0.04140	0.00099
0.00	0.80	0.00	10.00	0.00	8.13406	0.00000	0.00070

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[89] / mM	Ratio (89:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	2.26564	0.00000	0.00095
0.80	0.00	50.00	10.09	0.20	2.22503	0.04061	0.00095
0.40	0.40	25.00	10.04	0.40	2.21240	0.05324	0.00034
0.30	0.50	18.75	10.03	0.53	2.20661	0.05903	0.00066
0.20	0.60	12.50	10.02	0.80	2.19792	0.06772	0.00017
0.15	0.65	9.37	10.01	1.07	2.18950	0.07614	0.00065
0.10	0.70	6.25	10.01	1.60	2.18247	0.08317	0.00035
0.05	0.75	3.12	10.00	3.20	2.17198	0.09366	0.00129

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[89] / mM	Ratio (89:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	4.78070	0.00000	0.00126
0.80	0.00	50.00	10.09	0.20	4.72879	0.05191	0.00080
0.40	0.40	25.00	10.04	0.40	4.71353	0.06717	0.00016
0.30	0.50	18.75	10.03	0.53	4.70712	0.07358	0.00063
0.20	0.60	12.50	10.02	0.80	4.69724	0.08347	0.00040
0.15	0.65	9.37	10.01	1.07	4.68794	0.09276	0.00088
0.10	0.70	6.25	10.01	1.60	4.67064	0.11007	0.00007
0.05	0.75	3.12	10.00	3.20	4.67075	0.10996	0.00011

Job Plot

	41 / g	89 / g	D_2O / mL	[41] / mM	[89] / mM
Solution X	0.1361	0.0000	25	10.00	0.00
Solution Y	0.0000	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[89]_{tot}$ / mM	Mf of 89	δ	[41•89] / mM	Error / mM
0.70	0.10	1.25	0.12	8.00565	0.48	0.02
0.60	0.20	2.50	0.25	8.01666	0.88	0.01
0.50	0.30	3.75	0.37	8.03333	1.13	0.00
0.40	0.40	5.00	0.50	8.05254	1.21	0.03
0.30	0.50	6.25	0.62	8.07280	1.12	0.00
0.20	0.60	7.50	0.75	8.09078	0.93	0.02
0.10	0.70	8.75	0.87	8.11274	0.49	0.01
0.00	0.80	10.00	1.00	8.13082	0.00	0.00

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•89] / mM	Error / mM
0.80	0.00	10.00	1.00	2.26564	0.00	0.00
0.70	0.10	8.75	0.88	2.25072	1.39	0.03
0.60	0.20	7.50	0.75	2.23701	2.29	0.13
0.50	0.30	6.25	0.63	2.22152	2.94	0.01
0.40	0.40	5.00	0.50	2.20682	3.14	0.10
0.30	0.50	3.75	0.38	2.19317	2.90	0.02
0.20	0.60	2.50	0.25	2.17880	2.32	0.07
0.10	0.70	1.25	0.13	2.16851	1.30	0.02

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•89] / mM	Error / mM
0.80	0.00	10.04	1.00	4.78070	0.00	0.00
0.70	0.10	8.78	0.88	4.76268	1.41	0.01
0.60	0.20	7.53	0.75	4.74589	2.34	0.08
0.50	0.30	6.27	0.63	4.72816	2.94	0.01
0.40	0.40	5.01	0.50	4.71091	3.12	0.08
0.30	0.50	3.76	0.38	4.69490	2.88	0.02
0.20	0.60	2.51	0.25	4.67055	2.47	0.01
0.10	0.70	1.25	0.13	4.67050	1.23	0.00

3.8 Electrochemistry

3.8.1 Preparations

Three electrolytes were prepared.

1. Buffer solution (50 mM): potassium dihydrogen phosphate (13.6090 g, 100.00 mmol) and sodium hydroxide (2.3318 g, 58.30 mmol) were dissolved in water (2000 mL). The measured pH of the buffered electrolyte was 7.0.
2. Ferrocyanide solution (5 mM): potassium ferrocyanide trihydrate (0.5280 g, 1.25 mmol) was dissolved in the buffered solution (250 mL).
3. Bromide solution (5 mM): sodium bromide (0.1286 g, 1.25 mmol) was dissolved in the buffered solution (250 mL).

Microband electrodes were snapped along a pre-scribed line to expose a fresh gold surface and the electrode was then immediately dipped into methanol solutions of one of the thiols **78**, **82**, **83** or **84**. The electrodes were removed from the solutions after 2 minutes and dried in air before being used.

3.8.2 Measurements

The measurements were carried out with an Eco Chemie Autolab. A cell with a three-electrode configuration surrounded by a Faraday cage was used. The counter and reference electrodes were platinium foil and saturated calomel electrode (SCE), respectively. A simplified instrumental set-up for cyclic voltammetric experiments is shown in Figure 3.1.

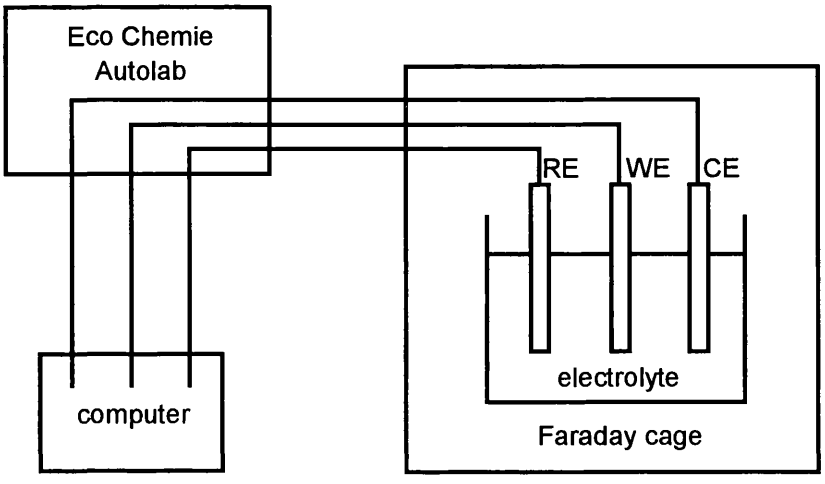


Figure 3.1 – Instrumental set-up for cyclic voltammetric experiments

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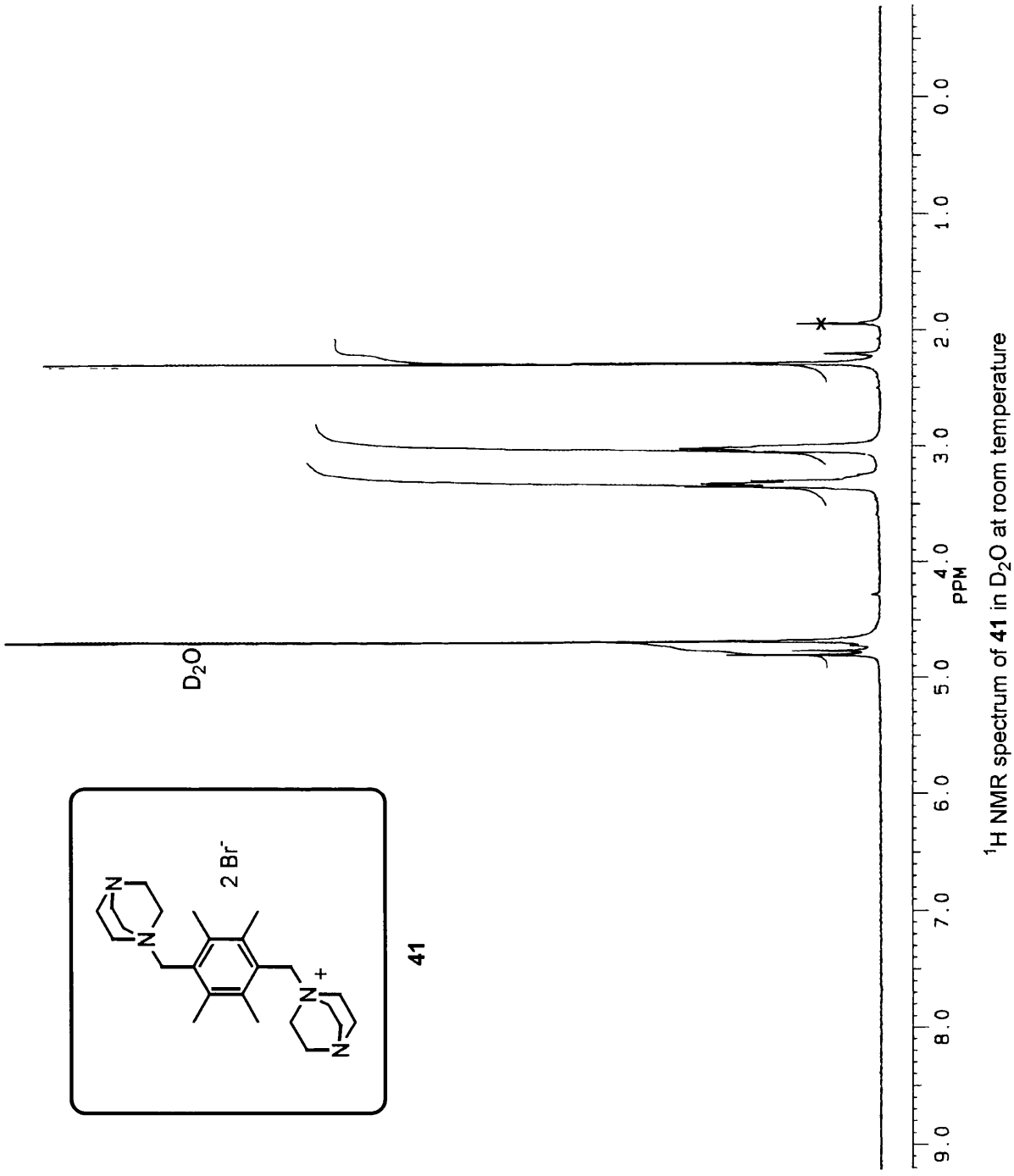
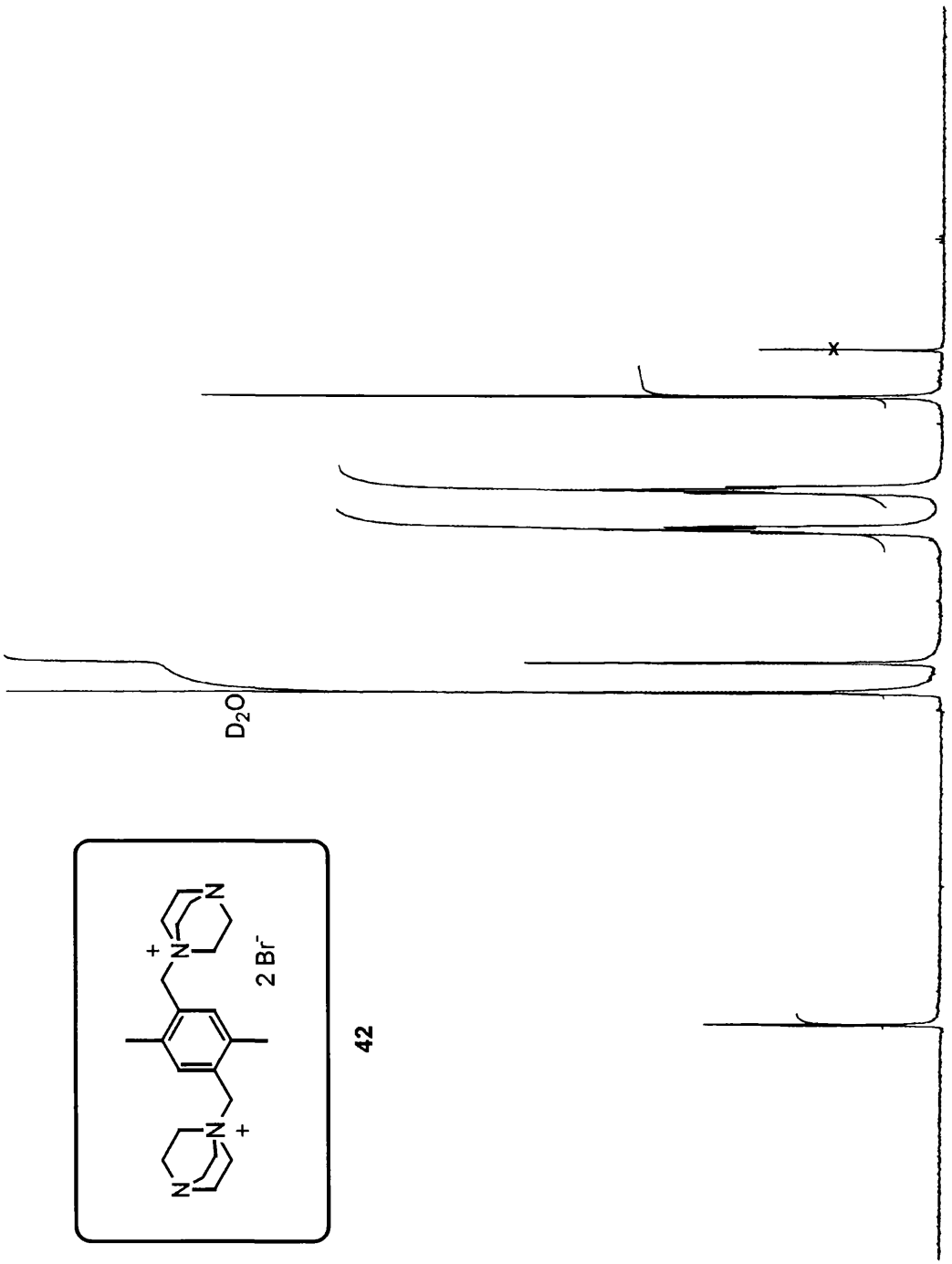
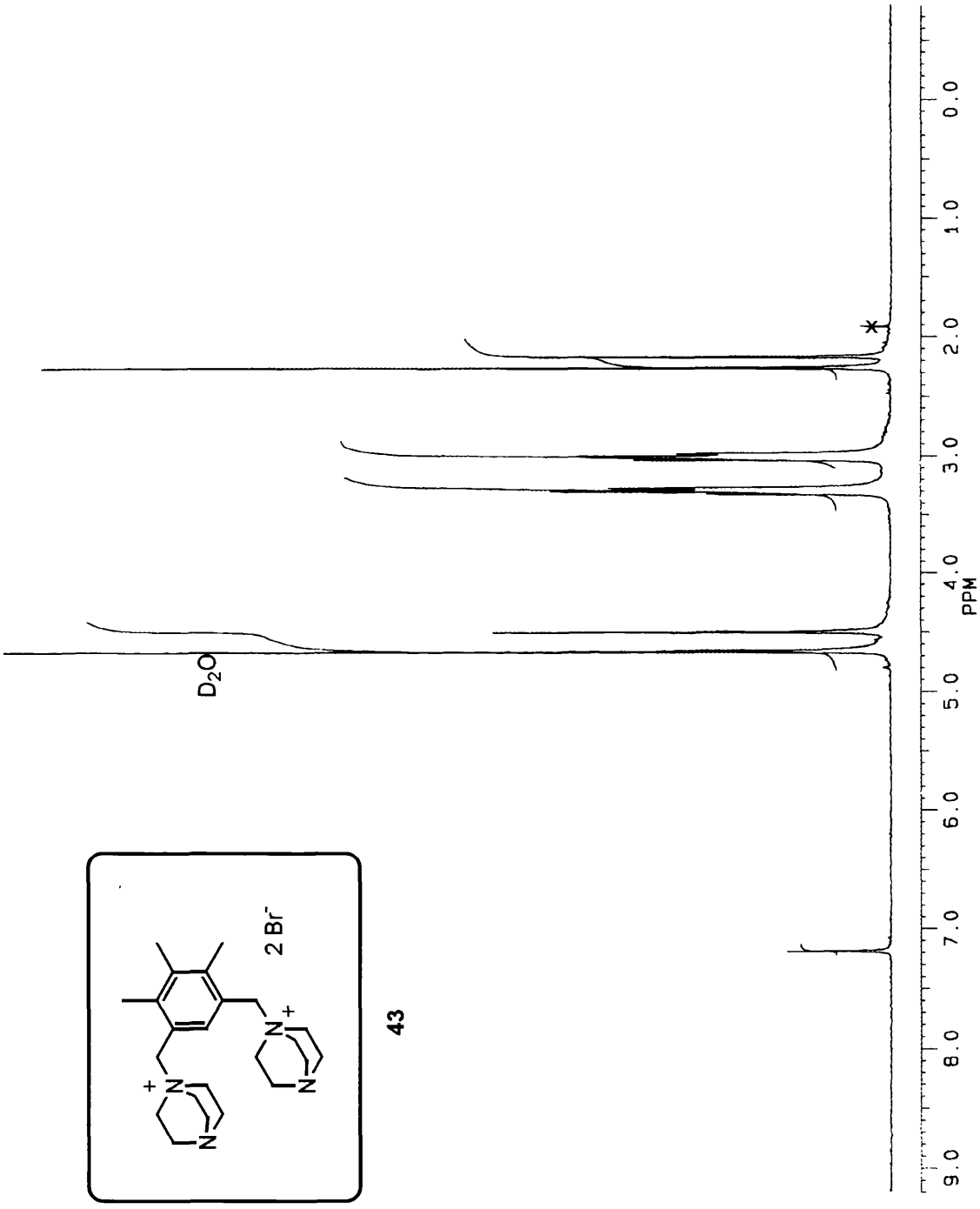


41

^{1}H NMR spectrum of **41** in D_2O at room temperature

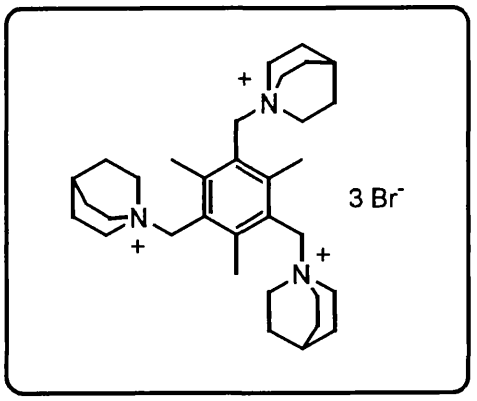


^{1}H NMR spectrum of **42** in D_2O at room temperature



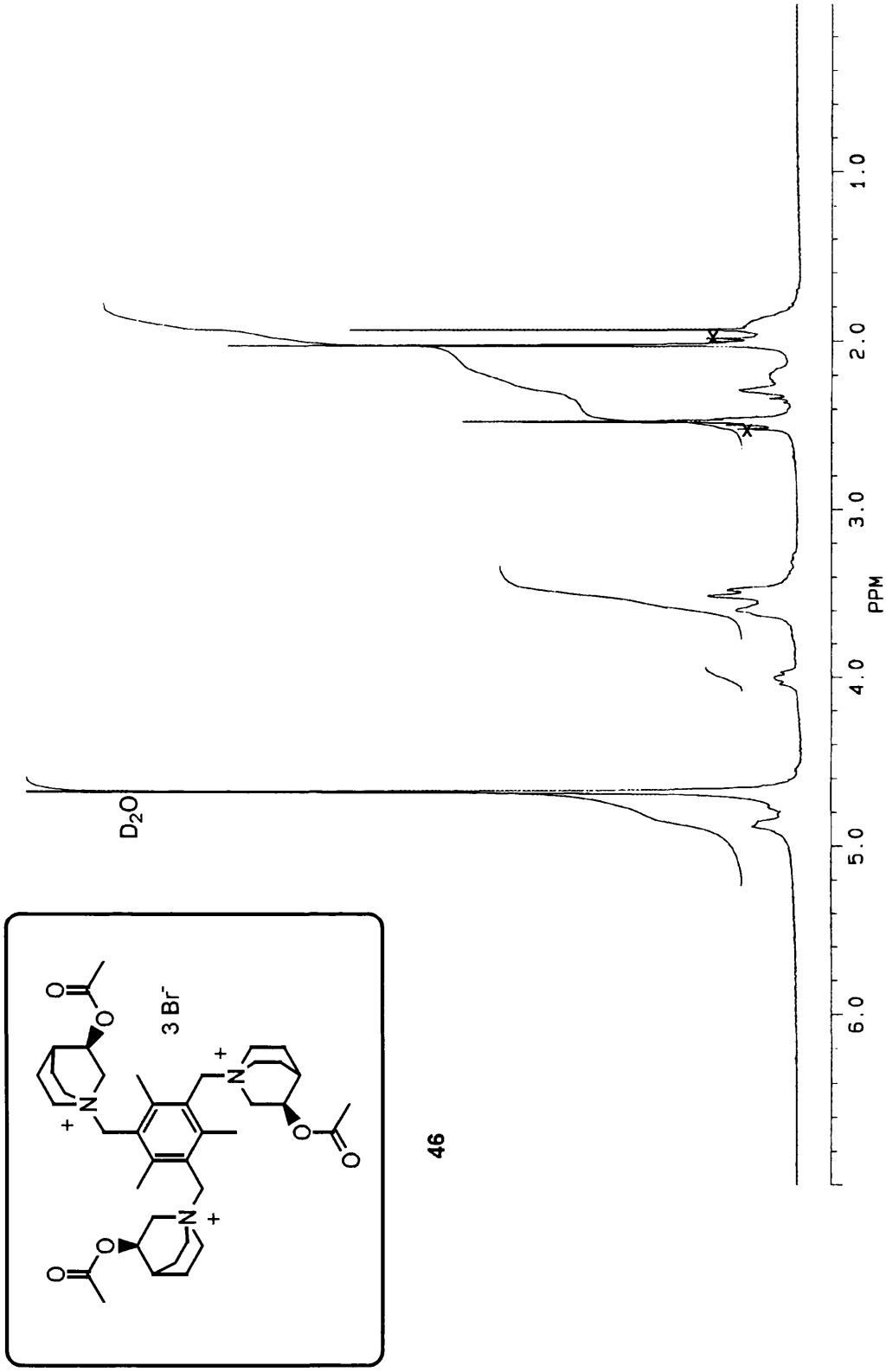
43

^{1}H NMR spectrum of **43** in D_2O at room temperature



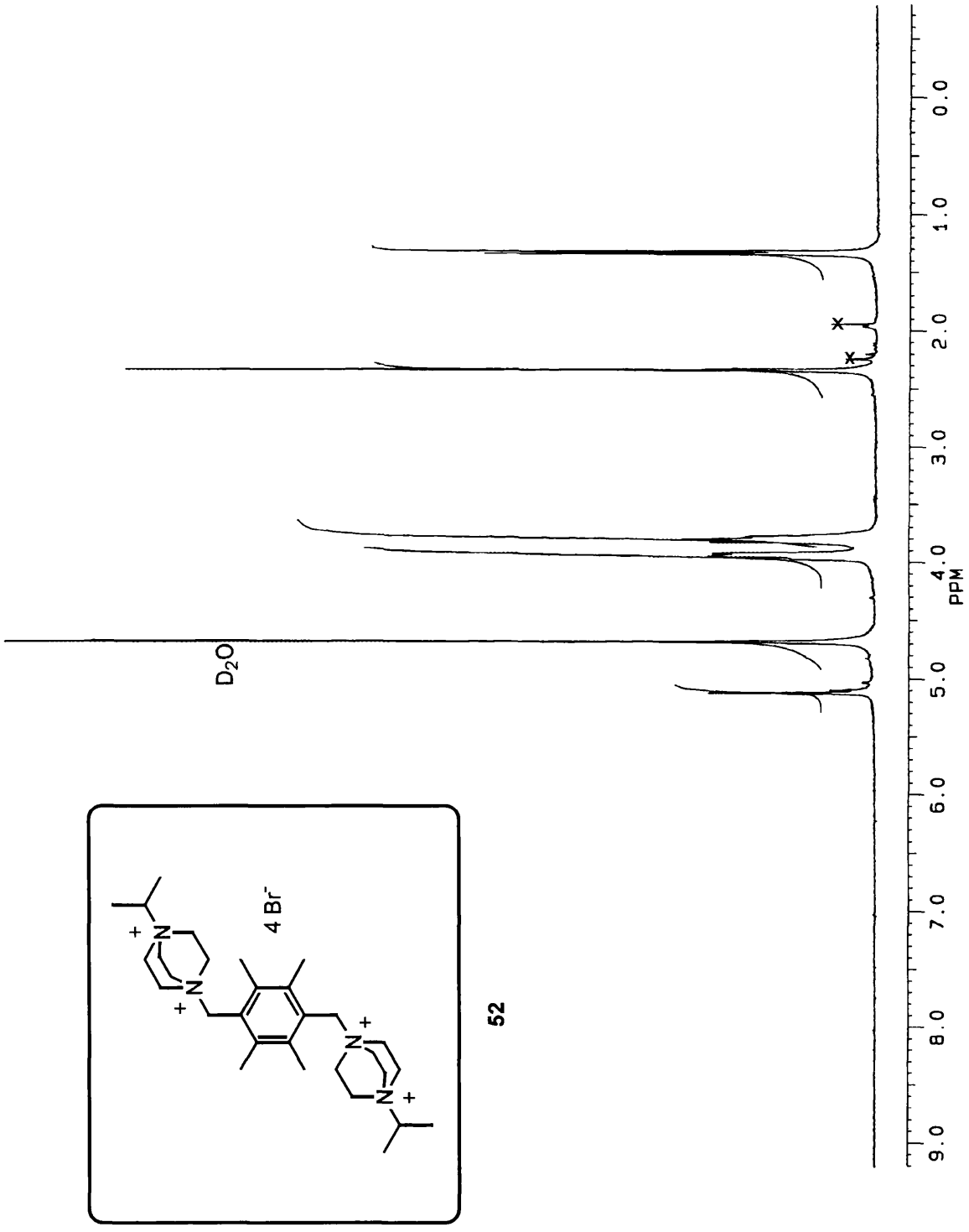
45

^{1}H NMR spectrum of **45** in D_2O at room temperature

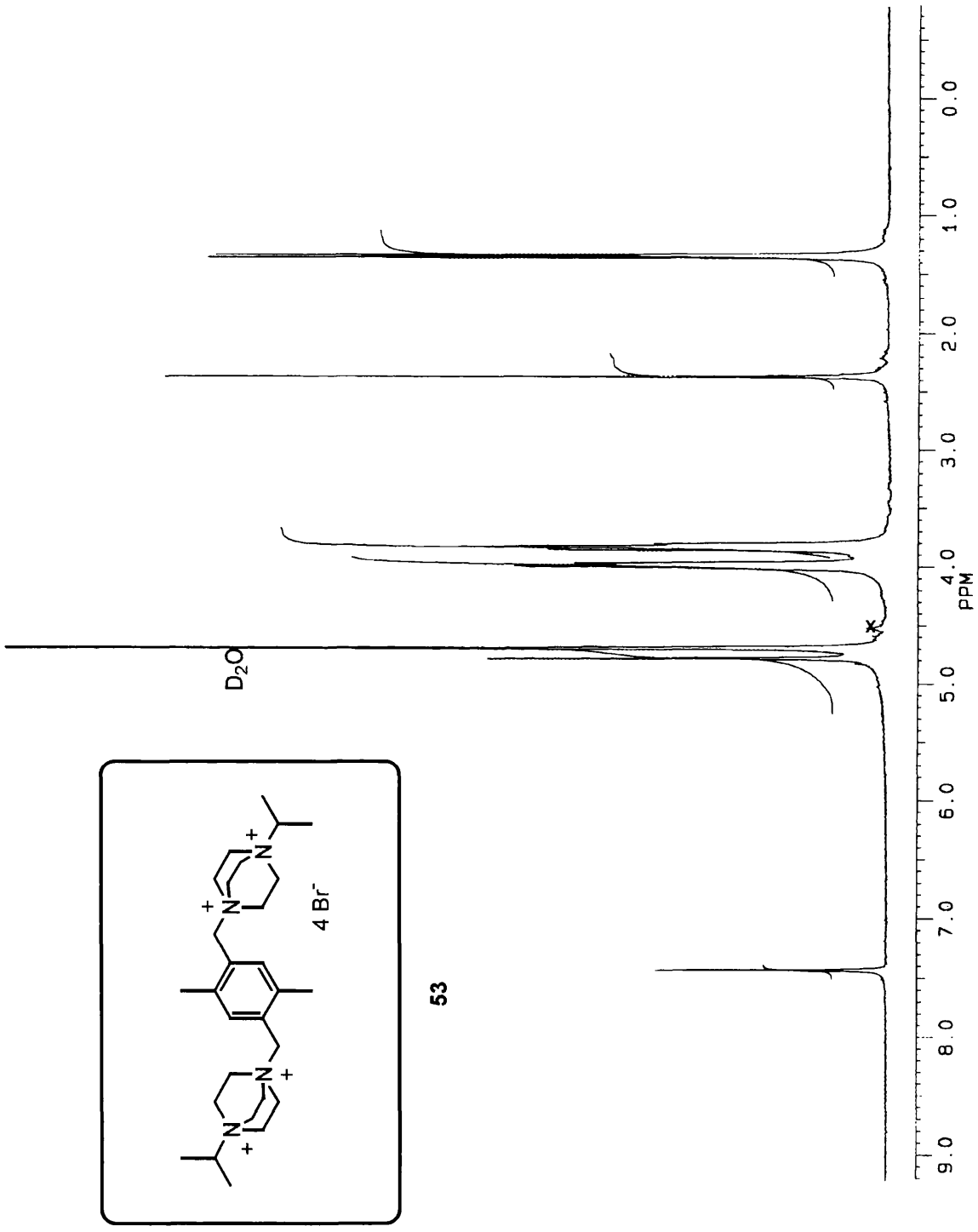


46

^{1}H NMR spectrum of **46** in D_2O at room temperature

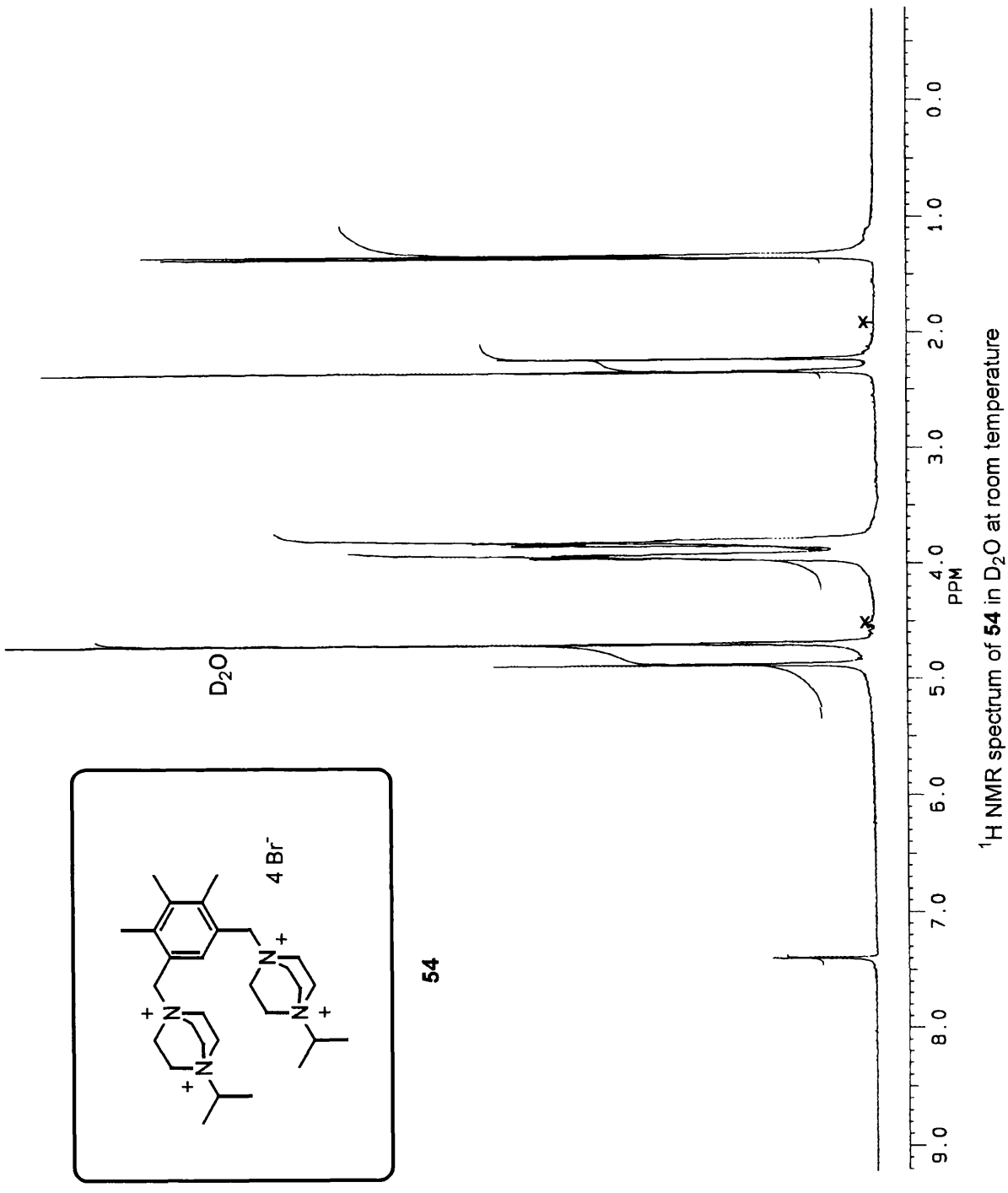


^{1}H NMR spectrum of **52** in D_2O at room temperature

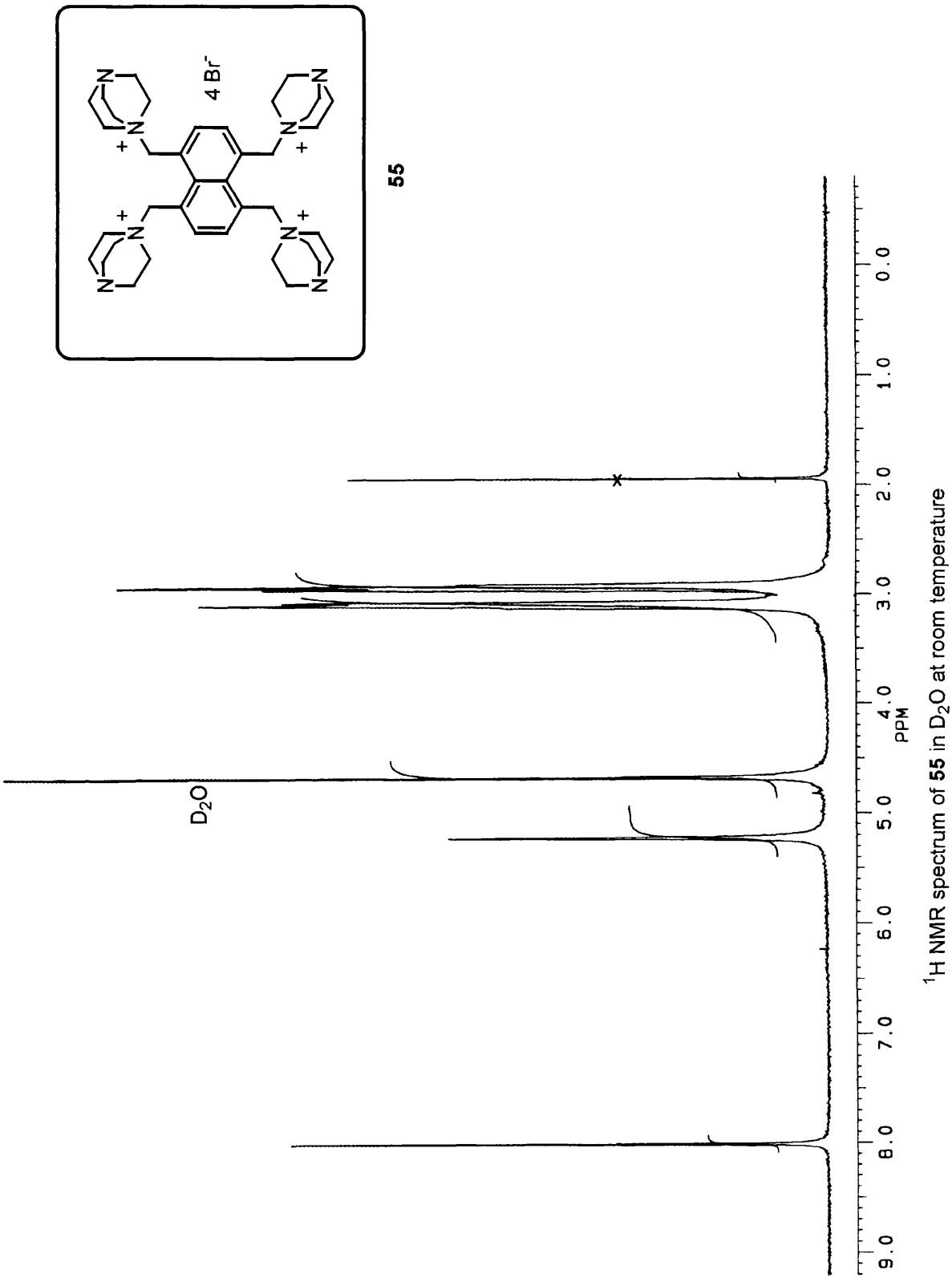


53

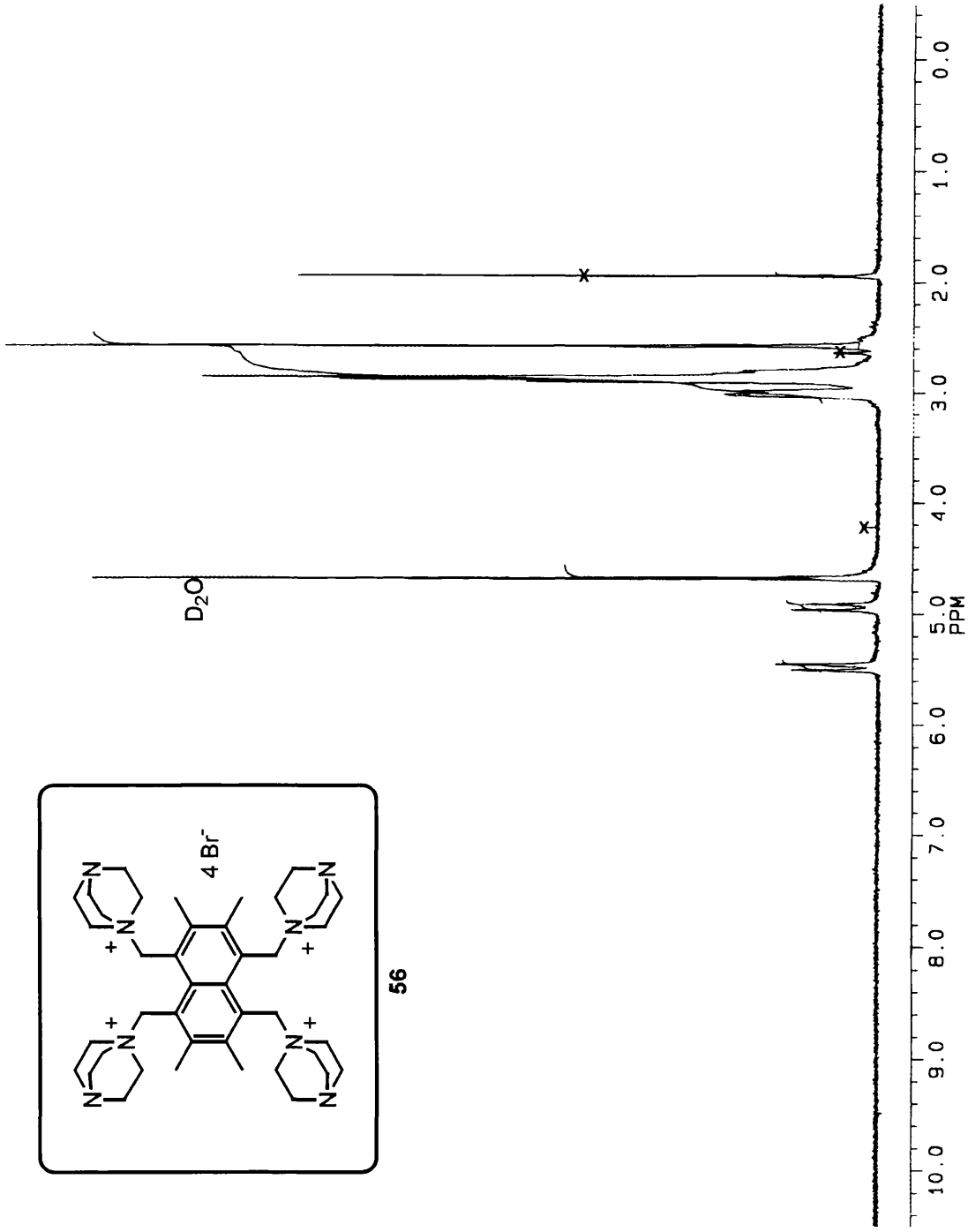
^{1}H NMR spectrum of **53** in D_2O at room temperature



^{1}H NMR spectrum of **54** in D_2O at room temperature

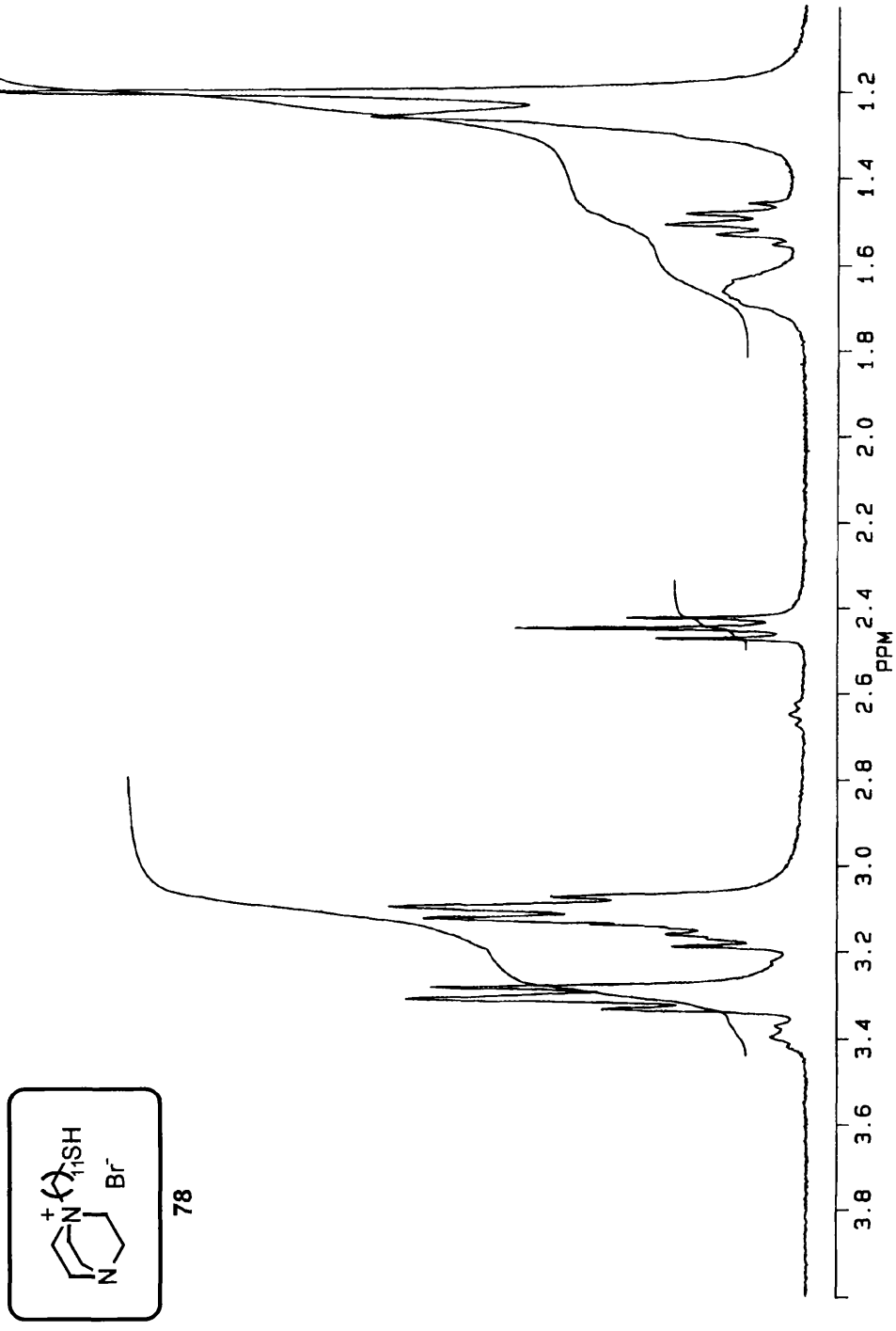


^{1}H NMR spectrum of **55** in D_2O at room temperature

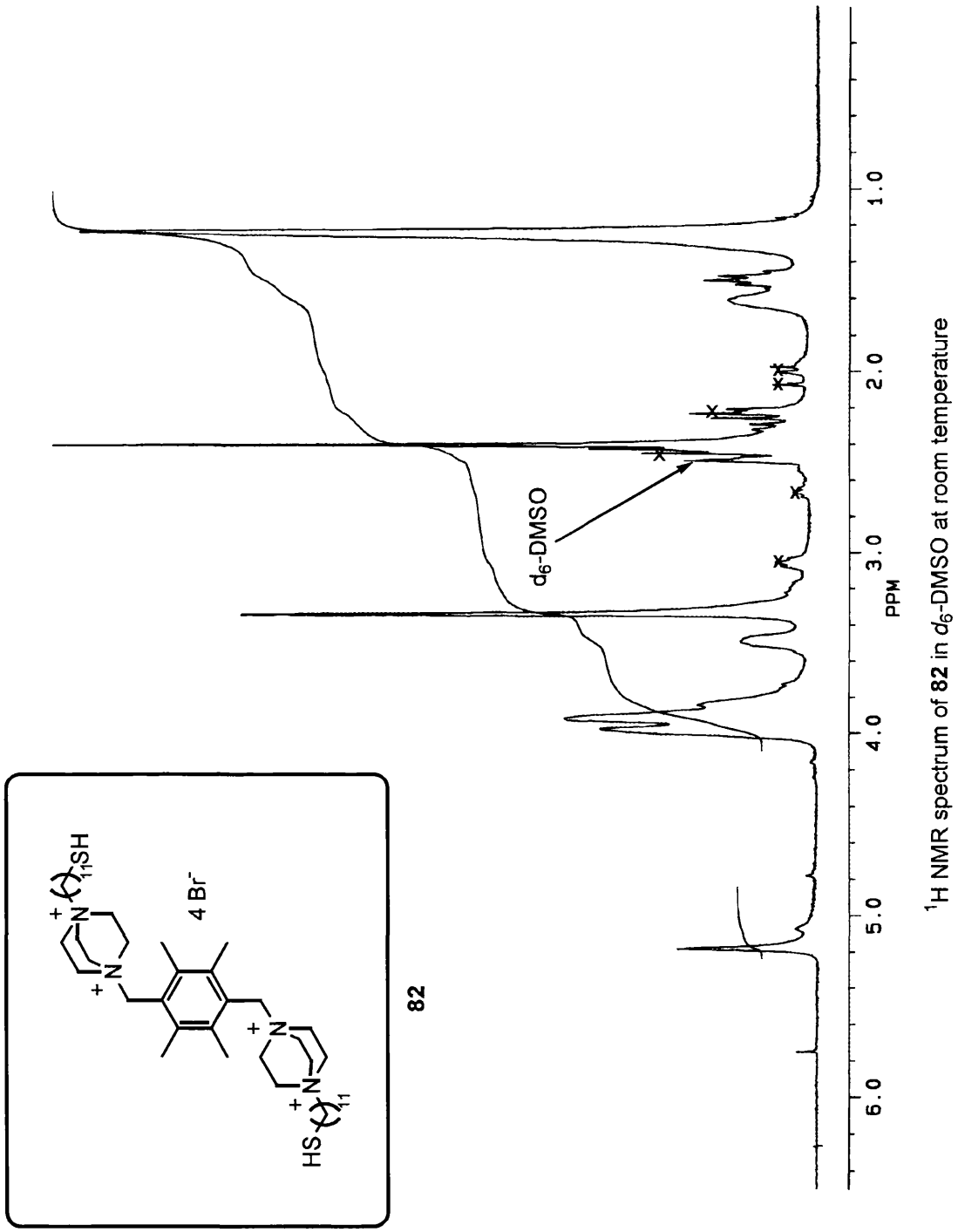


56

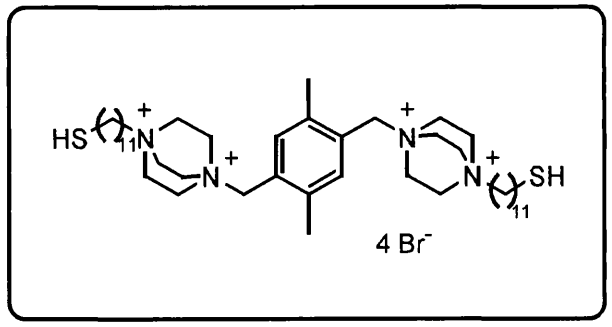
^{1}H NMR spectrum of **56** in D_2O at room temperature



^{1}H NMR spectrum of **78** in D_2O at room temperature

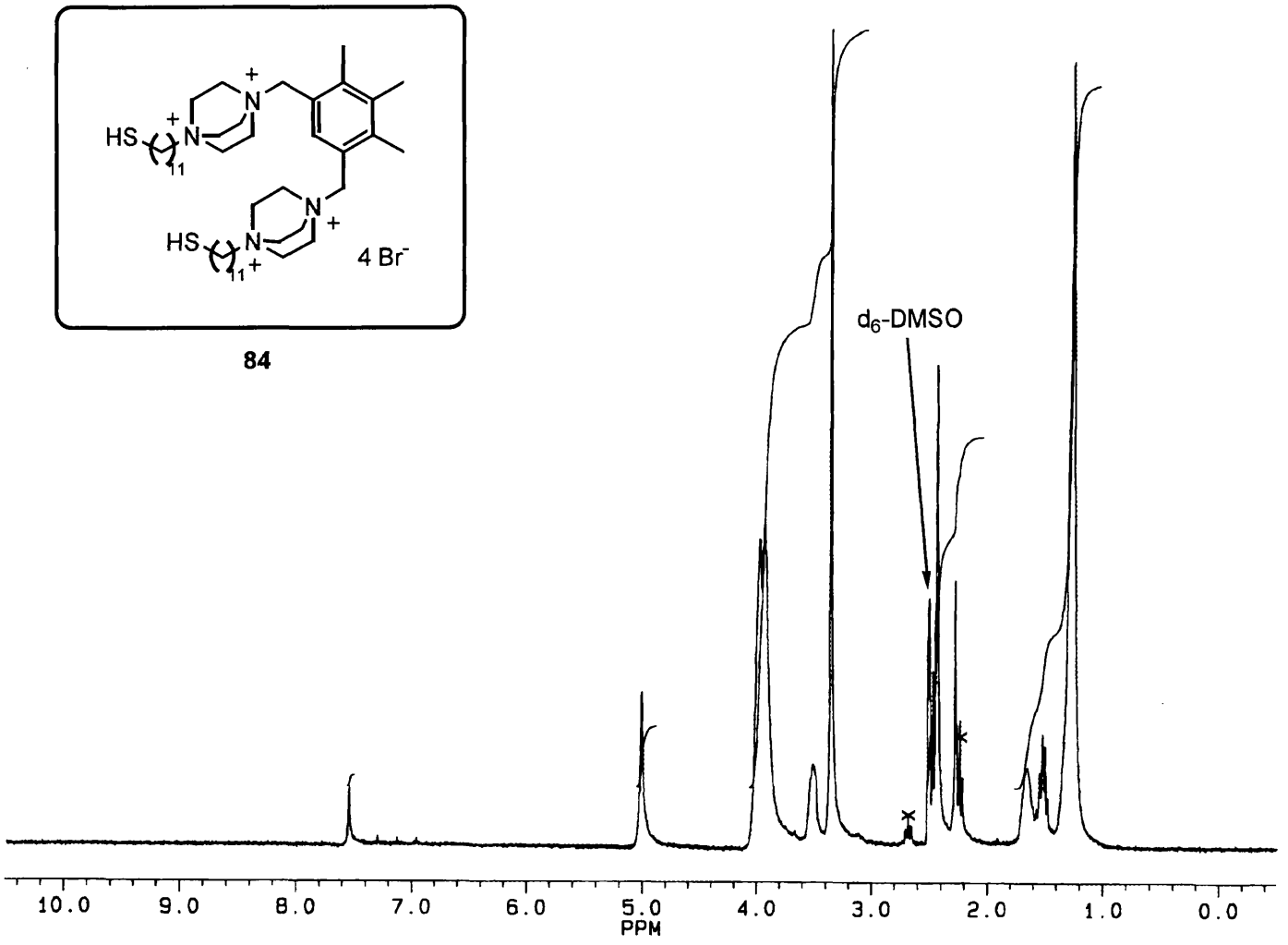


^{1}H NMR spectrum of **82** in d_6-DMSO at room temperature



83

^{1}H NMR spectrum of **83** in d_6-DMSO at room temperature



84

^{1}H NMR spectrum of **84** in d_6-DMSO at room temperature

Molecular Recognition Using Highly Charged Podands

(Appendix B – Results of NMR Titrations and Job Plots)

Part of a thesis presented to the University College London in partial fulfilment of the requirements for the degree of Doctor of Philosophy

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NMR Titrations and Job Plots

This section consists of a series of tables summarising results obtained from NMR titrations using dications **41-43**, trications **45-46** and tetracations **52-56** with a variety of polyanions synthesised. For anions where more than one chemical shift was observed, only the simplest and clearest signal was used for calculations, as all the chemical shifts moved equally and in the same direction as each other. The anionic signal used for each titration is indicated in bold later in this section. For the polycations, the benzyl and methyl signals were used for calculations, as they are usually the simplest and clearest. Where more than one titration was performed, the results shown are the average over all experiments.

A.1 General Procedure – NMR Titration

Two standardised solutions **X** and **Y** were prepared in deuterium oxide at known concentration. Solution **X** contains polycation and polyanion, whereas solution **Y** contains polyanion only. These solutions were then combined to give a constant volume of 0.8 mL and the ratio host:guest was varied stepwise from 5:1 to zero unless otherwise stated using 1.0 mL syringes. The accuracy of this syringe is ± 0.01 mL. ^{1}H NMR spectra were taken at 8 relative concentrations. Spectra were recorded at 300 MHz on a Bruker 300 instrument. Chemical shifts at different concentrations were observed and the changes in chemical shifts were plotted against host:guest ratio. This affords association constants of the complexes.

Experiment errors in chemical shifts were determined as follows:

$$\delta_{\varepsilon set1} = \delta_{ave} - \delta_{set1}$$

$$\delta_{\varepsilon set2} = \delta_{ave} - \delta_{set2}$$

$$\delta_{\varepsilon set3} = \delta_{ave} - \delta_{set3}$$

where δ_ε is the error in chemical shift, δ_{ave} is the average chemical shift of three sets of titrations and $\delta_{set n}$ is the chemical shift of one one titration for one specific concentration. The largest of the three δ_ε values was then used as the experimental error.

A.2 General Procedure – Job Plot

Standardised solutions of polycation and polyanion were prepared in deuterium oxide at same concentration. Solutions of different relative concentrations were prepared and the total concentration of host and guest remained constant using 1.0 mL syringes. The accuracy of this syringe is ± 0.01 mL. ^{1}H NMR spectra were taken at 9 relative concentrations. Spectra were recorded at 300 MHz on a Bruker AC300 instrument. The changes in chemical shifts of both cationic and anionic protons were recorded. The concentrations of the complex at different

$$[AC] = \frac{[A]_{tot}\,(\delta_{obs}-\delta_A)}{\delta_{AC}-\delta_A}$$

concentrations were estimated as follows:

where: [AC] = concentration of the complex

$[A]_{tot}$ = total concentration of A in solution

δ_{obs} = observed chemical shift

δ_A = chemical shift in the environment of A only

δ_{AC} = chemical shift in the complex (obtained from NMR titration data)

The same equation was used to determine the concentration of complex from measurements of the chemical shifts in the polycations. The concentration of complex was plotted against mole fraction. This leads to preferred stoichiometries of the complexes.

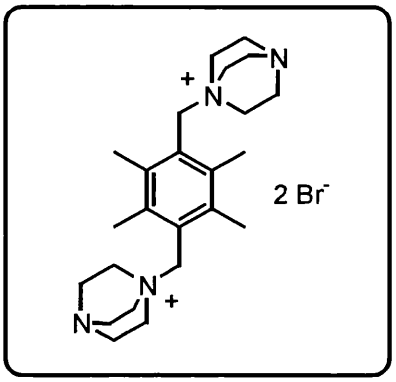
Experimental errors in the concentrations of the complex were calculated by using the same method described above to find the errors in δ_{obs} and δ_A which were then substituted into the equation below:

$$[AC]_\varepsilon = \left(\frac{[A]_{tot}\,((\delta_{obs} + \delta_{\varepsilon obs})-(\delta_A + \delta_{\varepsilon A}))}{\delta_{AC} - (\delta_A + \delta_{\varepsilon A})} \right) - [AC]$$

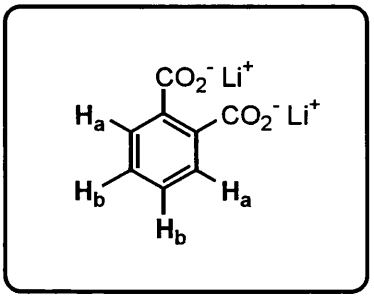
Where $[AC]_\varepsilon$ is the error in concentration of the complex, $\delta_{\varepsilon A}$ is the error in the chemical shift in the environment of A only and $\delta_{\varepsilon obs}$ is the error in the observed chemical shift.

Results of these experiments are available in separate appendix and one example is given below.

A.3 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and dilithium 1,2-benzenedicarboxylate



41



85

NMR Titration

	41 / g	85 / g	D_2O / mL	[41] / mM	[85] / mM
Solution X	0.2725	0.0190	10	50.05	10.67
Solution Y	0.0000	0.0453	25	0.00	10.18

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	[41] / mM	[85] / mM	Ratio (41:85)	δ	$\Delta\delta$	Error
0.80	0.00	50.05	10.67	4.69	7.24108	0.05538	0.00053
0.40	0.40	25.03	10.43	2.40	7.25799	0.03846	0.00046
0.30	0.50	18.77	10.37	1.81	7.26380	0.03266	0.00048
0.20	0.60	12.51	10.30	1.22	7.27071	0.02574	0.00005
0.15	0.65	9.39	10.27	0.91	7.27526	0.02119	0.00009
0.10	0.70	6.26	10.24	0.61	7.28054	0.01591	0.00013
0.05	0.75	3.13	10.21	0.31	7.28743	0.00902	0.00022
0.00	0.80	0.00	10.18	0.00	7.29645	0.00000	0.00057

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[85] / mM	Ratio (85:41)	δ	Δδ	Error
Cation reference		10.05	0.00	0.00	2.27439	0.00000	0.00013
0.80	0.00	50.05	10.67	0.21	2.26777	0.00662	0.00071
0.40	0.40	25.03	10.43	0.42	2.26617	0.00822	0.00028
0.30	0.50	18.77	10.37	0.55	2.26577	0.00862	0.00031
0.20	0.60	12.51	10.30	0.82	2.26481	0.00958	0.00031
0.15	0.65	9.39	10.27	1.10	2.26350	0.01089	0.00008
0.10	0.70	6.26	10.24	1.64	2.26277	0.01162	0.00045
0.05	0.75	3.13	10.21	3.26	2.26117	0.01322	0.00031

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[85] / mM	Ratio (85:41)	δ	Δδ	Error
Cation reference		10.05	0.00	0.00	4.77044	0.00000	0.00009
0.80	0.00	50.05	10.67	0.21	4.75836	0.01208	0.00053
0.40	0.40	25.03	10.43	0.42	4.75882	0.01162	0.00033
0.30	0.50	18.77	10.37	0.55	4.75826	0.01218	0.00017
0.20	0.60	12.51	10.30	0.82	4.75725	0.01319	0.00011
0.15	0.65	9.39	10.27	1.10	4.75632	0.01412	0.00010
0.10	0.70	6.26	10.24	1.64	4.75521	0.01523	0.00015
0.05	0.75	3.13	10.21	3.26	4.75376	0.01668	0.00025

Job Plot

	41 / g	85 / g	D_2O / mL	[41] / mM	[85] / mM
Solution X	0.0821	0.0000	15	10.05	0.00
Solution Y	0.0000	0.0453	25	0.00	10.18

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	$[85]_{tot}$ / mM	Mf of 85	δ	[41•85] / mM	Error / mM
0.70	0.10	1.29	0.13	7.27109	0.39	0.01
0.60	0.20	2.57	0.25	7.27457	0.67	0.02
0.50	0.30	3.85	0.38	7.27787	0.86	0.01
0.40	0.40	5.12	0.50	7.28129	0.93	0.02
0.30	0.50	6.39	0.63	7.28505	0.86	0.01
0.20	0.60	7.66	0.75	7.28800	0.76	0.03
0.10	0.70	8.92	0.88	7.29188	0.46	0.02
0.00	0.80	10.18	1.00	7.29614	0.00	0.00

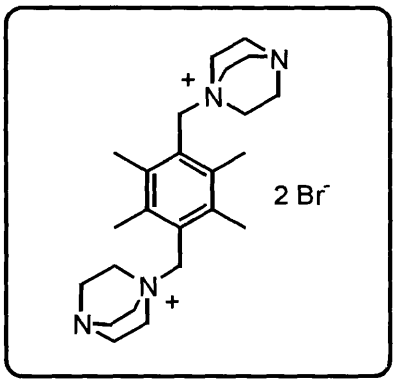
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•85] / mM	Error / mM
0.80	0.00	10.05	1.00	2.27439	0.00	0.00
0.70	0.10	8.78	0.87	2.27228	0.70	0.03
0.60	0.20	7.52	0.75	2.27028	1.17	0.02
0.50	0.30	6.25	0.62	2.26825	1.46	0.04
0.40	0.40	5.00	0.50	2.26585	1.62	0.10
0.30	0.50	3.74	0.37	2.26434	1.43	0.00
0.20	0.60	2.49	0.25	2.26194	1.18	0.08
0.10	0.70	1.24	0.12	2.26038	0.66	0.01

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•85] / mM	Error / mM
0.80	0.00	10.05	1.00	4.77044	0.00	0.00
0.70	0.10	8.78	0.87	4.76804	0.45	0.01
0.60	0.20	7.52	0.75	4.76573	0.75	0.03
0.50	0.30	6.25	0.62	4.76340	0.93	0.02
0.40	0.40	5.00	0.50	4.76087	1.01	0.02
0.30	0.50	3.74	0.37	4.75889	0.91	0.01
0.20	0.60	2.49	0.25	4.75602	0.76	0.04
0.10	0.70	1.24	0.12	4.75387	0.43	0.00

A.4 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and disodium 1,2-benzenedicarboxylate



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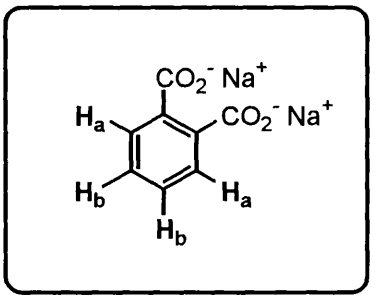


86

NMR Titration

	41 / g	86 / g	D_2O / mL	[41] / mM	[86] / mM
Solution X	0.2724	0.0210	10	50.04	10.00
Solution Y	0.0000	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	[41] / mM	[86] / mM	Ratio (41:86)	δ	$\Delta\delta$	Error
0.80	0.00	50.04	10.00	5.01	7.24559	0.05954	0.00419
0.40	0.40	25.02	10.00	2.50	7.26385	0.04128	0.00314
0.30	0.50	18.76	10.00	1.88	7.27041	0.03472	0.00367
0.20	0.60	12.51	10.00	1.25	7.27801	0.02712	0.00316
0.15	0.65	9.38	10.00	0.94	7.28329	0.02184	0.00218
0.10	0.70	6.25	10.00	0.63	7.28916	0.01596	0.00178
0.05	0.75	3.13	10.00	0.31	7.29568	0.00945	0.00226
0.00	0.80	0.00	10.00	0.00	7.30513	0.00000	0.00192

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[86] / mM	Ratio (86:41)	δ	Δδ	Error
Cation reference		10.02	0.00	0.00	2.28155	0.00000	0.00071
0.80	0.00	50.04	10.00	0.20	2.27616	0.00539	0.00417
0.40	0.40	25.02	10.00	0.40	2.27516	0.00638	0.00355
0.30	0.50	18.76	10.00	0.53	2.27465	0.00689	0.00313
0.20	0.60	12.51	10.00	0.80	2.27327	0.00828	0.00293
0.15	0.65	9.38	10.00	1.07	2.27274	0.00881	0.00223
0.10	0.70	6.25	10.00	1.60	2.27173	0.00981	0.00180
0.05	0.75	3.13	10.00	3.20	2.26980	0.01174	0.00175

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[86] / mM	Ratio (86:41)	δ	Δδ	Error
Cation reference		10.02	0.00	0.00	4.77779	0.00000	0.00084
0.80	0.00	50.04	10.00	0.20	4.76901	0.00878	0.00390
0.40	0.40	25.02	10.00	0.40	4.76854	0.00925	0.00308
0.30	0.50	18.76	10.00	0.53	4.76792	0.00987	0.00310
0.20	0.60	12.51	10.00	0.80	4.76666	0.01113	0.00284
0.15	0.65	9.38	10.00	1.07	4.76619	0.01160	0.00203
0.10	0.70	6.25	10.00	1.60	4.76517	0.01262	0.00169
0.05	0.75	3.13	10.00	3.20	4.76331	0.01449	0.00175

Job Plot

	41 / g	86 / g	D_2O / mL	[41] / mM	[86] / mM
Solution X	0.0818	0.0000	15	10.02	0.00
Solution Y	0.0000	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	$[86]_{tot}$ / mM	Mf of 86	δ	[41•86] / mM	Error / mM
0.70	0.10	1.25	0.12	7.27908	0.35	0.01
0.60	0.20	2.49	0.25	7.28232	0.61	0.01
0.50	0.30	3.74	0.37	7.28549	0.78	0.02
0.40	0.40	4.99	0.50	7.28913	0.84	0.03
0.30	0.50	6.24	0.62	7.29264	0.80	0.02
0.20	0.60	7.49	0.75	7.29619	0.66	0.01
0.10	0.70	8.74	0.87	7.30051	0.34	0.03
0.00	0.80	10.00	1.00	7.30393	0.00	0.00

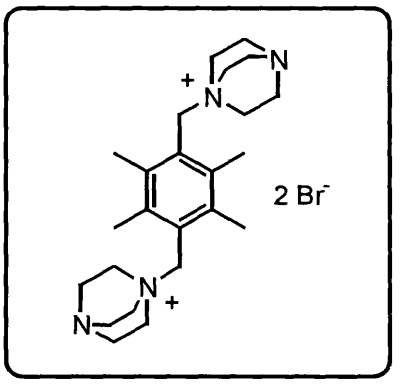
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•86] / mM	Error / mM
0.80	0.00	10.02	1.00	2.28155	0.00	0.00
0.70	0.10	8.77	0.88	2.27957	1.50	0.34
0.60	0.20	7.52	0.75	2.27769	2.51	0.28
0.50	0.30	6.27	0.63	2.27564	3.21	0.43
0.40	0.40	5.01	0.50	2.27397	3.29	0.26
0.30	0.50	3.76	0.38	2.27184	3.16	0.19
0.20	0.60	2.51	0.25	2.26990	2.53	0.15
0.10	0.70	1.25	0.13	2.26777	1.50	0.12

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•86] / mM	Error / mM
0.80	0.00	10.02	1.00	4.77779	0.00	0.00
0.70	0.10	8.77	0.88	4.77551	0.53	0.08
0.60	0.20	7.52	0.75	4.77338	0.88	0.04
0.50	0.30	6.27	0.63	4.77100	1.13	0.08
0.40	0.40	5.01	0.50	4.76889	1.18	0.03
0.30	0.50	3.76	0.38	4.76662	1.11	0.01
0.20	0.60	2.51	0.25	4.76424	0.90	0.00
0.10	0.70	1.25	0.13	4.76211	0.52	0.01

A.5 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and dipotassium 1,2-benzenedicarboxylate



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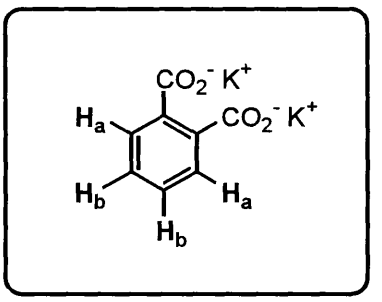


87

NMR Titration

	41 / g	87 / g	D_2O / mL	[41] / mM	[87] / mM
Solution X	0.2722	0.0242	10	50.00	9.99
Solution Y	0	0.0606	25	0.00	10.00

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	[41] / mM	[87] / mM	Ratio (41:87)	δ	$\Delta\delta$	Error
0.80	0.00	50.00	9.99	5.01	7.23941	0.05617	0.00100
0.40	0.40	25.00	10.00	2.50	7.25590	0.03968	0.00087
0.30	0.50	18.75	10.00	1.88	7.26440	0.03118	0.00065
0.20	0.60	12.50	10.00	1.25	7.27019	0.02539	0.00068
0.15	0.65	9.37	10.00	0.94	7.27699	0.01859	0.00080
0.10	0.70	6.25	10.00	0.62	7.28014	0.01544	0.00056
0.05	0.75	3.12	10.00	0.31	7.28925	0.00633	0.00112
0.00	0.80	0.00	10.00	0.00	7.29558	0.00000	0.00017

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[87] / mM	Ratio (87:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	2.27146	0.00000	0.00196
0.80	0.00	50.00	9.99	0.20	2.26903	0.00243	0.00074
0.40	0.40	25.00	10.00	0.40	2.26550	0.00596	0.00099
0.30	0.50	18.75	10.00	0.53	2.26698	0.00448	0.00042
0.20	0.60	12.50	10.00	0.80	2.26326	0.00821	0.00078
0.15	0.65	9.37	10.00	1.07	2.26464	0.00682	0.00072
0.10	0.70	6.25	10.00	1.60	2.26061	0.01085	0.00065
0.05	0.75	3.12	10.00	3.20	2.26124	0.01022	0.00095

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[87] / mM	Ratio (41:87)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	4.76791	0.00000	0.00160
0.80	0.00	50.00	9.99	0.20	4.76171	0.00620	0.00077
0.40	0.40	25.00	10.00	0.40	4.75921	0.00870	0.00088
0.30	0.50	18.75	10.00	0.53	4.76029	0.00761	0.00041
0.20	0.60	12.50	10.00	0.80	4.75684	0.01107	0.00073
0.15	0.65	9.37	10.00	1.07	4.75800	0.00990	0.00069
0.10	0.70	6.25	10.00	1.60	4.75433	0.01358	0.00054
0.05	0.75	3.12	10.00	3.20	4.75465	0.01326	0.00083

Job Plot

	41 / g	87 / g	D_2O / mL	[41] / mM	[87] / mM
Solution X	0.1361	0.0000	25	10.00	0.00
Solution Y	0.0000	0.0606	25	0.00	10.00

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	$[87]_{tot}$ / mM	Mf of 87	δ	[41•87] / mM	Error / mM
0.70	0.10	1.25	0.13	7.27010	0.36	0.00
0.60	0.20	2.50	0.25	7.27361	0.62	0.01
0.50	0.30	3.75	0.38	7.27734	0.78	0.00
0.40	0.40	5.00	0.50	7.28098	0.84	0.01
0.30	0.50	6.25	0.63	7.28407	0.83	0.00
0.20	0.60	7.50	0.75	7.28838	0.64	0.02
0.10	0.70	8.75	0.88	7.29140	0.45	0.05
0.00	0.80	10.00	1.00	7.29602	0.00	0.00

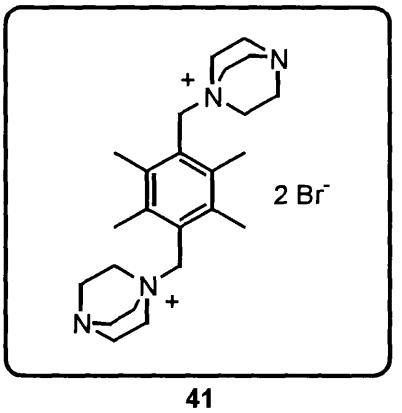
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•87] / mM	Error / mM
0.80	0.00	10.00	1.00	2.27146	0.00	0.00
0.70	0.10	8.75	0.87	2.26943	1.70	0.76
0.60	0.20	7.50	0.75	2.26752	2.83	0.25
0.50	0.30	6.25	0.62	2.26566	3.46	0.03
0.40	0.40	5.00	0.50	2.26408	3.53	0.42
0.30	0.50	3.75	0.37	2.26178	3.47	0.40
0.20	0.60	2.50	0.25	2.26015	2.70	0.52
0.10	0.70	1.25	0.12	2.25769	1.64	0.21

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•87] / mM	Error / mM
0.80	0.00	10.00	1.00	4.76791	0.00	0.00
0.70	0.10	8.75	0.87	4.76569	0.43	0.25
0.60	0.20	7.50	0.75	4.76358	0.72	0.05
0.50	0.30	6.25	0.62	4.76134	0.91	0.14
0.40	0.40	5.00	0.50	4.75941	0.95	0.04
0.30	0.50	3.75	0.37	4.75673	0.93	0.03
0.20	0.60	2.50	0.25	4.75462	0.74	0.03
0.10	0.70	1.25	0.12	4.75175	0.45	0.02

A.6 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and dilithium 1,3-benzenedicarboxylate



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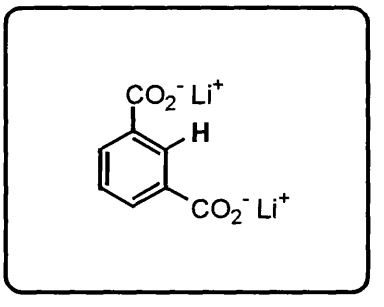


88

NMR Titration

	41 / g	88 / g	D_2O / mL	[41] / mM	[88] / mM
Solution X	0.2052	0.0179	10	37.69	10.06
Solution Y	0	0.0448	25	0.00	10.07

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[88] / mM	Ratio (41:88)	δ	Δδ	Error
0.80	0.00	37.69	10.06	3.75	7.93138	0.20972	0.00247
0.40	0.40	18.85	10.06	1.87	7.98970	0.15139	0.00257
0.30	0.50	14.13	10.06	1.40	8.01434	0.12676	0.00373
0.20	0.60	9.42	10.06	0.94	8.04067	0.10042	0.00435
0.15	0.65	7.07	10.07	0.70	8.05713	0.08396	0.00234
0.10	0.70	4.71	10.07	0.47	8.07764	0.06345	0.00205
0.05	0.75	2.36	10.07	0.23	8.10251	0.03858	0.00197
0.00	0.80	0.00	10.07	0.00	8.14109	0.00000	0.00323

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[88] / mM	Ratio (88:41)	δ	Δδ	Error
Cation reference		10.04	0.00	0.00	2.27491	0.00000	0.00093
0.80	0.00	37.69	10.06	0.27	2.23585	0.03907	0.00171
0.40	0.40	18.85	10.06	0.53	2.22401	0.05090	0.00387
0.30	0.50	14.13	10.06	0.71	2.21894	0.05597	0.00272
0.20	0.60	9.42	10.06	1.07	2.21055	0.06436	0.00188
0.15	0.65	7.07	10.07	1.42	2.20456	0.07035	0.00259
0.10	0.70	4.71	10.07	2.14	2.19688	0.07803	0.00099
0.05	0.75	2.36	10.07	4.27	2.18741	0.08750	0.00420

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[88] / mM	Ratio (88:41)	δ	Δδ	Error
Cation reference		10.04	0.00	0.00	4.78940	0.00000	0.00120
0.80	0.00	37.69	10.06	0.27	4.72991	0.05949	0.00155
0.40	0.40	18.85	10.06	0.53	4.71636	0.07304	0.00198
0.30	0.50	14.13	10.06	0.71	4.71073	0.07867	0.00101
0.20	0.60	9.42	10.06	1.07	4.70218	0.08722	0.00166
0.15	0.65	7.07	10.07	1.42	4.69556	0.09384	0.00198
0.10	0.70	4.71	10.07	2.14	4.68782	0.10158	0.00132
0.05	0.75	2.36	10.07	4.27	4.67064	0.11876	0.00031

Job Plot

	41 / g	88 / g	D_2O / mL	[41] / mM	[88] / mM
Solution X	0.0820	0.0000	15	10.04	0.00
Solution Y	0.0000	0.0448	25	0.00	10.07

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[88]_{tot}$ / mM	Mf of 88	δ	[41•88] / mM	Error / mM
0.70	0.10	1.26	0.13	8.01564	0.57	0.01
0.60	0.20	2.52	0.25	8.02664	1.04	0.01
0.50	0.30	3.78	0.38	8.04405	1.32	0.00
0.40	0.40	5.04	0.50	8.06351	1.41	0.03
0.30	0.50	6.30	0.63	8.07944	1.41	0.04
0.20	0.60	7.56	0.75	8.09989	1.14	0.02
0.10	0.70	8.81	0.88	8.12193	0.63	0.06
0.00	0.80	10.07	1.00	8.14208	0.00	0.00

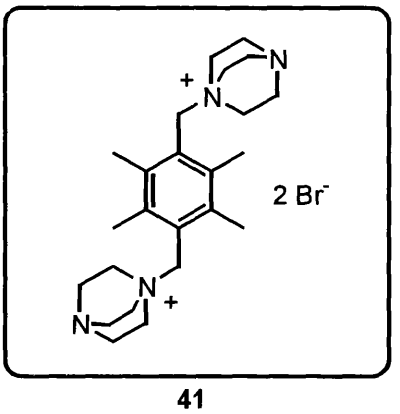
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•88] / mM	Error / mM
0.80	0.00	10.04	1.00	2.27491	0.00	0.00
0.70	0.10	8.78	0.87	2.26391	1.09	0.05
0.60	0.20	7.53	0.75	2.24839	2.25	0.00
0.50	0.30	6.27	0.62	2.23881	2.55	0.06
0.40	0.40	5.01	0.50	2.22863	2.61	0.00
0.30	0.50	3.76	0.37	2.21406	2.57	0.01
0.20	0.60	2.51	0.25	2.20295	2.03	0.07
0.10	0.70	1.25	0.12	2.19377	1.14	0.01

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•88] / mM	Error / mM
0.80	0.00	10.04	1.00	4.78940	0.00	0.00
0.70	0.10	8.78	0.87	4.77568	1.00	0.03
0.60	0.20	7.53	0.75	4.75739	2.00	0.01
0.50	0.30	6.27	0.62	4.74254	2.44	0.03
0.40	0.40	5.01	0.50	4.72811	2.55	0.01
0.30	0.50	3.76	0.37	4.71014	2.47	0.01
0.20	0.60	2.51	0.25	4.69529	1.96	0.05
0.10	0.70	1.25	0.12	4.67135	1.23	0.00

A.7 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and disodium 1,3-benzenedicarboxylate



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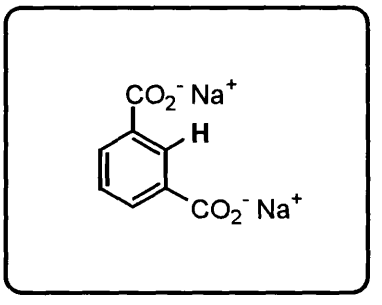


89

NMR Titration

	41 / g	89 / g	D_2O / mL	[41] / mM	[89] / mM
Solution X	0.2722	0.0212	10	50.00	10.09
Solution Y	0	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[89] / mM	Ratio (41:89)	δ	Δδ	Error
0.80	0.00	50.00	10.09	4.96	7.90543	0.22864	0.00115
0.40	0.40	25.00	10.04	2.49	7.96177	0.17230	0.00020
0.30	0.50	18.75	10.03	1.87	7.98608	0.14799	0.00081
0.20	0.60	12.50	10.02	1.25	8.01763	0.11643	0.00060
0.15	0.65	9.37	10.01	0.94	8.03516	0.09891	0.00044
0.10	0.70	6.25	10.01	0.62	8.06504	0.06902	0.00313
0.05	0.75	3.12	10.00	0.31	8.09266	0.04140	0.00099
0.00	0.80	0.00	10.00	0.00	8.13406	0.00000	0.00070

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[89] / mM	Ratio (89:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	2.26564	0.00000	0.00095
0.80	0.00	50.00	10.09	0.20	2.22503	0.04061	0.00095
0.40	0.40	25.00	10.04	0.40	2.21240	0.05324	0.00034
0.30	0.50	18.75	10.03	0.53	2.20661	0.05903	0.00066
0.20	0.60	12.50	10.02	0.80	2.19792	0.06772	0.00017
0.15	0.65	9.37	10.01	1.07	2.18950	0.07614	0.00065
0.10	0.70	6.25	10.01	1.60	2.18247	0.08317	0.00035
0.05	0.75	3.12	10.00	3.20	2.17198	0.09366	0.00129

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[89] / mM	Ratio (89:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	4.78070	0.00000	0.00126
0.80	0.00	50.00	10.09	0.20	4.72879	0.05191	0.00080
0.40	0.40	25.00	10.04	0.40	4.71353	0.06717	0.00016
0.30	0.50	18.75	10.03	0.53	4.70712	0.07358	0.00063
0.20	0.60	12.50	10.02	0.80	4.69724	0.08347	0.00040
0.15	0.65	9.37	10.01	1.07	4.68794	0.09276	0.00088
0.10	0.70	6.25	10.01	1.60	4.67064	0.11007	0.00007
0.05	0.75	3.12	10.00	3.20	4.67075	0.10996	0.00011

Job Plot

	41 / g	89 / g	D_2O / mL	[41] / mM	[89] / mM
Solution X	0.1361	0.0000	25	10.00	0.00
Solution Y	0.0000	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[89]_{tot}$ / mM	Mf of 89	δ	[41•89] / mM	Error / mM
0.70	0.10	1.25	0.12	8.00565	0.48	0.02
0.60	0.20	2.50	0.25	8.01666	0.88	0.01
0.50	0.30	3.75	0.37	8.03333	1.13	0.00
0.40	0.40	5.00	0.50	8.05254	1.21	0.03
0.30	0.50	6.25	0.62	8.07280	1.12	0.00
0.20	0.60	7.50	0.75	8.09078	0.93	0.02
0.10	0.70	8.75	0.87	8.11274	0.49	0.01
0.00	0.80	10.00	1.00	8.13082	0.00	0.00

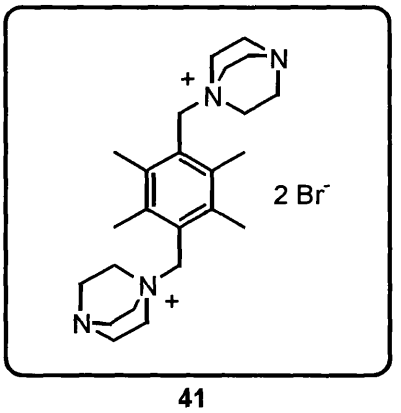
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•89] / mM	Error / mM
0.80	0.00	10.00	1.00	2.26564	0.00	0.00
0.70	0.10	8.75	0.88	2.25072	1.39	0.03
0.60	0.20	7.50	0.75	2.23701	2.29	0.13
0.50	0.30	6.25	0.63	2.22152	2.94	0.01
0.40	0.40	5.00	0.50	2.20682	3.14	0.10
0.30	0.50	3.75	0.38	2.19317	2.90	0.02
0.20	0.60	2.50	0.25	2.17880	2.32	0.07
0.10	0.70	1.25	0.13	2.16851	1.30	0.02

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•89] / mM	Error / mM
0.80	0.00	10.04	1.00	4.78070	0.00	0.00
0.70	0.10	8.78	0.88	4.76268	1.41	0.01
0.60	0.20	7.53	0.75	4.74589	2.34	0.08
0.50	0.30	6.27	0.63	4.72816	2.94	0.01
0.40	0.40	5.01	0.50	4.71091	3.12	0.08
0.30	0.50	3.76	0.38	4.69490	2.88	0.02
0.20	0.60	2.51	0.25	4.67055	2.47	0.01
0.10	0.70	1.25	0.13	4.67050	1.23	0.00

A.8 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and dipotassium 1,3-benzenedicarboxylate



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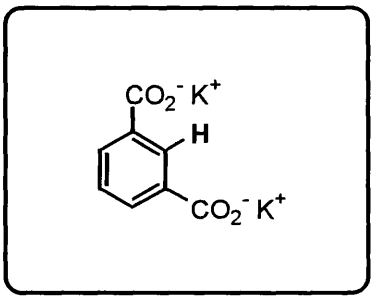


90

NMR Titration

	41 / g	90 / g	D_2O / mL	[41] / mM	[90] / mM
Solution X	0.2707	0.0252	10	49.72	10.40
Solution Y	0	0.0606	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[90] / mM	Ratio (41:90)	δ	Δδ	Error
0.80	0.00	49.72	10.40	4.78	7.92370	0.25228	0.00298
0.40	0.40	24.86	10.20	2.44	7.99299	0.18299	0.00225
0.30	0.50	18.65	10.15	1.84	8.01921	0.15677	0.00286
0.20	0.60	12.43	10.10	1.23	8.05128	0.12470	0.00097
0.15	0.65	9.32	10.08	0.93	8.07202	0.10396	0.00125
0.10	0.70	6.22	10.05	0.62	8.09459	0.08139	0.00510
0.05	0.75	3.11	10.03	0.31	8.12708	0.04890	0.00282
0.00	0.80	0.00	10.00	0.00	8.17598	0.00000	0.00234

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[90] / mM	Ratio (90:41)	δ	Δδ	Error
Cation reference		10.04	0.00	0.00	2.27912	0.00000	0.00180
0.80	0.00	49.72	10.40	0.21	2.24045	0.03867	0.00216
0.40	0.40	24.86	10.20	0.41	2.22764	0.05148	0.00161
0.30	0.50	18.65	10.15	0.54	2.22122	0.05791	0.00255
0.20	0.60	12.43	10.10	0.81	2.21167	0.06745	0.00152
0.15	0.65	9.32	10.08	1.08	2.20600	0.07313	0.00122
0.10	0.70	6.22	10.05	1.62	2.19873	0.08040	0.00284
0.05	0.75	3.11	10.03	3.23	2.18882	0.09031	0.00560

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[90] / mM	Ratio (90:41)	δ	Δδ	Error
Cation reference		10.04	0.00	0.00	4.79343	0.00000	0.00171
0.80	0.00	49.72	10.40	0.21	4.73108	0.06235	0.00211
0.40	0.40	24.86	10.20	0.41	4.71771	0.07572	0.00173
0.30	0.50	18.65	10.15	0.54	4.71061	0.08283	0.00238
0.20	0.60	12.43	10.10	0.81	4.70009	0.09334	0.00145
0.15	0.65	9.32	10.08	1.08	4.69348	0.09996	0.00130
0.10	0.70	6.22	10.05	1.62	4.68463	0.10881	0.00311
0.05	0.75	3.11	10.03	3.23	4.67166	0.12177	0.00015

Job Plot

	41 / g	90 / g	D_2O / mL	[41] / mM	[90] / mM
Solution X	0.0820	0.0000	15	10.04	0.00
Solution Y	0.0000	0.0606	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[90]_{tot}$ / mM	Mf of 90	δ	[41•90] / mM	Error / mM
0.70	0.10	1.25	0.12	8.02878	0.54	0.01
0.60	0.20	2.49	0.25	8.05160	0.91	0.01
0.50	0.30	3.74	0.37	8.07363	1.12	0.03
0.40	0.40	4.99	0.50	8.09420	1.19	0.01
0.30	0.50	6.24	0.62	8.11225	1.17	0.03
0.20	0.60	7.50	0.75	8.13500	0.90	0.03
0.10	0.70	8.75	0.87	8.15734	0.48	0.04
0.00	0.80	10.00	1.00	8.17632	0.00	0.00

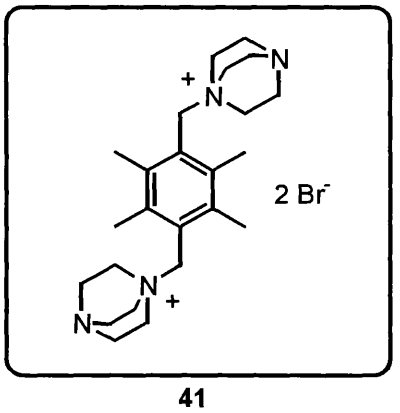
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•90] / mM	Error / mM
0.80	0.00	10.04	1.00	2.27912	0.00	0.00
0.70	0.10	8.79	0.88	2.26198	1.19	0.03
0.60	0.20	7.54	0.75	2.24838	1.82	0.16
0.50	0.30	6.28	0.63	2.23715	2.08	0.00
0.40	0.40	5.03	0.50	2.22394	2.18	0.10
0.30	0.50	3.77	0.38	2.20917	2.08	0.06
0.20	0.60	2.52	0.25	2.19750	1.62	0.02
0.10	0.70	1.26	0.13	2.18781	0.90	0.01

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•90] / mM	Error / mM
0.80	0.00	10.04	1.00	4.79343	0.00	0.00
0.70	0.10	8.79	0.88	4.77231	0.97	0.03
0.60	0.20	7.54	0.75	4.75448	1.53	0.05
0.50	0.30	6.28	0.63	4.73763	1.83	0.00
0.40	0.40	5.03	0.50	4.71987	1.93	0.06
0.30	0.50	3.77	0.38	4.70103	1.82	0.03
0.20	0.60	2.52	0.25	4.67138	1.61	0.01
0.10	0.70	1.26	0.13	4.64449	0.98	0.08

A.9 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and calcium 1,3-benzenedicarboxylate



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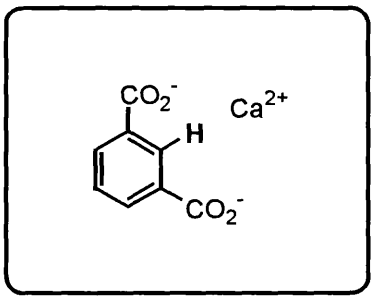


91

NMR Titration

	41 / g	91 / g	D_2O / mL	[41] / mM	[91] / mM
Solution X	0.2722	0.0209	10	50.00	10.24
Solution Y	0	0.0511	25	0.00	10.01

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[91] / mM	Ratio (41:91)	δ	Δδ	Error
0.80	0.00	50.00	10.24	4.89	7.94003	0.23071	0.00398
0.40	0.40	25.00	10.12	2.47	8.00337	0.16737	0.00200
0.30	0.50	18.75	10.09	1.86	8.02864	0.14210	0.00187
0.20	0.60	12.50	10.07	1.24	8.05964	0.11110	0.00257
0.15	0.65	9.37	10.05	0.93	8.07896	0.09178	0.00052
0.10	0.70	6.25	10.04	0.62	8.10094	0.06980	0.00113
0.05	0.75	3.12	10.02	0.31	8.13026	0.04048	0.00047
0.00	0.80	0.00	10.01	0.00	8.17074	0.00000	0.00173

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[91] / mM	Ratio (91:41)	δ	Δδ	Error
Cation reference		9.99	0.00	0.00	2.27727	0.00000	0.00113
0.80	0.00	50.00	10.24	0.20	2.24442	0.03286	0.00269
0.40	0.40	25.00	10.12	0.40	2.23279	0.04449	0.00160
0.30	0.50	18.75	10.09	0.54	2.22704	0.05024	0.00176
0.20	0.60	12.50	10.07	0.81	2.21925	0.05802	0.00201
0.15	0.65	9.37	10.05	1.07	2.21397	0.06330	0.00082
0.10	0.70	6.25	10.04	1.61	2.20693	0.07035	0.00165
0.05	0.75	3.12	10.02	3.21	2.19849	0.07878	0.00145

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[91] / mM	Ratio (91:41)	δ	Δδ	Error
Cation reference		9.99	0.00	0.00	4.79151	0.00000	0.00076
0.80	0.00	50.00	10.24	0.20	4.73640	0.05511	0.00249
0.40	0.40	25.00	10.12	0.40	4.72532	0.06619	0.00151
0.30	0.50	18.75	10.09	0.54	4.71978	0.07174	0.00176
0.20	0.60	12.50	10.07	0.81	4.71102	0.08049	0.00215
0.15	0.65	9.37	10.05	1.07	4.70483	0.08669	0.00077
0.10	0.70	6.25	10.04	1.61	4.69680	0.09471	0.00164
0.05	0.75	3.12	10.02	3.21	4.67256	0.11896	0.00005

Job Plot

	41 / g	91 / g	D_2O / mL	[41] / mM	[91] / mM
Solution X	0.0816	0.0000	15	9.99	0.00
Solution Y	0.0000	0.0511	25	0.00	10.01

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[91]_{tot}$ / mM	Mf of 91	δ	[41•91] / mM	Error / mM
0.70	0.10	1.25	0.13	8.03522	0.53	0.01
0.60	0.20	2.51	0.25	8.05363	0.92	0.01
0.50	0.30	3.76	0.38	8.07456	1.13	0.00
0.40	0.40	5.01	0.50	8.09377	1.21	0.00
0.30	0.50	6.26	0.63	8.11273	1.13	0.02
0.20	0.60	7.51	0.75	8.13215	0.90	0.03
0.10	0.70	8.76	0.88	8.15003	0.55	0.00
0.00	0.80	10.01	1.00	8.17004	0.00	0.00

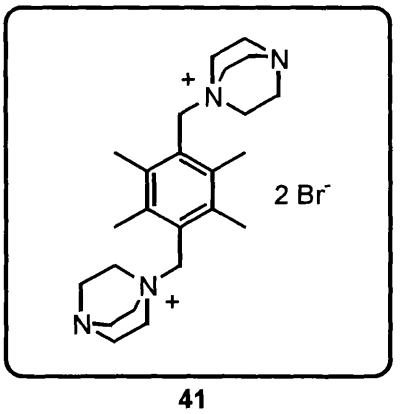
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•91] / mM	Error / mM
0.80	0.00	9.99	1.00	2.27727	0.00	0.00
0.70	0.10	8.74	0.87	2.26246	1.48	0.03
0.60	0.20	7.49	0.75	2.24978	2.36	0.12
0.50	0.30	6.24	0.62	2.24029	2.64	0.06
0.40	0.40	4.99	0.50	2.22837	2.80	0.06
0.30	0.50	3.74	0.37	2.21782	2.55	0.08
0.20	0.60	2.49	0.25	2.20824	1.97	0.04
0.10	0.70	1.25	0.12	2.19734	1.14	0.02

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•91] / mM	Error / mM
0.80	0.00	9.99	1.00	4.79151	0.00	0.00
0.70	0.10	8.74	0.87	4.77312	1.35	0.03
0.60	0.20	7.49	0.75	4.75787	2.11	0.09
0.50	0.30	6.24	0.62	4.74268	2.55	0.06
0.40	0.40	4.99	0.50	4.72691	2.70	0.05
0.30	0.50	3.74	0.37	4.71304	2.46	0.06
0.20	0.60	2.49	0.25	4.69991	1.91	0.02
0.10	0.70	1.25	0.12	4.67240	1.24	0.00

A.10 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and disodium 1,4-benzenedicarboxylate



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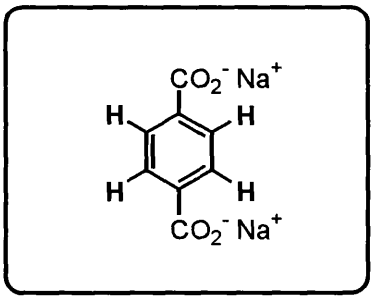


92

NMR Titration

	41 / g	92 / g	D_2O / mL	[41] / mM	[92] / mM
Solution X	0.2722	0.0212	10	50.00	10.09
Solution Y	0	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[92] / mM	Ratio (41:92)	δ	Δδ	Error
0.80	0.00	50.00	10.09	4.96	7.44970	0.27872	0.00049
0.40	0.40	25.00	10.04	2.49	7.52498	0.20344	0.00133
0.30	0.50	18.75	10.03	1.87	7.55594	0.17248	0.00102
0.20	0.60	12.50	10.02	1.25	7.59227	0.13615	0.00233
0.15	0.65	9.37	10.01	0.94	7.61786	0.11056	0.00282
0.10	0.70	6.25	10.01	0.62	7.64288	0.08554	0.00276
0.05	0.75	3.12	10.00	0.31	7.67760	0.05082	0.00240
0.00	0.80	0.00	10.00	0.00	7.72842	0.00000	0.00017

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[92] / mM	Ratio (92:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	2.26481	0.00000	0.00130
0.80	0.00	50.00	10.09	0.20	2.23132	0.03349	0.00033
0.40	0.40	25.00	10.04	0.40	2.21503	0.04978	0.00021
0.30	0.50	18.75	10.03	0.53	2.21026	0.05455	0.00056
0.20	0.60	12.50	10.02	0.80	2.20024	0.06458	0.00057
0.15	0.65	9.37	10.01	1.07	2.19524	0.06957	0.00175
0.10	0.70	6.25	10.01	1.60	2.18783	0.07698	0.00074
0.05	0.75	3.12	10.00	3.20	2.18093	0.08388	0.00216

Job Plot

	41 / g	92 / g	D_2O / mL	[41] / mM	[92] / mM
Solution X	0.1361	0.0000	25	10.00	0.00
Solution Y	0.0000	0.0525	25	0.00	10.00

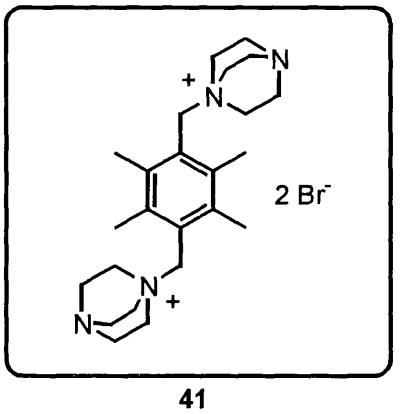
Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[92]_{tot}$ / mM	Mf of 92	δ	[41•92] / mM	Error / mM
0.70	0.10	1.25	0.12	7.57137	0.51	0.00
0.60	0.20	2.50	0.25	7.59260	0.87	0.01
0.50	0.30	3.75	0.37	7.61049	1.13	0.05
0.40	0.40	5.00	0.50	7.63601	1.18	0.02
0.30	0.50	6.25	0.62	7.65949	1.09	0.00
0.20	0.60	7.50	0.75	7.68214	0.86	0.02
0.10	0.70	8.75	0.87	7.70378	0.51	0.02
0.00	0.80	10.00	1.00	7.72606	0.00	0.00

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•92] / mM	Error / mM
0.80	0.00	10.00	1.00	2.26481	0.00	0.00
0.70	0.10	8.75	0.88	2.24758	1.44	0.04
0.60	0.20	7.50	0.75	2.23545	2.10	0.04
0.50	0.30	6.25	0.63	2.21862	2.75	0.21
0.40	0.40	5.00	0.50	2.20824	2.70	0.06
0.30	0.50	3.75	0.38	2.19612	2.46	0.01
0.20	0.60	2.50	0.25	2.18457	1.91	0.02
0.10	0.70	1.25	0.13	2.17488	1.07	0.02

A.11 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and disodium dipicolinate



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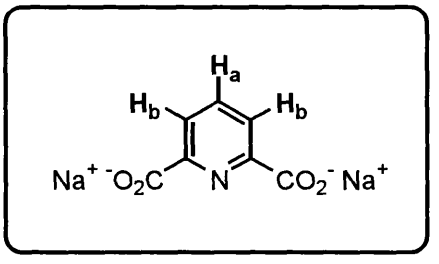


93

NMR Titration

	41 / g	93 / g	D_2O / mL	[41] / mM	[93] / mM
Solution X	0.2722	0.0211	10	50.00	10.00
Solution Y	0	0.0528	25	0.00	10.01

Anion proton shift (average of 3 runs) – average of δH_a and 2 δH_b

X / mL	Y / mL	[41] / mM	[93] / mM	Ratio (41:93)	δ	$\Delta\delta$	Error
0.80	0.00	50.00	10.00	5.00	7.60477	0.25795	0.00276
0.40	0.40	25.00	10.00	2.50	7.68328	0.17945	0.00168
0.30	0.50	18.75	10.00	1.87	7.71286	0.14987	0.00218
0.20	0.60	12.50	10.00	1.25	7.74635	0.11638	0.00178
0.15	0.65	9.37	10.00	0.94	7.76722	0.09551	0.00180
0.10	0.70	6.25	10.00	0.62	7.79114	0.07159	0.00177
0.05	0.75	3.12	10.01	0.31	7.81956	0.04316	0.00081
0.00	0.80	0.00	10.01	0.00	7.86272	0.00000	0.00184

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[93] / mM	Ratio (93:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	2.27990	0.00000	0.00142
0.80	0.00	50.00	10.00	0.20	2.24585	0.03405	0.00234
0.40	0.40	25.00	10.00	0.40	2.23482	0.04508	0.00103
0.30	0.50	18.75	10.00	0.53	2.23077	0.04913	0.00223
0.20	0.60	12.50	10.00	0.80	2.22329	0.05661	0.00124
0.15	0.65	9.37	10.00	1.07	2.21942	0.06048	0.00181
0.10	0.70	6.25	10.00	1.60	2.21367	0.06623	0.00166
0.05	0.75	3.12	10.01	3.20	2.20677	0.07313	0.00075

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[93] / mM	Ratio (93:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	4.77564	0.00000	0.00133
0.80	0.00	50.00	10.00	0.20	4.73655	0.03909	0.00218
0.40	0.40	25.00	10.00	0.40	4.72627	0.04937	0.00104
0.30	0.50	18.75	10.00	0.53	4.72203	0.05361	0.00212
0.20	0.60	12.50	10.00	0.80	4.71411	0.06153	0.00127
0.15	0.65	9.37	10.00	1.07	4.71000	0.06565	0.00168
0.10	0.70	6.25	10.00	1.60	4.70372	0.07192	0.00162
0.05	0.75	3.12	10.01	3.20	4.69566	0.07998	0.00081

Job Plot

	41 / g	93 / g	D_2O / mL	[41] / mM	[93] / mM
Solution X	0.1361	0.0000	25	10.00	0.00
Solution Y	0.0000	0.0528	25	0.00	10.01

Anion proton shift (average of 3 runs) – average of δH_a and 2 δH_b

X / mL	Y / mL	$[93]_{tot}$ / mM	Mf of 93	δ	[41•93] / mM	Error / mM
0.70	0.10	1.25	0.13	7.74089	0.40	0.00
0.60	0.20	2.50	0.25	7.75695	0.69	0.01
0.50	0.30	3.75	0.38	7.77373	0.88	0.01
0.40	0.40	5.00	0.50	7.79167	0.94	0.01
0.30	0.50	6.25	0.63	7.80992	0.87	0.00
0.20	0.60	7.51	0.75	7.82794	0.70	0.01
0.10	0.70	8.76	0.88	7.84657	0.39	0.01
0.00	0.80	10.01	1.00	7.86358	0.00	0.00

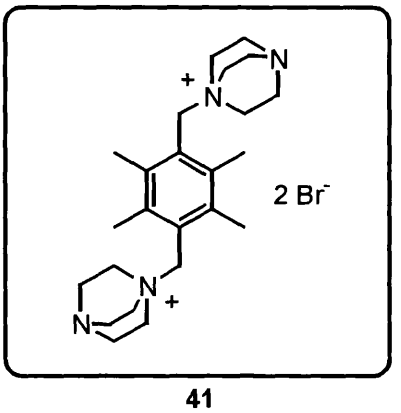
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•93] / mM	Error / mM
0.80	0.00	10.00	1.00	2.27990	0.00	0.00
0.70	0.10	8.75	0.87	2.26575	1.49	0.07
0.60	0.20	7.50	0.75	2.25661	2.11	0.05
0.50	0.30	6.25	0.62	2.24596	2.56	0.05
0.40	0.40	5.00	0.50	2.23545	2.68	0.05
0.30	0.50	3.75	0.37	2.22526	2.47	0.02
0.20	0.60	2.50	0.25	2.21538	1.94	0.05
0.10	0.70	1.25	0.12	2.20710	1.10	0.00

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•93] / mM	Error / mM
0.80	0.00	10.00	1.00	4.77564	0.00	0.00
0.70	0.10	8.75	0.87	4.76269	1.50	0.07
0.60	0.20	7.50	0.75	4.75046	2.50	0.05
0.50	0.30	6.25	0.62	4.73805	3.11	0.03
0.40	0.40	5.00	0.50	4.72588	3.29	0.07
0.30	0.50	3.75	0.37	4.71405	3.05	0.01
0.20	0.60	2.50	0.25	4.70767	2.25	0.06
0.10	0.70	1.25	0.12	4.70100	1.23	0.07

A.12 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and calcium dipicolinate



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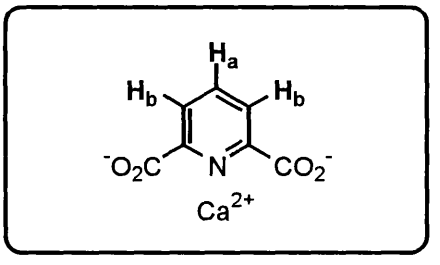


94

NMR Titration

	41 / g	94 / g	D_2O / mL	[41] / mM	[94] / mM
Solution X	0.2726	0.0207	10	50.07	10.09
Solution Y	0	0.0512	25	0.00	9.98

Anion proton shift (average of 3 runs) – average of δH_a and 2 δH_b

X / mL	Y / mL	[41] / mM	[94] / mM	Ratio (41:94)	δ	$\Delta\delta$	Error
0.80	0.00	50.07	10.09	4.96	7.93351	0.07639	0.00111
0.40	0.40	25.04	10.03	2.49	7.96453	0.04537	0.00152
0.30	0.50	18.78	10.02	1.87	7.97249	0.03741	0.00031
0.20	0.60	12.52	10.01	1.25	7.98388	0.02602	0.00167
0.15	0.65	9.39	10.00	0.94	7.98974	0.02016	0.00019
0.10	0.70	6.26	9.99	0.63	7.99441	0.01549	0.00211
0.05	0.75	3.13	9.99	0.31	7.99952	0.01038	0.00080
0.00	0.80	0.00	9.98	0.00	8.00990	0.00000	0.00116

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[94] / mM	Ratio (94:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	2.27851	0.00000	0.00089
0.80	0.00	50.07	10.09	0.20	2.27530	0.00321	0.00148
0.40	0.40	25.04	10.03	0.40	2.27287	0.00565	0.00040
0.30	0.50	18.78	10.02	0.53	2.27050	0.00801	0.00076
0.20	0.60	12.52	10.01	0.80	2.27046	0.00805	0.00112
0.15	0.65	9.39	10.00	1.07	2.27068	0.00783	0.00037
0.10	0.70	6.26	9.99	1.60	2.26852	0.00999	0.00204
0.05	0.75	3.13	9.99	3.19	2.26505	0.01346	0.00072

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[94] / mM	Ratio (94:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	4.77402	0.00000	0.00064
0.80	0.00	50.07	10.09	0.20	4.76920	0.00482	0.00116
0.40	0.40	25.04	10.03	0.40	4.76893	0.00509	0.00121
0.30	0.50	18.78	10.02	0.53	4.76753	0.00649	0.00040
0.20	0.60	12.52	10.01	0.80	4.76756	0.00646	0.00134
0.15	0.65	9.39	10.00	1.07	4.76756	0.00646	0.00006
0.10	0.70	6.26	9.99	1.60	4.76562	0.00840	0.00183
0.05	0.75	3.13	9.99	3.19	4.76316	0.01086	0.00061

Job Plot

	41 / g	94 / g	D_2O / mL	[41] / mM	[94] / mM
Solution X	0.0817	0.0000	15	10.00	0.00
Solution Y	0.0000	0.0512	25	0.00	9.98

Anion proton shift (average of 3 runs) – average of δH_a and 2 δH_b

X / mL	Y / mL	$[94]_{tot}$ / mM	Mf of 94	δ	[41•94] / mM	Error / mM
0.70	0.10	1.25	0.12	7.98279	0.17	0.01
0.60	0.20	2.49	0.25	7.98909	0.26	0.01
0.50	0.30	3.74	0.37	7.99343	0.30	0.01
0.40	0.40	4.98	0.50	7.99706	0.30	0.03
0.30	0.50	6.23	0.62	7.99866	0.31	0.02
0.20	0.60	7.48	0.75	8.00241	0.22	0.00
0.10	0.70	8.73	0.87	8.00480	0.15	0.06
0.00	0.80	9.98	1.00	8.00784	0.00	0.00

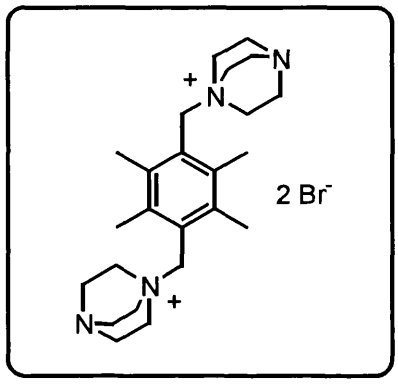
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•94] / mM	Error / mM
0.80	0.00	10.00	1.00	2.27851	0.00	0.00
0.70	0.10	8.76	0.88	2.27654	1.19	0.46
0.60	0.20	7.51	0.75	2.27399	2.34	0.18
0.50	0.30	6.26	0.63	2.27270	2.51	0.23
0.40	0.40	5.01	0.50	2.27122	2.52	0.38
0.30	0.50	3.76	0.38	2.26834	2.63	0.24
0.20	0.60	2.51	0.25	2.26650	2.07	0.11
0.10	0.70	1.25	0.13	2.26331	1.31	0.16

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•94] / mM	Error / mM
0.80	0.00	10.00	1.00	4.77402	0.00	0.00
0.70	0.10	8.76	0.88	4.77286	0.92	0.57
0.60	0.20	7.51	0.75	4.77080	2.19	0.15
0.50	0.30	6.26	0.63	4.76962	2.50	0.25
0.40	0.40	5.01	0.50	4.76838	2.56	0.47
0.30	0.50	3.76	0.38	4.76569	2.84	0.29
0.20	0.60	2.51	0.25	4.76427	2.22	0.13
0.10	0.70	1.25	0.13	4.76212	1.35	0.21

A.13 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and trisodium 1,3,5-benzene-tricarboxylate



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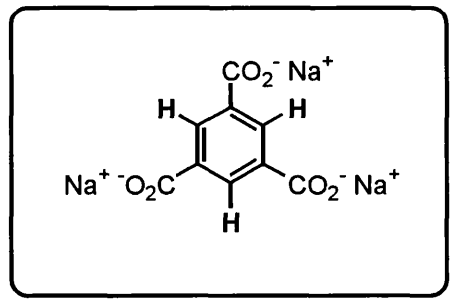


95

NMR Titration

	41 / g	95 / g	D_2O / mL	[41] / mM	[95] / mM
Solution X	0.2751	0.0276	10	50.53	10.00
Solution Y	0	0.0692	25	0.00	10.03

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[95] / mM	Ratio (41:95)	δ	Δδ	Error
0.80	0.00	50.53	10.00	5.05	7.87666	0.38337	0.00242
0.40	0.40	25.27	10.01	2.52	7.94945	0.31058	0.00407
0.30	0.50	18.95	10.01	1.89	7.98726	0.27277	0.00155
0.20	0.60	12.63	10.02	1.26	8.04323	0.21680	0.00103
0.15	0.65	9.47	10.02	0.95	8.08220	0.17783	0.00123
0.10	0.70	6.32	10.02	0.63	8.12737	0.13266	0.00070
0.05	0.75	3.16	10.02	0.32	8.18397	0.07606	0.00157
0.00	0.80	0.00	10.03	0.00	8.26003	0.00000	0.00122

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[95] / mM	Ratio (95:41)	δ	Δδ	Error
Cation reference		10.09	0.00	0.00	2.28164	0.00000	0.00188
0.80	0.00	50.53	10.00	0.20	2.20809	0.07356	0.00222
0.40	0.40	25.27	10.01	0.40	2.16500	0.11664	0.00233
0.30	0.50	18.95	10.01	0.53	2.14611	0.13554	0.00187
0.20	0.60	12.63	10.02	0.79	2.12362	0.15802	0.00066
0.15	0.65	9.47	10.02	1.06	2.11085	0.17079	0.00106
0.10	0.70	6.32	10.02	1.59	2.09953	0.18212	0.00086
0.05	0.75	3.16	10.02	3.17	2.08930	0.19234	0.00082

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[95] / mM	Ratio (95:41)	δ	Δδ	Error
Cation reference		10.09	0.00	0.00	4.79652	0.00000	0.00191
0.80	0.00	50.53	10.00	0.20	4.68942	0.10711	0.00256
0.40	0.40	25.27	10.01	0.40	4.64296	0.15356	0.00249
0.30	0.50	18.95	10.01	0.53	4.62271	0.17381	0.00182
0.20	0.60	12.63	10.02	0.79	4.59998	0.19654	0.00075
0.15	0.65	9.47	10.02	1.06	4.58766	0.20886	0.00087
0.10	0.70	6.32	10.02	1.59	4.57721	0.21931	0.00077
0.05	0.75	3.16	10.02	3.17	4.56868	0.22785	0.00080

Job Plot

	41 / g	95 / g	D_2O / mL	[41] / mM	[95] / mM
Solution X	0.0824	0.0000	15	10.09	0.00
Solution Y	0.0000	0.0692	25	0.00	10.03

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[95]_{tot}$ / mM	Mf of 95	δ	[41•95] / mM	Error / mM
0.70	0.10	1.25	0.12	7.96701	0.78	0.01
0.60	0.20	2.49	0.25	8.00355	1.37	0.02
0.50	0.30	3.74	0.37	8.04557	1.72	0.02
0.40	0.40	5.00	0.50	8.09422	1.77	0.01
0.30	0.50	6.25	0.62	8.14164	1.57	0.00
0.20	0.60	7.51	0.75	8.18599	1.17	0.00
0.10	0.70	8.77	0.87	8.22187	0.69	0.01
0.00	0.80	10.03	1.00	8.25808	0.00	0.00

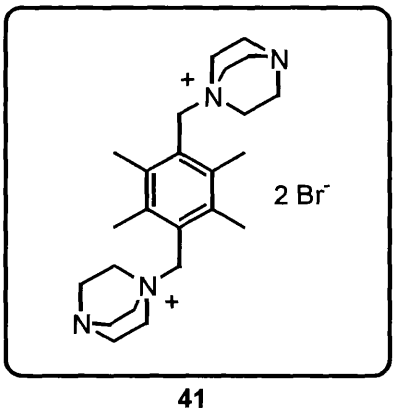
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•95] / mM	Error / mM
0.80	0.00	10.09	1.00	2.28164	0.00	0.00
0.70	0.10	8.84	0.88	2.24159	1.27	0.04
0.60	0.20	7.58	0.75	2.20243	2.15	0.04
0.50	0.30	6.32	0.63	2.16510	2.64	0.01
0.40	0.40	5.06	0.50	2.13508	2.66	0.01
0.30	0.50	3.80	0.38	2.11381	2.29	0.01
0.20	0.60	2.53	0.25	2.09867	1.66	0.00
0.10	0.70	1.27	0.13	2.08937	0.88	0.00

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•95] / mM	Error / mM
0.80	0.00	10.09	1.00	4.79652	0.00	0.00
0.70	0.10	8.84	0.88	4.74318	1.50	0.03
0.60	0.20	7.58	0.75	4.69350	2.49	0.04
0.50	0.30	6.32	0.63	4.65020	2.95	0.01
0.40	0.40	5.06	0.50	4.61600	2.91	0.01
0.30	0.50	3.80	0.38	4.59329	2.46	0.01
0.20	0.60	2.53	0.25	4.57852	1.76	0.00
0.10	0.70	1.27	0.13	4.56951	0.92	0.00

A.14 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and tetrasodium 1,2,4,5-benzene-tetracarboxylate



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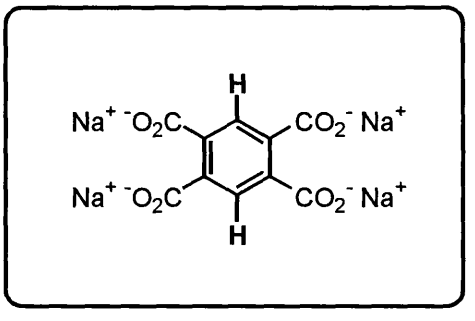


96

NMR Titration

	41 / g	96 / g	D_2O / mL	[41] / mM	[96] / mM
Solution X	0.2722	0.0354	10	50.00	10.35
Solution Y	0	0.0855	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[96] / mM	Ratio (41:96)	δ	Δδ	Error
0.80	0.00	50.00	10.35	4.83	7.31235	0.03896	0.00528
0.40	0.40	25.00	10.17	2.46	7.31762	0.03369	0.00163
0.30	0.50	18.75	10.13	1.85	7.32032	0.03099	0.00307
0.20	0.60	12.50	10.09	1.24	7.32769	0.02362	0.00169
0.15	0.65	9.37	10.06	0.93	7.32931	0.02200	0.00355
0.10	0.70	6.25	10.04	0.62	7.33595	0.01536	0.00154
0.05	0.75	3.12	10.02	0.31	7.34061	0.01070	0.00237
0.00	0.80	0.00	10.00	0.00	7.35131	0.00000	0.00212

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[96] / mM	Ratio (96:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	2.25558	0.00000	0.00083
0.80	0.00	50.00	10.35	0.21	2.25118	0.00440	0.00300
0.40	0.40	25.00	10.17	0.41	2.24841	0.00717	0.00191
0.30	0.50	18.75	10.13	0.54	2.24603	0.00955	0.00302
0.20	0.60	12.50	10.09	0.81	2.24511	0.01048	0.00118
0.15	0.65	9.37	10.06	1.07	2.24168	0.01391	0.00362
0.10	0.70	6.25	10.04	1.61	2.24175	0.01384	0.00148
0.05	0.75	3.12	10.02	3.21	2.23805	0.01753	0.00201

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[96] / mM	Ratio (96:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	4.77124	0.00000	0.00046
0.80	0.00	50.00	10.35	0.21	4.76104	0.01021	0.00478
0.40	0.40	25.00	10.17	0.41	4.76267	0.00858	0.00197
0.30	0.50	18.75	10.13	0.54	4.76200	0.00924	0.00271
0.20	0.60	12.50	10.09	0.81	4.76269	0.00855	0.00124
0.15	0.65	9.37	10.06	1.07	4.75999	0.01125	0.00320
0.10	0.70	6.25	10.04	1.61	4.76055	0.01069	0.00143
0.05	0.75	3.12	10.02	3.21	4.75784	0.01340	0.00188

Job Plot

	41 / g	96 / g	D_2O / mL	[41] / mM	[96] / mM
Solution X	0.1361	0.0000	25	10.00	0.00
Solution Y	0.0000	0.0855	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[96]_{tot}$ / mM	Mf of 96	δ	[41•96] / mM	Error / mM
0.70	0.10	1.25	0.12	7.30270	1.42	0.02
0.60	0.20	2.50	0.25	7.31212	2.23	0.08
0.50	0.30	3.75	0.37	7.31626	2.94	0.15
0.40	0.40	5.00	0.50	7.32629	2.63	0.16
0.30	0.50	6.25	0.62	7.32972	2.72	0.15
0.20	0.60	7.50	0.75	7.33710	1.83	0.03
0.10	0.70	8.75	0.87	7.34280	0.85	0.01
0.00	0.80	10.00	1.00	7.34652	0.00	0.00

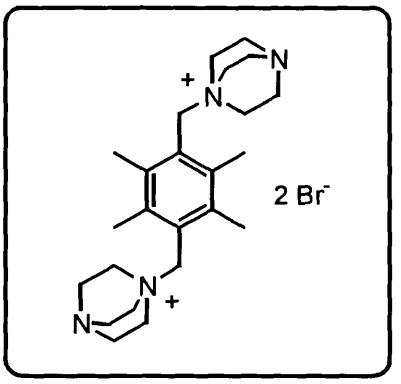
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•96] / mM	Error / mM
0.80	0.00	10.00	1.00	2.25558	0.00	0.00
0.70	0.10	8.75	0.88	2.24767	3.07	0.09
0.60	0.20	7.50	0.75	2.24706	2.83	0.33
0.50	0.30	6.25	0.63	2.24074	4.11	0.31
0.40	0.40	5.00	0.50	2.24148	3.12	0.24
0.30	0.50	3.75	0.38	2.23639	3.19	0.25
0.20	0.60	2.50	0.25	2.23657	2.10	0.17
0.10	0.70	1.25	0.13	2.23496	1.14	0.05

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•96] / mM	Error / mM
0.80	0.00	10.00	1.00	4.77124	0.00	0.00
0.70	0.10	8.75	0.88	4.76445	3.51	0.04
0.60	0.20	7.50	0.75	4.76431	3.07	0.55
0.50	0.30	6.25	0.63	4.75937	4.38	0.63
0.40	0.40	5.00	0.50	4.76017	3.27	0.35
0.30	0.50	3.75	0.38	4.75607	3.36	0.33
0.20	0.60	2.50	0.25	4.75639	2.19	0.21
0.10	0.70	1.25	0.13	4.75527	1.18	0.06

A.15 3,6-Bis(DABCO-N-methyl)-1,2,4,5-tetramethylbenzene dibromide and tetrasodium 1,4,5,8-naphthalene-tetracarboxylate



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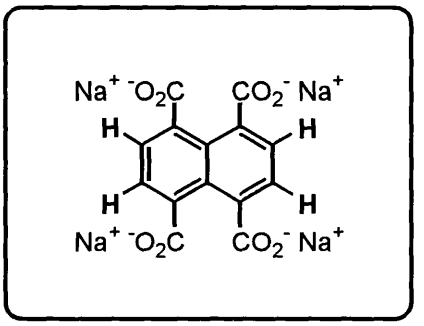


97

NMR Titration

	41 / g	97 / g	D_2O / mL	[41] / mM	[97] / mM
Solution X	0.2722	0.0392	10	50.00	10.00
Solution Y	0	0.0980	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[97] / mM	Ratio (41:97)	δ	Δδ	Error
0.80	0.00	50.00	10.00	5.00	7.41677	0.13691	0.00115
0.40	0.40	25.00	10.00	2.50	7.45230	0.10137	0.00153
0.30	0.50	18.75	10.00	1.88	7.46643	0.08725	0.00130
0.20	0.60	12.50	10.00	1.25	7.48513	0.06855	0.00166
0.15	0.65	9.37	10.00	0.94	7.49830	0.05537	0.00060
0.10	0.70	6.25	10.00	0.63	7.51354	0.04014	0.00178
0.05	0.75	3.12	10.00	0.31	7.53120	0.02248	0.00224
0.00	0.80	0.00	10.00	0.00	7.55368	0.00000	0.00134

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[97] / mM	Ratio (97:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	2.27660	0.00000	0.00213
0.80	0.00	50.00	10.00	0.20	2.26008	0.01652	0.00095
0.40	0.40	25.00	10.00	0.40	2.25283	0.02377	0.00138
0.30	0.50	18.75	10.00	0.53	2.25042	0.02618	0.00126
0.20	0.60	12.50	10.00	0.80	2.24686	0.02974	0.00145
0.15	0.65	9.37	10.00	1.07	2.24451	0.03209	0.00142
0.10	0.70	6.25	10.00	1.60	2.24256	0.03404	0.00197
0.05	0.75	3.12	10.00	3.20	2.23929	0.03731	0.00242

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[41] / mM	[97] / mM	Ratio (97:41)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	4.79110	0.00000	0.00208
0.80	0.00	50.00	10.00	0.20	4.76563	0.02547	0.00097
0.40	0.40	25.00	10.00	0.40	4.76502	0.02608	0.00126
0.30	0.50	18.75	10.00	0.53	4.76311	0.02799	0.00095
0.20	0.60	12.50	10.00	0.80	4.76023	0.03087	0.00132
0.15	0.65	9.37	10.00	1.07	4.75858	0.03252	0.00124
0.10	0.70	6.25	10.00	1.60	4.75725	0.03385	0.00163
0.05	0.75	3.12	10.00	3.20	4.75467	0.03643	0.00207

Job Plot

	41 / g	97 / g	D_2O / mL	[41] / mM	[97] / mM
Solution X	0.1361	0.0000	25	10.00	0.00
Solution Y	0.0000	0.0980	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[97]_{tot}$ / mM	Mf of 97	δ	[41•97] / mM	Error / mM
0.70	0.10	1.25	0.12	7.44734	0.84	0.01
0.60	0.20	2.50	0.25	7.46818	1.36	0.01
0.50	0.30	3.75	0.37	7.48664	1.61	0.03
0.40	0.40	5.00	0.50	7.50393	1.62	0.01
0.30	0.50	6.25	0.62	7.52080	1.37	0.02
0.20	0.60	7.50	0.75	7.53530	0.98	0.05
0.10	0.70	8.75	0.87	7.54589	0.57	0.11
0.00	0.80	10.00	1.00	7.55651	0.00	0.00

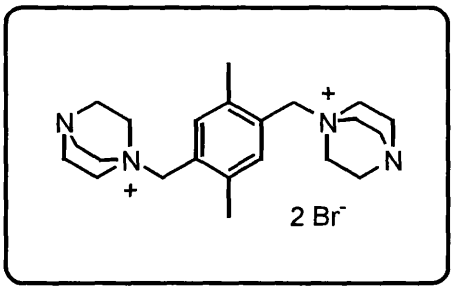
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•97] / mM	Error / mM
0.80	0.00	10.00	1.00	2.27660	0.00	0.00
0.70	0.10	8.75	0.88	2.26890	1.33	0.08
0.60	0.20	7.50	0.75	2.26331	1.97	0.15
0.50	0.30	6.25	0.63	2.25634	2.50	0.15
0.40	0.40	5.00	0.50	2.25068	2.56	0.03
0.30	0.50	3.75	0.38	2.24786	2.13	0.05
0.20	0.60	2.50	0.25	2.24451	1.59	0.04
0.10	0.70	1.25	0.13	2.23955	0.92	0.00

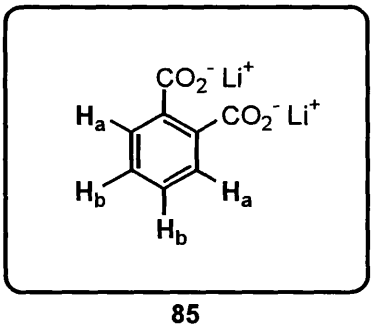
Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[41]_{tot}$ / mM	Mf of 41	δ	[41•97] / mM	Error / mM
0.80	0.00	10.00	1.00	4.79110	0.00	0.00
0.70	0.10	8.75	0.88	4.78417	1.24	0.06
0.60	0.20	7.50	0.75	4.77851	1.92	0.16
0.50	0.30	6.25	0.63	4.77151	2.49	0.12
0.40	0.40	5.00	0.50	4.76605	2.55	0.02
0.30	0.50	3.75	0.38	4.76317	2.13	0.05
0.20	0.60	2.50	0.25	4.75996	1.59	0.05
0.10	0.70	1.25	0.13	4.75518	0.91	0.01

A.16 2,5-Bis(DABCO-N-methyl)-1,4-dimethylbenzene dibromide and dilithium 1,2-benzenedicarboxylate



42



85

NMR Titration

	42 / g	85 / g	D_2O / mL	[42] / mM	[85] / mM
Solution X	0.2615	0.0182	10	50.64	10.22
Solution Y	0	0.0447	25	0.00	10.04

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	[42] / mM	[85] / mM	Ratio (42:85)	δ	$\Delta\delta$	Error
0.80	0.00	50.64	10.22	4.95	7.23721	0.05755	0.01165
0.40	0.40	25.32	10.13	2.50	7.25911	0.03565	0.00155
0.30	0.50	18.99	10.11	1.88	7.26516	0.02960	0.00088
0.20	0.60	12.66	10.09	1.25	7.27217	0.02259	0.00176
0.15	0.65	9.50	10.08	0.94	7.27442	0.02035	0.00068
0.10	0.70	6.33	10.07	0.63	7.28083	0.01393	0.00074
0.05	0.75	3.17	10.06	0.31	7.28581	0.00895	0.00211
0.00	0.80	0.00	10.04	0.00	7.29476	0.00000	0.00040

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[85] / mM	Ratio (85:42)	δ	Δδ	Error
Cation reference		10.04	0.00	0.00	2.30648	0.00000	0.00096
0.80	0.00	50.64	10.22	0.20	2.30842	0.00194	0.00042
0.40	0.40	25.32	10.13	0.40	2.30098	0.00550	0.00135
0.30	0.50	18.99	10.11	0.53	2.30008	0.00640	0.00078
0.20	0.60	12.66	10.09	0.80	2.29898	0.00750	0.00165
0.15	0.65	9.50	10.08	1.06	2.29583	0.01065	0.00052
0.10	0.70	6.33	10.07	1.59	2.29617	0.01031	0.00081
0.05	0.75	3.17	10.06	3.18	2.29441	0.01207	0.00223

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[85] / mM	Ratio (85:42)	δ	Δδ	Error
Cation reference		10.04	0.00	0.00	4.43500	0.00000	0.00088
0.80	0.00	50.64	10.22	0.20	4.43272	0.00228	0.00032
0.40	0.40	25.32	10.13	0.40	4.42538	0.00962	0.00119
0.30	0.50	18.99	10.11	0.53	4.42443	0.01057	0.00079
0.20	0.60	12.66	10.09	0.80	4.42294	0.01206	0.00152
0.15	0.65	9.50	10.08	1.06	4.41969	0.01531	0.00049
0.10	0.70	6.33	10.07	1.59	4.41960	0.01540	0.00082
0.05	0.75	3.17	10.06	3.18	4.41771	0.01729	0.00201

Job Plot

	42 / g	85 / g	D_2O / mL	[42] / mM	[85] / mM
Solution X	0.0778	0.0000	15	10.04	0.00
Solution Y	0.0000	0.0447	25	0.00	10.04

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	$[85]_{tot}$ / mM	Mf of 85	δ	[42•85] / mM	Error / mM
0.70	0.10	1.26	0.13	7.24961	0.56	0.05
0.60	0.20	2.51	0.25	7.26310	0.80	0.03
0.50	0.30	3.77	0.38	7.27659	0.73	0.02
0.40	0.40	5.02	0.50	7.28187	0.73	0.05
0.30	0.50	6.28	0.63	7.28545	0.70	0.03
0.20	0.60	7.53	0.75	7.29050	0.48	0.00
0.10	0.70	8.79	0.88	7.29372	0.30	0.01
0.00	0.80	10.04	1.00	7.29738	0.00	0.00

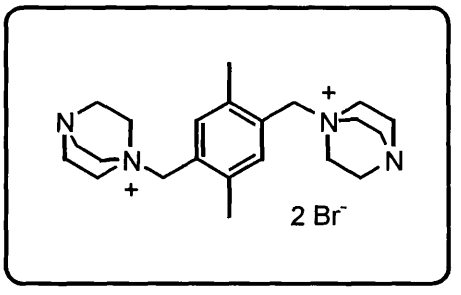
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•85] / mM	Error / mM
0.80	0.00	10.04	1.00	2.30648	0.00	0.00
0.70	0.10	8.79	0.87	2.30488	1.04	0.18
0.60	0.20	7.53	0.75	2.30255	2.19	0.25
0.50	0.30	6.28	0.62	2.30186	2.15	0.07
0.40	0.40	5.02	0.50	2.29982	2.48	0.35
0.30	0.50	3.77	0.37	2.29766	2.46	0.31
0.20	0.60	2.51	0.25	2.29664	1.83	0.06
0.10	0.70	1.26	0.12	2.29425	1.14	0.09

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•85] / mM	Error / mM
0.80	0.00	10.04	1.00	4.43500	0.00	0.00
0.70	0.10	8.79	0.87	4.43250	1.29	0.03
0.60	0.20	7.53	0.75	4.42960	2.39	0.23
0.50	0.30	6.28	0.62	4.42810	2.55	0.06
0.40	0.40	5.02	0.50	4.42536	2.85	0.32
0.30	0.50	3.77	0.37	4.42250	2.77	0.25
0.20	0.60	2.51	0.25	4.42087	2.09	0.10
0.10	0.70	1.26	0.12	4.41763	1.28	0.08

A.17 2,5-Bis(DABCO-N-methyl)-1,4-dimethylbenzene dibromide and disodium 1,2-benzenedicarboxylate



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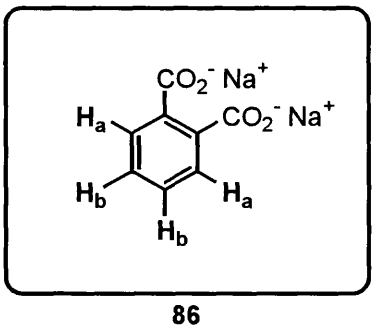


86

NMR Titration

	42 / g	86 / g	D_2O / mL	[42] / mM	[86] / mM
Solution X	0.2583	0.0210	10	50.02	10.00
Solution Y	0	0.0524	25	0.00	9.98

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	[42] / mM	[86] / mM	Ratio (42:86)	δ	$\Delta\delta$	Error
0.80	0.00	50.02	10.00	5.00	7.23871	0.06348	0.00778
0.40	0.40	25.01	9.99	2.50	7.26549	0.03670	0.00076
0.30	0.50	18.76	9.98	1.88	7.27033	0.03186	0.00076
0.20	0.60	12.51	9.98	1.25	7.27684	0.02535	0.00124
0.15	0.65	9.38	9.98	0.94	7.28205	0.02014	0.00243
0.10	0.70	6.25	9.98	0.63	7.28640	0.01579	0.00107
0.05	0.75	3.13	9.98	0.31	7.29401	0.00818	0.00236
0.00	0.80	0.00	9.98	0.00	7.30219	0.00000	0.00114

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[86] / mM	Ratio (86:42)	δ	Δδ	Error
Cation reference		9.99	0.00	0.00	2.31240	0.00000	0.00149
0.80	0.00	50.02	10.00	0.20	2.31394	0.00153	0.00110
0.40	0.40	25.01	9.99	0.40	2.30771	0.00469	0.00079
0.30	0.50	18.76	9.98	0.53	2.30573	0.00667	0.00099
0.20	0.60	12.51	9.98	0.80	2.30348	0.00892	0.00108
0.15	0.65	9.38	9.98	1.06	2.30221	0.01019	0.00108
0.10	0.70	6.25	9.98	1.60	2.30055	0.01185	0.00128
0.05	0.75	3.13	9.98	3.19	2.29858	0.01382	0.00155

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[86] / mM	Ratio (86:42)	δ	Δδ	Error
Cation reference		9.99	0.00	0.00	4.44075	0.00000	0.00131
0.80	0.00	50.02	10.00	0.20	4.43901	0.00175	0.00105
0.40	0.40	25.01	9.99	0.40	4.43273	0.00802	0.00069
0.30	0.50	18.76	9.98	0.53	4.43061	0.01014	0.00088
0.20	0.60	12.51	9.98	0.80	4.42797	0.01278	0.00102
0.15	0.65	9.38	9.98	1.06	4.42627	0.01448	0.00092
0.10	0.70	6.25	9.98	1.60	4.42453	0.01622	0.00110
0.05	0.75	3.13	9.98	3.19	4.42240	0.01835	0.00127

Job Plot

	42 / g	86 / g	D_2O / mL	[42] / mM	[86] / mM
Solution X	0.0774	0.0000	15	9.99	0.00
Solution Y	0.0000	0.0524	25	0.00	9.98

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	$[86]_{tot}$ / mM	Mf of 86	δ	[42•86] / mM	Error / mM
0.70	0.10	1.25	0.12	7.27196	0.33	0.06
0.60	0.20	2.49	0.25	7.27404	0.62	0.00
0.50	0.30	3.74	0.37	7.27995	0.76	0.02
0.40	0.40	4.98	0.50	7.28538	0.80	0.01
0.30	0.50	6.23	0.62	7.29320	0.62	0.01
0.20	0.60	7.48	0.75	7.29791	0.48	0.02
0.10	0.70	8.73	0.87	7.30221	0.27	0.06
0.00	0.80	9.98	1.00	7.30615	0.00	0.00

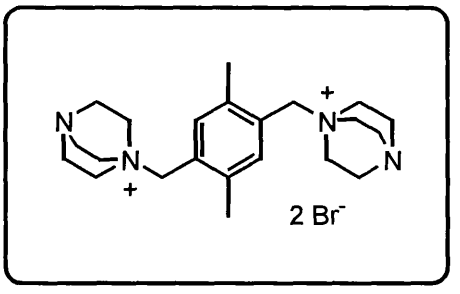
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•86] / mM	Error / mM
0.80	0.00	9.99	1.00	2.31240	0.00	0.00
0.70	0.10	8.75	0.88	2.31071	0.96	0.03
0.60	0.20	7.50	0.75	2.30896	1.68	0.19
0.50	0.30	6.25	0.63	2.30770	1.91	0.23
0.40	0.40	5.00	0.50	2.30581	2.14	0.11
0.30	0.50	3.75	0.38	2.30466	1.89	0.13
0.20	0.60	2.50	0.25	2.30316	1.50	0.07
0.10	0.70	1.25	0.13	2.30189	0.85	0.01

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•86] / mM	Error / mM
0.80	0.00	9.99	1.00	4.44075	0.00	0.00
0.70	0.10	8.75	0.88	4.43838	1.11	0.02
0.60	0.20	7.50	0.75	4.43617	1.83	0.08
0.50	0.30	6.25	0.63	4.43404	2.24	0.22
0.40	0.40	5.00	0.50	4.43168	2.42	0.13
0.30	0.50	3.75	0.38	4.42977	2.20	0.16
0.20	0.60	2.50	0.25	4.42761	1.75	0.08
0.10	0.70	1.25	0.13	4.42533	1.03	0.01

A.18 2,5-Bis(DABCO-N-methyl)-1,4-dimethylbenzene dibromide and dipotassium 1,2-benzenedicarboxylate



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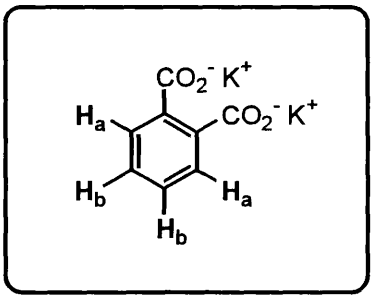


87

NMR Titration

	42 / g	87 / g	D_2O / mL	[42] / mM	[87] / mM
Solution X	0.2600	0.0258	10	50.35	10.65
Solution Y	0	0.0614	25	0.00	10.14

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	[42] / mM	[87] / mM	Ratio (42:87)	δ	$\Delta\delta$	Error
0.80	0.00	50.35	10.65	4.73	7.24340	0.06529	0.01262
0.40	0.40	25.18	10.39	2.42	7.26887	0.03982	0.00315
0.30	0.50	18.88	10.33	1.83	7.27654	0.03215	0.00379
0.20	0.60	12.59	10.26	1.23	7.28288	0.02581	0.00331
0.15	0.65	9.44	10.23	0.92	7.28962	0.01907	0.00308
0.10	0.70	6.29	10.20	0.62	7.29185	0.01684	0.00218
0.05	0.75	3.15	10.17	0.31	7.29799	0.01070	0.00164
0.00	0.80	0.00	10.14	0.00	7.30869	0.00000	0.00147

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[87] / mM	Ratio (87:42)	δ	Δδ	Error
Cation reference		10.14	0.00	0.00	2.31673	0.00000	0.00106
0.80	0.00	50.35	10.65	0.21	2.31454	0.00219	0.00425
0.40	0.40	25.18	10.39	0.41	2.31049	0.00624	0.00309
0.30	0.50	18.88	10.33	0.55	2.30892	0.00781	0.00331
0.20	0.60	12.59	10.26	0.82	2.30804	0.00869	0.00300
0.15	0.65	9.44	10.23	1.08	2.30724	0.00949	0.00261
0.10	0.70	6.29	10.20	1.62	2.30598	0.01075	0.00185
0.05	0.75	3.15	10.17	3.23	2.30455	0.01218	0.00136

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[87] / mM	Ratio (87:42)	δ	Δδ	Error
Cation reference		10.14	0.00	0.00	4.44445	0.00000	0.00094
0.80	0.00	50.35	10.65	0.21	4.43855	0.00590	0.00412
0.40	0.40	25.18	10.39	0.41	4.43433	0.01012	0.00297
0.30	0.50	18.88	10.33	0.55	4.43289	0.01157	0.00325
0.20	0.60	12.59	10.26	0.82	4.43130	0.01316	0.00286
0.15	0.65	9.44	10.23	1.08	4.43043	0.01402	0.00259
0.10	0.70	6.29	10.20	1.62	4.42900	0.01545	0.00179
0.05	0.75	3.15	10.17	3.23	4.42729	0.01716	0.00136

Job Plot

	42 / g	87 / g	D_2O / mL	[42] / mM	[87] / mM
Solution X	0.0785	0.0000	15	10.14	0.00
Solution Y	0.0000	0.0614	25	0.00	10.14

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	$[87]_{tot}$ / mM	Mf of 87	δ	[42•87] / mM	Error / mM
0.70	0.10	1.27	0.13	7.28591	0.25	0.00
0.60	0.20	2.53	0.25	7.29033	0.41	0.00
0.50	0.30	3.80	0.38	7.29336	0.53	0.01
0.40	0.40	5.07	0.50	7.29551	0.62	0.00
0.30	0.50	6.34	0.63	7.29802	0.66	0.01
0.20	0.60	7.60	0.75	7.30316	0.49	0.00
0.10	0.70	8.87	0.88	7.30737	0.30	0.02
0.00	0.80	10.14	1.00	7.31187	0.00	0.00

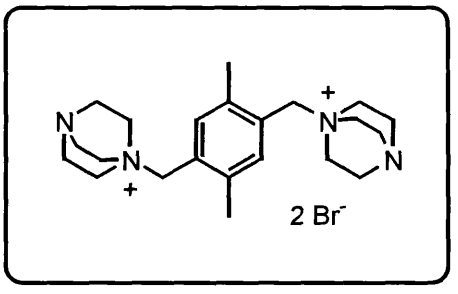
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•87] / mM	Error / mM
0.80	0.00	10.14	1.00	2.31673	0.00	0.00
0.70	0.10	8.87	0.87	2.31532	0.98	0.16
0.60	0.20	7.60	0.75	2.31367	1.83	0.22
0.50	0.30	6.33	0.62	2.31219	2.26	0.12
0.40	0.40	5.07	0.50	2.31078	2.37	0.41
0.30	0.50	3.80	0.37	2.30894	2.32	0.27
0.20	0.60	2.53	0.25	2.30786	1.76	0.13
0.10	0.70	1.27	0.12	2.30619	1.05	0.06

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•87] / mM	Error / mM
0.80	0.00	10.14	1.00	4.44445	0.00	0.00
0.70	0.10	8.87	0.87	4.44232	1.03	0.15
0.60	0.20	7.60	0.75	4.43993	1.86	0.16
0.50	0.30	6.33	0.62	4.43783	2.27	0.09
0.40	0.40	5.07	0.50	4.43583	2.37	0.22
0.30	0.50	3.80	0.37	4.43302	2.35	0.21
0.20	0.60	2.53	0.25	4.43119	1.82	0.09
0.10	0.70	1.27	0.12	4.42872	1.08	0.04

A.19 2,5-Bis(DABCO-N-methyl)-1,4-dimethylbenzene dibromide and dilithium 1,3-benzenedicarboxylate



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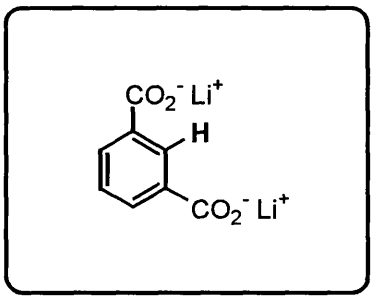


88

NMR Titration

	42 / g	88 / g	D_2O / mL	[42] / mM	[88] / mM
Solution X	0.2281	0.0179	10	44.17	10.06
Solution Y	0	0.0448	25	0.00	10.07

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[88] / mM	Ratio (42:88)	δ	Δδ	Error
0.80	0.00	44.17	10.06	4.39	8.00883	0.13062	0.00023
0.40	0.40	22.09	10.06	2.20	8.04324	0.09621	0.00089
0.30	0.50	16.57	10.06	1.65	8.05652	0.08293	0.00111
0.20	0.60	11.04	10.06	1.10	8.07388	0.06557	0.00078
0.15	0.65	8.28	10.07	0.82	8.08469	0.05476	0.00064
0.10	0.70	5.52	10.07	0.55	8.09780	0.04165	0.00078
0.05	0.75	2.76	10.07	0.27	8.11459	0.02486	0.00030
0.00	0.80	0.00	10.07	0.00	8.13945	0.00000	0.00039

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[88] / mM	Ratio (88:42)	δ	Δδ	Error
Cation reference		10.06	0.00	0.00	2.30528	0.00000	0.00161
0.80	0.00	44.17	10.06	0.23	2.28237	0.02290	0.00021
0.40	0.40	22.09	10.06	0.46	2.26727	0.03801	0.00044
0.30	0.50	16.57	10.06	0.61	2.26131	0.04397	0.00077
0.20	0.60	11.04	10.06	0.91	2.25356	0.05172	0.00052
0.15	0.65	8.28	10.07	1.22	2.24773	0.05755	0.00025
0.10	0.70	5.52	10.07	1.82	2.24166	0.06362	0.00025
0.05	0.75	2.76	10.07	3.65	2.23408	0.07119	0.00070

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[88] / mM	Ratio (88:42)	δ	Δδ	Error
Cation reference		10.06	0.00	0.00	4.43384	0.00000	0.00158
0.80	0.00	44.17	10.06	0.23	4.39976	0.03408	0.00018
0.40	0.40	22.09	10.06	0.46	4.38062	0.05323	0.00047
0.30	0.50	16.57	10.06	0.61	4.37263	0.06122	0.00052
0.20	0.60	11.04	10.06	0.91	4.36235	0.07149	0.00064
0.15	0.65	8.28	10.07	1.22	4.35486	0.07898	0.00022
0.10	0.70	5.52	10.07	1.82	4.34673	0.08711	0.00025
0.05	0.75	2.76	10.07	3.65	4.33672	0.09712	0.00066

Job Plot

	42 / g	88 / g	D_2O / mL	[42] / mM	[88] / mM
Solution X	0.0779	0.0000	15	10.06	0.00
Solution Y	0.0000	0.0448	25	0.00	10.07

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[88]_{tot}$ / mM	Mf of 88	δ	[42•88] / mM	Error / mM
0.70	0.10	1.26	0.13	8.05943	0.60	0.01
0.60	0.20	2.52	0.25	8.06989	1.05	0.02
0.50	0.30	3.78	0.38	8.08085	1.33	0.03
0.40	0.40	5.04	0.50	8.09346	1.41	0.05
0.30	0.50	6.29	0.63	8.10511	1.33	0.08
0.20	0.60	7.55	0.75	8.11618	1.11	0.02
0.10	0.70	8.81	0.88	8.12895	0.64	0.03
0.00	0.80	10.07	1.00	8.14135	0.00	0.00

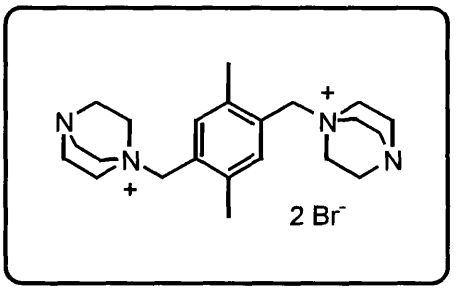
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•88] / mM	Error / mM
0.80	0.00	10.06	1.00	2.30528	0.00	0.00
0.70	0.10	8.80	0.87	2.29397	1.38	0.06
0.60	0.20	7.54	0.75	2.28270	2.36	0.06
0.50	0.30	6.28	0.62	2.27272	2.83	0.00
0.40	0.40	5.03	0.50	2.26340	2.91	0.26
0.30	0.50	3.77	0.37	2.25340	2.71	0.22
0.20	0.60	2.51	0.25	2.24352	2.15	0.06
0.10	0.70	1.26	0.12	2.23504	1.22	0.05

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•88] / mM	Error / mM
0.80	0.00	10.06	1.00	4.43384	0.00	0.00
0.70	0.10	8.80	0.87	4.41876	1.36	0.04
0.60	0.20	7.54	0.75	4.40379	2.32	0.02
0.50	0.30	6.28	0.62	4.38993	2.82	0.01
0.40	0.40	5.03	0.50	4.37667	2.94	0.19
0.30	0.50	3.77	0.37	4.36307	2.73	0.16
0.20	0.60	2.51	0.25	4.34939	2.17	0.04
0.10	0.70	1.26	0.12	4.33739	1.24	0.03

A.20 2,5-Bis(DABCO-N-methyl)-1,4-dimethylbenzene dibromide and disodium 1,3-benzenedicarboxylate



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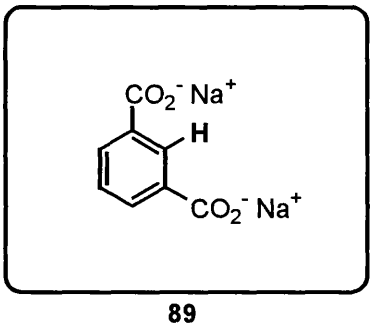


89

NMR Titration

	42 / g	89 / g	D_2O / mL	[42] / mM	[89] / mM
Solution X	0.2006	0.0212	10	38.85	10.09
Solution Y	0	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[89] / mM	Ratio (42:89)	δ	Δδ	Error
0.80	0.00	38.85	10.09	3.85	8.00996	0.13273	0.00036
0.40	0.40	19.42	10.04	1.93	8.04805	0.09464	0.00337
0.30	0.50	14.57	10.03	1.45	8.06172	0.08097	0.00041
0.20	0.60	9.71	10.02	0.97	8.07559	0.06710	0.00018
0.15	0.65	7.28	10.01	0.73	8.08679	0.05590	0.00042
0.10	0.70	4.86	10.01	0.49	8.10514	0.03755	0.00125
0.05	0.75	2.43	10.00	0.24	8.12266	0.02003	0.00090
0.00	0.80	0.00	10.00	0.00	8.14269	0.00000	0.00095

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[89] / mM	Ratio (89:42)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	2.30568	0.00000	0.00037
0.80	0.00	38.85	10.09	0.26	2.28290	0.02278	0.00037
0.40	0.40	19.42	10.04	0.52	2.27188	0.03380	0.00271
0.30	0.50	14.57	10.03	0.69	2.26585	0.03983	0.00052
0.20	0.60	9.71	10.02	1.03	2.25519	0.05049	0.00055
0.15	0.65	7.28	10.01	1.37	2.24951	0.05617	0.00060
0.10	0.70	4.86	10.01	2.06	2.24694	0.05874	0.00132
0.05	0.75	2.43	10.00	4.12	2.24016	0.06552	0.00133

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[89] / mM	Ratio (89:42)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	4.43411	0.00000	0.00036
0.80	0.00	38.85	10.09	0.26	4.40102	0.03309	0.00029
0.40	0.40	19.42	10.04	0.52	4.38550	0.04861	0.00271
0.30	0.50	14.57	10.03	0.69	4.37756	0.05655	0.00025
0.20	0.60	9.71	10.02	1.03	4.36447	0.06964	0.00041
0.15	0.65	7.28	10.01	1.37	4.35727	0.07684	0.00061
0.10	0.70	4.86	10.01	2.06	4.35290	0.08121	0.00133
0.05	0.75	2.43	10.00	4.12	4.34347	0.09064	0.00123

Job Plot

	42 / g	89 / g	D_2O / mL	[42] / mM	[89] / mM
Solution X	0.0775	0.0000	15	10.01	0.00
Solution Y	0.0000	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[89]_{tot}$ / mM	Mf of 89	δ	[42•89] / mM	Error / mM
0.70	0.10	1.25	0.12	8.05943	0.59	0.02
0.60	0.20	2.50	0.25	8.07105	1.03	0.00
0.50	0.30	3.75	0.37	8.07876	1.39	0.01
0.40	0.40	4.99	0.50	8.09080	1.52	0.00
0.30	0.50	6.24	0.62	8.10587	1.38	0.00
0.20	0.60	7.49	0.75	8.11580	1.25	0.01
0.10	0.70	8.74	0.87	8.12933	0.81	0.01
0.00	0.80	10.00	1.00	8.14611	0.00	0.00

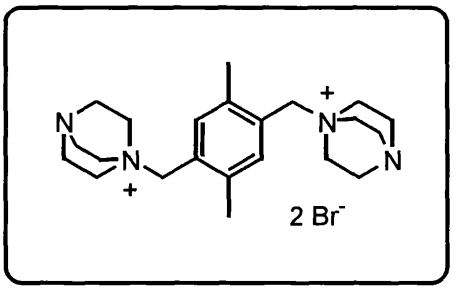
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•89] / mM	Error / mM
0.80	0.00	10.01	1.00	2.30568	0.00	0.00
0.70	0.10	8.76	0.88	2.29710	1.13	0.28
0.60	0.20	7.51	0.75	2.28952	1.82	0.01
0.50	0.30	6.26	0.63	2.27719	2.67	0.05
0.40	0.40	5.01	0.50	2.26747	2.87	0.07
0.30	0.50	3.75	0.38	2.26035	2.55	0.00
0.20	0.60	2.50	0.25	2.24807	2.16	0.01
0.10	0.70	1.25	0.13	2.23916	1.25	0.02

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•89] / mM	Error / mM
0.80	0.00	10.01	1.00	4.43411	0.00	0.00
0.70	0.10	8.76	0.88	4.42210	1.14	0.19
0.60	0.20	7.51	0.75	4.41127	1.86	0.02
0.50	0.30	6.26	0.63	4.39561	2.61	0.03
0.40	0.40	5.01	0.50	4.38214	2.82	0.04
0.30	0.50	3.75	0.38	4.37128	2.56	0.00
0.20	0.60	2.50	0.25	4.35541	2.14	0.01
0.10	0.70	1.25	0.13	4.34280	1.24	0.01

A.21 2,5-Bis(DABCO-N-methyl)-1,4-dimethylbenzene dibromide and dipotassium 1,3-benzenedicarboxylate



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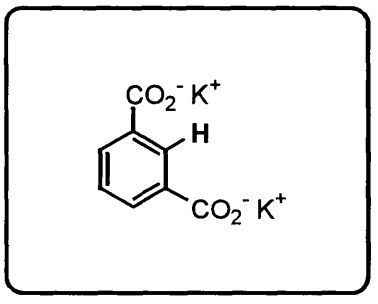


90

NMR Titration

	42 / g	90 / g	D_2O / mL	[42] / mM	[90] / mM
Solution X	0.2678	0.0244	10	51.86	10.07
Solution Y	0	0.0609	25	0.00	10.05

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[90] / mM	Ratio (42:90)	δ	Δδ	Error
0.80	0.00	51.86	10.07	5.15	8.01570	0.15129	0.00244
0.40	0.40	25.93	10.06	2.58	8.05493	0.11206	0.00169
0.30	0.50	19.45	10.06	1.93	8.06963	0.09736	0.00180
0.20	0.60	12.97	10.06	1.29	8.09112	0.07587	0.00080
0.15	0.65	9.72	10.06	0.97	8.10774	0.05925	0.00503
0.10	0.70	6.48	10.06	0.64	8.11825	0.04874	0.00106
0.05	0.75	3.24	10.05	0.32	8.13742	0.02957	0.00189
0.00	0.80	0.00	10.05	0.00	8.16699	0.00000	0.00039

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[90] / mM	Ratio (90:42)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	2.29918	0.00000	0.00123
0.80	0.00	51.86	10.07	0.19	2.27920	0.01998	0.00144
0.40	0.40	25.93	10.06	0.39	2.26348	0.03570	0.00149
0.30	0.50	19.45	10.06	0.52	2.25876	0.04042	0.00026
0.20	0.60	12.97	10.06	0.78	2.25140	0.04778	0.00137
0.15	0.65	9.72	10.06	1.03	2.24540	0.05377	0.00066
0.10	0.70	6.48	10.06	1.55	2.24010	0.05907	0.00111
0.05	0.75	3.24	10.05	3.10	2.23171	0.06746	0.00188

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[90] / mM	Ratio (90:42)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	4.42791	0.00000	0.00117
0.80	0.00	51.86	10.07	0.19	4.39787	0.03004	0.00153
0.40	0.40	25.93	10.06	0.39	4.37875	0.04916	0.00145
0.30	0.50	19.45	10.06	0.52	4.37199	0.05592	0.00019
0.20	0.60	12.97	10.06	0.78	4.36226	0.06565	0.00111
0.15	0.65	9.72	10.06	1.03	4.35464	0.07327	0.00038
0.10	0.70	6.48	10.06	1.55	4.34729	0.08062	0.00107
0.05	0.75	3.24	10.05	3.10	4.33637	0.09153	0.00194

Job Plot

	42 / g	90 / g	D_2O / mL	[42] / mM	[90] / mM
Solution X	0.0775	0.0000	15	10.01	0.00
Solution Y	0.0000	0.0609	25	0.00	10.05

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[90]_{tot}$ / mM	Mf of 90	δ	[42•90] / mM	Error / mM
0.70	0.10	1.26	0.13	8.07820	0.56	0.00
0.60	0.20	2.52	0.25	8.09254	0.95	0.00
0.50	0.30	3.78	0.38	8.10740	1.14	0.01
0.40	0.40	5.04	0.50	8.11966	1.22	0.02
0.30	0.50	6.29	0.63	8.13103	1.17	0.02
0.20	0.60	7.55	0.75	8.14336	0.94	0.01
0.10	0.70	8.80	0.88	8.15462	0.61	0.01
0.00	0.80	10.05	1.00	8.16865	0.00	0.00

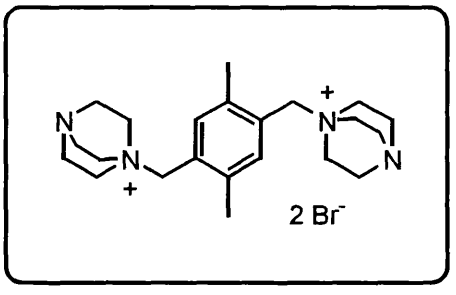
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•90] / mM	Error / mM
0.80	0.00	10.01	1.00	2.29918	0.00	0.00
0.70	0.10	8.75	0.87	2.28842	1.40	0.03
0.60	0.20	7.50	0.75	2.27842	2.32	0.03
0.50	0.30	6.24	0.62	2.26907	2.80	0.02
0.40	0.40	4.99	0.50	2.25786	3.07	0.07
0.30	0.50	3.74	0.37	2.24822	2.84	0.03
0.20	0.60	2.49	0.25	2.23871	2.24	0.04
0.10	0.70	1.25	0.12	2.22875	1.31	0.02

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•90] / mM	Error / mM
0.80	0.00	10.01	1.00	4.42791	0.00	0.00
0.70	0.10	8.75	0.87	4.41412	1.31	0.04
0.60	0.20	7.50	0.75	4.40052	2.23	0.02
0.50	0.30	6.24	0.62	4.38740	2.75	0.01
0.40	0.40	4.99	0.50	4.37292	2.99	0.05
0.30	0.50	3.74	0.37	4.35928	2.79	0.03
0.20	0.60	2.49	0.25	4.34612	2.22	0.03
0.10	0.70	1.25	0.12	4.33263	1.29	0.02

A.22 2,5-Bis(DABCO-N-methyl)-1,4-dimethylbenzene dibromide and calcium 1,3-benzenedicarboxylate



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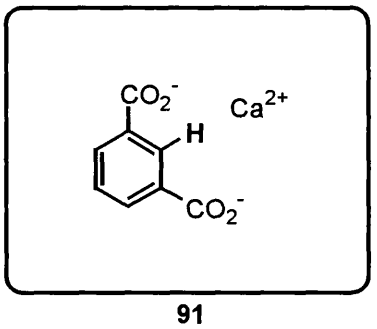


91

NMR Titration

	42 / g	91 / g	D_2O / mL	[42] / mM	[91] / mM
Solution X	0.2596	0.0212	10	50.28	10.38
Solution Y	0	0.0525	25	0.00	10.28

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[91] / mM	Ratio (42:91)	δ	$\Delta\delta$	Error
0.80	0.00	50.28	10.38	4.84	8.01326	0.16042	0.00099
0.40	0.40	25.14	10.33	2.43	8.05647	0.11722	0.00041
0.30	0.50	18.85	10.32	1.83	8.07248	0.10120	0.00019
0.20	0.60	12.57	10.31	1.22	8.09264	0.08105	0.00047
0.15	0.65	9.43	10.30	0.91	8.10539	0.06829	0.00031
0.10	0.70	6.28	10.30	0.61	8.12098	0.05271	0.00026
0.05	0.75	3.14	10.29	0.31	8.14232	0.03136	0.00065
0.00	0.80	0.00	10.28	0.00	8.17369	0.00000	0.00009

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[91] / mM	Ratio (91:42)	δ	Δδ	Error
Cation reference		10.10	0.00	0.00	2.31039	0.00000	0.00067
0.80	0.00	50.28	10.38	0.21	2.29214	0.01825	0.00076
0.40	0.40	25.14	10.33	0.41	2.27962	0.03077	0.00054
0.30	0.50	18.85	10.32	0.55	2.27457	0.03582	0.00019
0.20	0.60	12.57	10.31	0.82	2.26783	0.04256	0.00024
0.15	0.65	9.43	10.30	1.09	2.26318	0.04721	0.00040
0.10	0.70	6.28	10.30	1.64	2.25788	0.05251	0.00034
0.05	0.75	3.14	10.29	3.27	2.25057	0.05982	0.00031

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[91] / mM	Ratio (91:42)	δ	Δδ	Error
Cation reference		10.10	0.00	0.00	4.43862	0.00000	0.00059
0.80	0.00	50.28	10.38	0.21	4.41165	0.02697	0.00069
0.40	0.40	25.14	10.33	0.41	4.39616	0.04246	0.00054
0.30	0.50	18.85	10.32	0.55	4.38965	0.04897	0.00021
0.20	0.60	12.57	10.31	0.82	4.38098	0.05764	0.00024
0.15	0.65	9.43	10.30	1.09	4.37506	0.06356	0.00040
0.10	0.70	6.28	10.30	1.64	4.36790	0.07072	0.00040
0.05	0.75	3.14	10.29	3.27	4.35836	0.08026	0.00048

Job Plot

	42 / g	91 / g	D_2O / mL	[42] / mM	[91] / mM
Solution X	0.0782	0.0000	15	10.10	0.00
Solution Y	0.0000	0.0525	25	0.00	10.28

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[91]_{tot}$ / mM	Mf of 91	δ	[42•91] / mM	Error / mM
0.70	0.10	1.31	0.13	8.07355	0.63	0.00
0.60	0.20	2.61	0.25	8.08996	1.05	0.00
0.50	0.30	3.90	0.38	8.10486	1.29	0.00
0.40	0.40	5.19	0.50	8.11885	1.38	0.01
0.30	0.50	6.47	0.63	8.13277	1.30	0.00
0.20	0.60	7.75	0.75	8.14664	1.05	0.01
0.10	0.70	9.02	0.88	8.16071	0.62	0.00
0.00	0.80	10.28	1.00	8.17527	0.00	0.00

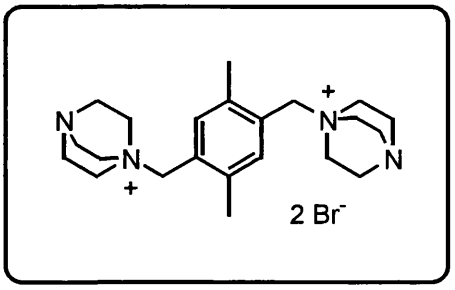
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•91] / mM	Error / mM
0.80	0.00	10.10	1.00	2.31039	0.00	0.00
0.70	0.10	8.81	0.87	2.30093	1.38	0.04
0.60	0.20	7.54	0.75	2.29277	2.20	0.04
0.50	0.30	6.27	0.62	2.28411	2.73	0.03
0.40	0.40	5.00	0.50	2.27595	2.85	0.06
0.30	0.50	3.74	0.37	2.26744	2.66	0.02
0.20	0.60	2.49	0.25	2.25920	2.11	0.03
0.10	0.70	1.24	0.12	2.25082	1.22	0.01

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•91] / mM	Error / mM
0.80	0.00	10.10	1.00	4.43862	0.00	0.00
0.70	0.10	8.81	0.87	4.42603	1.38	0.05
0.60	0.20	7.54	0.75	4.41501	2.21	0.06
0.50	0.30	6.27	0.62	4.40342	2.74	0.03
0.40	0.40	5.00	0.50	4.39230	2.87	0.04
0.30	0.50	3.74	0.37	4.38081	2.68	0.02
0.20	0.60	2.49	0.25	4.36932	2.14	0.02
0.10	0.70	1.24	0.12	4.35819	1.24	0.01

A.23 2,5-Bis(DABCO-N-methyl)-1,4-dimethylbenzene dibromide and disodium 1,4-benzenedicarboxylate



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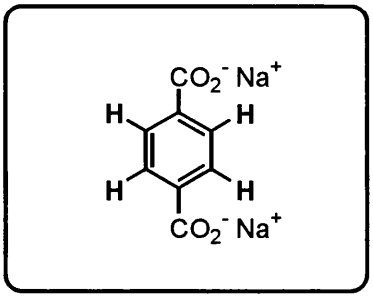


92

NMR Titration

	42 / g	92 / g	D_2O / mL	[42] / mM	[92] / mM
Solution X	0.2582	0.0210	10	50.00	10.00
Solution Y	0	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[92] / mM	Ratio (42:92)	δ	$\Delta\delta$	Error
0.80	0.00	50.00	10.00	5.00	7.60114	0.13940	0.00169
0.40	0.40	25.00	10.00	2.50	7.63646	0.10408	0.00090
0.30	0.50	18.75	10.00	1.88	7.64975	0.09079	0.00060
0.20	0.60	12.50	10.00	1.25	7.66924	0.07130	0.00116
0.15	0.65	9.38	10.00	0.94	7.68114	0.05940	0.00267
0.10	0.70	6.25	10.00	0.63	7.69361	0.04693	0.00166
0.05	0.75	3.13	10.00	0.31	7.71200	0.02854	0.00236
0.00	0.80	0.00	10.00	0.00	7.74054	0.00000	0.00053

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[92] / mM	Ratio (92:42)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	2.30850	0.00000	0.00166
0.80	0.00	50.00	10.00	0.20	2.29242	0.01608	0.00143
0.40	0.40	25.00	10.00	0.40	2.27575	0.03275	0.00087
0.30	0.50	18.75	10.00	0.53	2.26817	0.04033	0.00065
0.20	0.60	12.50	10.00	0.80	2.26448	0.04402	0.00081
0.15	0.65	9.38	10.00	1.07	2.25946	0.04904	0.00260
0.10	0.70	6.25	10.00	1.60	2.25090	0.05760	0.00153
0.05	0.75	3.13	10.00	3.20	2.24524	0.06326	0.00193

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[92] / mM	Ratio (92:42)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	4.43696	0.00000	0.00154
0.80	0.00	50.00	10.00	0.20	4.40960	0.02736	0.00136
0.40	0.40	25.00	10.00	0.40	4.38865	0.04831	0.00083
0.30	0.50	18.75	10.00	0.53	4.37934	0.05762	0.00058
0.20	0.60	12.50	10.00	0.80	4.37292	0.06404	0.00079
0.15	0.65	9.38	10.00	1.07	4.36615	0.07081	0.00254
0.10	0.70	6.25	10.00	1.60	4.35546	0.08150	0.00147
0.05	0.75	3.13	10.00	3.20	4.34686	0.09010	0.00178

Job Plot

	42 / g	92 / g	D_2O / mL	[42] / mM	[92] / mM
Solution X	0.0775	0.0000	15	10.01	0.00
Solution Y	0.0000	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[92]_{tot}$ / mM	Mf of 92	δ	[42•92] / mM	Error / mM
0.70	0.10	1.25	0.12	7.66004	0.55	0.00
0.60	0.20	2.50	0.25	7.67029	0.95	0.01
0.50	0.30	3.75	0.37	7.68232	1.18	0.01
0.40	0.40	5.00	0.50	7.69123	1.32	0.02
0.30	0.50	6.25	0.62	7.70272	1.25	0.01
0.20	0.60	7.50	0.75	7.71567	0.95	0.01
0.10	0.70	8.75	0.87	7.72636	0.58	0.01
0.00	0.80	10.00	1.00	7.73826	0.00	0.00

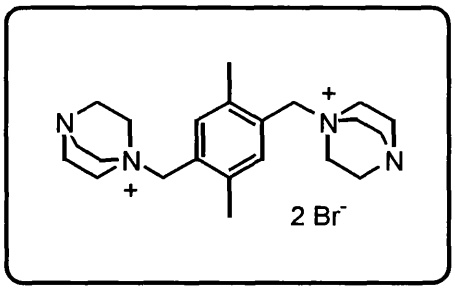
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•92] / mM	Error / mM
0.80	0.00	10.01	1.00	2.30850	0.00	0.00
0.70	0.10	8.76	0.88	2.29715	1.59	0.02
0.60	0.20	7.51	0.75	2.28854	2.40	0.09
0.50	0.30	6.26	0.63	2.28005	2.85	0.03
0.40	0.40	5.01	0.50	2.26894	3.17	0.11
0.30	0.50	3.75	0.38	2.25960	2.94	0.09
0.20	0.60	2.50	0.25	2.25194	2.27	0.05
0.10	0.70	1.25	0.13	2.24296	1.31	0.04

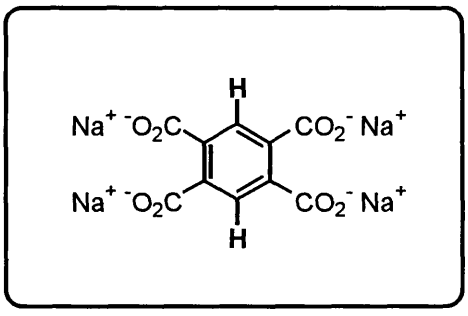
Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•92] / mM	Error / mM
0.80	0.00	10.01	1.00	4.43696	0.00	0.00
0.70	0.10	8.76	0.88	4.42176	1.50	0.01
0.60	0.20	7.51	0.75	4.40904	2.36	0.05
0.50	0.30	6.26	0.63	4.39664	2.84	0.02
0.40	0.40	5.01	0.50	4.38156	3.12	0.07
0.30	0.50	3.75	0.38	4.36828	2.90	0.06
0.20	0.60	2.50	0.25	4.35681	2.26	0.04
0.10	0.70	1.25	0.13	4.34427	1.30	0.03

A.24 2,5-Bis(DABCO-N-methyl)-1,4-dimethylbenzene dibromide and tetrasodium 1,2,4,5-benzene-tetracarboxylate



42



96

NMR Titration

	42 / g	96 / g	D_2O / mL	[42] / mM	[96] / mM
Solution X	0.2586	0.0342	10	50.08	10.00
Solution Y	0	0.0855	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[96] / mM	Ratio (42:96)	δ	Δδ	Error
0.80	0.00	50.08	10.00	5.01	7.32011	0.04950	0.00273
0.40	0.40	25.04	10.00	2.50	7.33045	0.03917	0.00198
0.30	0.50	18.78	10.00	1.88	7.33500	0.03462	0.00078
0.20	0.60	12.52	10.00	1.25	7.34116	0.02846	0.00128
0.15	0.65	9.39	10.00	0.94	7.34649	0.02312	0.00171
0.10	0.70	6.26	10.00	0.63	7.35103	0.01859	0.00140
0.05	0.75	3.13	10.00	0.31	7.36075	0.00887	0.00062
0.00	0.80	0.00	10.00	0.00	7.36962	0.00000	0.00051

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[96] / mM	Ratio (96:42)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	2.30883	0.00000	0.00216
0.80	0.00	50.08	10.00	0.20	2.30646	0.00237	0.00064
0.40	0.40	25.04	10.00	0.40	2.29923	0.00960	0.00194
0.30	0.50	18.78	10.00	0.53	2.29711	0.01172	0.00058
0.20	0.60	12.52	10.00	0.80	2.29304	0.01579	0.00137
0.15	0.65	9.39	10.00	1.06	2.29145	0.01738	0.00184
0.10	0.70	6.26	10.00	1.60	2.28720	0.02163	0.00106
0.05	0.75	3.13	10.00	3.19	2.28611	0.02271	0.00071

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[42] / mM	[96] / mM	Ratio (96:42)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	4.43739	0.00000	0.00213
0.80	0.00	50.08	10.00	0.20	4.43369	0.00371	0.00053
0.40	0.40	25.04	10.00	0.40	4.42661	0.01078	0.00179
0.30	0.50	18.78	10.00	0.53	4.42446	0.01293	0.00056
0.20	0.60	12.52	10.00	0.80	4.42083	0.01656	0.00121
0.15	0.65	9.39	10.00	1.06	4.41903	0.01836	0.00152
0.10	0.70	6.26	10.00	1.60	4.41491	0.02248	0.00094
0.05	0.75	3.13	10.00	3.19	4.41367	0.02372	0.00060

Job Plot

	42 / g	96 / g	D_2O / mL	[42] / mM	[96] / mM
Solution X	0.1291	0.0000	25	10.00	0.00
Solution Y	0.0000	0.0855	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[96]_{tot}$ / mM	Mf of 96	δ	[42•96] / mM	Error / mM
0.70	0.10	1.25	0.12	7.32767	0.87	0.04
0.60	0.20	2.50	0.25	7.33234	1.56	0.04
0.50	0.30	3.75	0.37	7.33861	1.96	0.07
0.40	0.40	5.00	0.50	7.34614	2.01	0.01
0.30	0.50	6.25	0.62	7.35367	1.75	0.04
0.20	0.60	7.50	0.75	7.35932	1.42	0.04
0.10	0.70	8.75	0.87	7.36559	0.77	0.10
0.00	0.80	10.00	1.00	7.37104	0.00	0.00

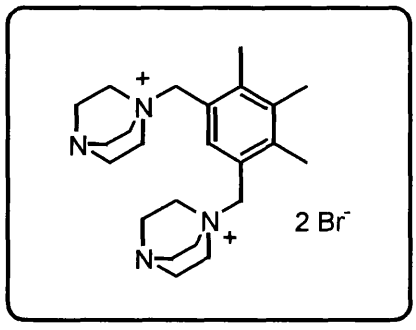
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•96] / mM	Error / mM
0.80	0.00	10.00	1.00	2.30883	0.00	0.00
0.70	0.10	8.75	0.88	2.30260	2.29	0.16
0.60	0.20	7.50	0.75	2.29930	3.00	0.19
0.50	0.30	6.25	0.63	2.29428	3.82	0.20
0.40	0.40	5.00	0.50	2.29148	3.64	0.14
0.30	0.50	3.75	0.38	2.28821	3.25	0.11
0.20	0.60	2.50	0.25	2.28520	2.48	0.18
0.10	0.70	1.25	0.13	2.28368	1.32	0.09

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[42]_{tot}$ / mM	Mf of 42	δ	[42•96] / mM	Error / mM
0.80	0.00	10.00	1.00	4.43739	0.00	0.00
0.70	0.10	8.75	0.88	4.43097	2.30	0.06
0.60	0.20	7.50	0.75	4.42747	3.05	0.19
0.50	0.30	6.25	0.63	4.42224	3.88	0.14
0.40	0.40	5.00	0.50	4.41921	3.73	0.13
0.30	0.50	3.75	0.38	4.41599	3.29	0.12
0.20	0.60	2.50	0.25	4.41303	2.50	0.15
0.10	0.70	1.25	0.13	4.41138	1.33	0.09

A.25 4,6-Bis(DABCO-N-methyl)-1,2,3-trimethylbenzene dibromide and dilithium 1,2-benzenedicarboxylate



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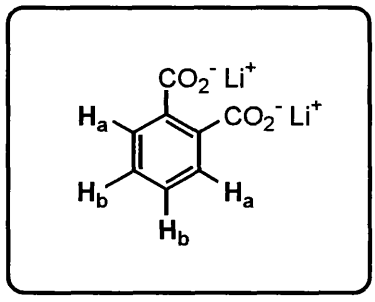


85

NMR Titration

	43 / g	85 / g	D_2O / mL	[43] / mM	[85] / mM
Solution X	0.2698	0.0186	10	50.87	10.45
Solution Y	0	0.0450	25	0.00	10.11

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	[43] / mM	[85] / mM	Ratio (43:85)	δ	Δδ	Error
0.80	0.00	50.87	10.45	4.87	7.25631	0.04047	0.00205
0.40	0.40	25.43	10.28	2.47	7.26736	0.02943	0.00216
0.30	0.50	19.08	10.24	1.86	7.27149	0.02529	0.00206
0.20	0.60	12.72	10.20	1.25	7.27615	0.02063	0.00161
0.15	0.65	9.54	10.18	0.94	7.27925	0.01754	0.00133
0.10	0.70	6.36	10.15	0.63	7.28305	0.01374	0.00094
0.05	0.75	3.18	10.13	0.31	7.28813	0.00866	0.00115
0.00	0.80	0.00	10.11	0.00	7.29679	0.00000	0.00263

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[85] / mM	Ratio (85:43)	δ	Δδ	Error
Cation reference		10.03	0.00	0.00	2.27564	0.00000	0.00028
0.80	0.00	50.87	10.45	0.21	2.27936	0.00371	0.00224
0.40	0.40	25.43	10.28	0.40	2.27588	0.00023	0.00203
0.30	0.50	19.08	10.24	0.54	2.27425	0.00139	0.00184
0.20	0.60	12.72	10.20	0.80	2.27166	0.00398	0.00170
0.15	0.65	9.54	10.18	1.07	2.27040	0.00524	0.00141
0.10	0.70	6.36	10.15	1.60	2.26867	0.00697	0.00106
0.05	0.75	3.18	10.13	3.19	2.26724	0.00840	0.00137

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[85] / mM	Ratio (85:43)	δ	Δδ	Error
Cation reference		10.03	0.00	0.00	4.51469	0.00000	0.00031
0.80	0.00	50.87	10.45	0.21	4.52407	0.00938	0.00208
0.40	0.40	25.43	10.28	0.40	4.51499	0.00030	0.00192
0.30	0.50	19.08	10.24	0.54	4.51149	0.00320	0.00176
0.20	0.60	12.72	10.20	0.80	4.50675	0.00794	0.00156
0.15	0.65	9.54	10.18	1.07	4.50422	0.01047	0.00133
0.10	0.70	6.36	10.15	1.60	4.50099	0.01370	0.00097
0.05	0.75	3.18	10.13	3.19	4.49773	0.01696	0.00143

Job Plot

	43 / g	85 / g	D_2O / mL	[43] / mM	[85] / mM
Solution X	0.0798	0.0000	15	10.03	0.00
Solution Y	0.0000	0.0450	25	0.00	10.11

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	$[85]_{tot}$ / mM	Mf of 85	δ	[43•85] / mM	Error / mM
0.70	0.10	1.27	0.13	7.27359	0.53	0.03
0.60	0.20	2.54	0.25	7.27591	0.95	0.07
0.50	0.30	3.81	0.38	7.27922	1.17	0.10
0.40	0.40	5.08	0.50	7.28215	1.27	0.06
0.30	0.50	6.34	0.63	7.28543	1.17	0.07
0.20	0.60	7.60	0.75	7.28885	0.89	0.09
0.10	0.70	8.86	0.88	7.29144	0.59	0.02
0.00	0.80	10.11	1.00	7.29482	0.00	0.00

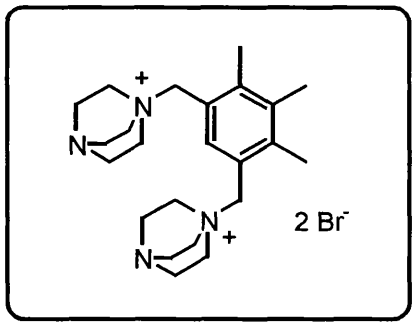
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•85] / mM	Error / mM
0.80	0.00	10.03	1.00	2.27564	0.00	0.00
0.70	0.10	8.77	0.87	2.27416	0.27	0.01
0.60	0.20	7.51	0.75	2.27285	0.43	0.06
0.50	0.30	6.25	0.62	2.27141	0.54	0.01
0.40	0.40	4.99	0.50	2.27003	0.58	0.11
0.30	0.50	3.74	0.37	2.26858	0.54	0.10
0.20	0.60	2.49	0.25	2.26723	0.43	0.07
0.10	0.70	1.24	0.12	2.26577	0.25	0.06

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•85] / mM	Error / mM
0.80	0.00	10.03	1.00	4.51469	0.00	0.00
0.70	0.10	8.77	0.87	4.51182	0.10	0.01
0.60	0.20	7.51	0.75	4.50892	0.17	0.00
0.50	0.30	6.25	0.62	4.50637	0.20	0.00
0.40	0.40	4.99	0.50	4.50363	0.22	0.02
0.30	0.50	3.74	0.37	4.50072	0.20	0.02
0.20	0.60	2.49	0.25	4.49807	0.16	0.02
0.10	0.70	1.24	0.12	4.49492	0.10	0.01

A.26 4,6-Bis(DABCO-N-methyl)-1,2,3-trimethylbenzene dibromide and disodium 1,2-benzenedicarboxylate



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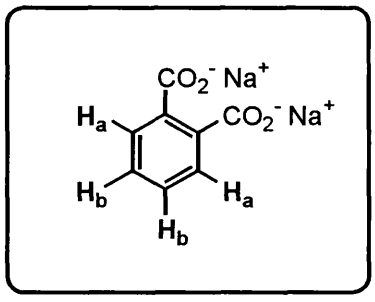


86

NMR Titration

	43 / g	86 / g	D_2O / mL	[43] / mM	[86] / mM
Solution X	0.2657	0.0214	10	50.10	10.19
Solution Y	0	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	[43] / mM	[86] / mM	Ratio (43:86)	δ	$\Delta\delta$	Error
0.80	0.00	50.10	10.19	4.92	7.24389	0.04361	0.00331
0.40	0.40	25.05	10.09	2.48	7.25745	0.03005	0.00130
0.30	0.50	18.79	10.07	1.87	7.26288	0.02462	0.00246
0.20	0.60	12.52	10.04	1.25	7.26910	0.01840	0.00198
0.15	0.65	9.39	10.03	0.94	7.27084	0.01666	0.00123
0.10	0.70	6.26	10.02	0.63	7.27501	0.01249	0.00191
0.05	0.75	3.13	10.01	0.31	7.28028	0.00722	0.00197
0.00	0.80	0.00	10.00	0.00	7.28750	0.00000	0.00266

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[86] / mM	Ratio (86:43)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	2.26846	0.00000	0.00306
0.80	0.00	50.10	10.19	0.20	2.26741	0.00105	0.00317
0.40	0.40	25.05	10.09	0.40	2.26438	0.00408	0.00132
0.30	0.50	18.79	10.07	0.54	2.26425	0.00421	0.00206
0.20	0.60	12.52	10.04	0.80	2.26358	0.00488	0.00191
0.15	0.65	9.39	10.03	1.07	2.26106	0.00740	0.00124
0.10	0.70	6.26	10.02	1.60	2.26015	0.00831	0.00195
0.05	0.75	3.13	10.01	3.20	2.25938	0.00908	0.00189

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[86] / mM	Ratio (86:43)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	4.50824	0.00000	0.00279
0.80	0.00	50.10	10.19	0.20	4.51383	0.00558	0.00307
0.40	0.40	25.05	10.09	0.40	4.50479	0.00345	0.00125
0.30	0.50	18.79	10.07	0.54	4.50277	0.00548	0.00198
0.20	0.60	12.52	10.04	0.80	4.49968	0.00856	0.00175
0.15	0.65	9.39	10.03	1.07	4.49583	0.01241	0.00113
0.10	0.70	6.26	10.02	1.60	4.49342	0.01482	0.00192
0.05	0.75	3.13	10.01	3.20	4.49063	0.01762	0.00172

Job Plot

	43 / g	86 / g	D_2O / mL	[43] / mM	[86] / mM
Solution X	0.0796	0.0000	15	10.01	0.00
Solution Y	0.0000	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	$[86]_{tot}$ / mM	Mf of 86	δ	[43•86] / mM	Error / mM
0.70	0.10	1.25	0.12	7.34102	0.15	0.00
0.60	0.20	2.50	0.25	7.34230	0.27	0.01
0.50	0.30	3.75	0.37	7.34494	0.34	0.00
0.40	0.40	5.00	0.50	7.34799	0.35	0.00
0.30	0.50	6.24	0.62	7.34941	0.37	0.02
0.20	0.60	7.49	0.75	7.35312	0.26	0.07
0.10	0.70	8.74	0.87	7.35506	0.18	0.02
0.00	0.80	10.00	1.00	7.35815	0.00	0.00

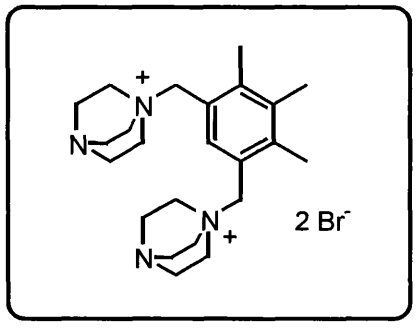
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•86] / mM	Error / mM
0.80	0.00	10.01	1.00	2.26846	0.00	0.00
0.70	0.10	8.76	0.88	2.26605	2.23	0.26
0.60	0.20	7.51	0.75	2.26592	2.02	0.09
0.50	0.30	6.26	0.63	2.26446	2.64	0.51
0.40	0.40	5.01	0.50	2.26207	3.38	0.15
0.30	0.50	3.75	0.38	2.26198	2.57	0.61
0.20	0.60	2.50	0.25	2.26119	1.92	0.33
0.10	0.70	1.25	0.13	2.25806	1.38	0.22

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•86] / mM	Error / mM
0.80	0.00	10.01	1.00	4.50824	0.00	0.00
0.70	0.10	8.76	0.88	4.50412	1.24	0.07
0.60	0.20	7.51	0.75	4.50306	1.33	0.07
0.50	0.30	6.26	0.63	4.50023	1.71	0.16
0.40	0.40	5.01	0.50	4.49651	2.01	0.06
0.30	0.50	3.75	0.38	4.49492	1.71	0.13
0.20	0.60	2.50	0.25	4.49262	1.34	0.06
0.10	0.70	1.25	0.13	4.48816	0.86	0.04

A.27 4,6-Bis(DABCO-N-methyl)-1,2,3-trimethylbenzene dibromide and dipotassium 1,2-benzenedicarboxylate



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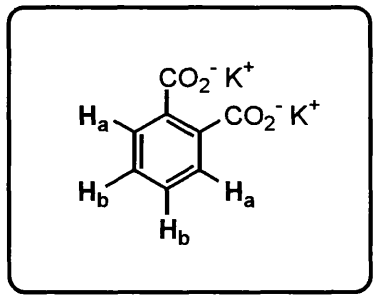


87

NMR Titration

	43 / g	87 / g	D_2O / mL	[43] / mM	[87] / mM
Solution X	0.2655	0.0242	10	50.06	9.99
Solution Y	0	0.0606	25	0.00	10.00

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	[43] / mM	[87] / mM	Ratio (43:87)	δ	$\Delta\delta$	Error
0.80	0.00	50.06	9.99	5.01	7.32081	0.03750	0.00099
0.40	0.40	25.03	10.00	2.50	7.33246	0.02585	0.00177
0.30	0.50	18.77	10.00	1.88	7.33489	0.02342	0.00037
0.20	0.60	12.51	10.00	1.25	7.34288	0.01543	0.00018
0.15	0.65	9.39	10.00	0.94	7.34435	0.01396	0.00107
0.10	0.70	6.26	10.00	0.63	7.34716	0.01115	0.00000
0.05	0.75	3.13	10.00	0.31	7.35401	0.00430	0.00095
0.00	0.80	0.00	10.00	0.00	7.35831	0.00000	0.00033

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[87] / mM	Ratio (87:43)	δ	Δδ	Error
Cation reference		10.02	0.00	0.00	2.28200	0.00000	0.00083
0.80	0.00	50.06	9.99	0.20	2.28375	0.00175	0.00102
0.40	0.40	25.03	10.00	0.40	2.28032	0.00168	0.00083
0.30	0.50	18.77	10.00	0.53	2.27749	0.00451	0.00089
0.20	0.60	12.51	10.00	0.80	2.27787	0.00413	0.00066
0.15	0.65	9.39	10.00	1.07	2.27543	0.00657	0.00101
0.10	0.70	6.26	10.00	1.60	2.27371	0.00829	0.00031
0.05	0.75	3.13	10.00	3.20	2.27439	0.00761	0.00079

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[87] / mM	Ratio (87:43)	δ	Δδ	Error
Cation reference		10.02	0.00	0.00	4.52085	0.00000	0.00072
0.80	0.00	50.06	9.99	0.20	4.52874	0.00789	0.00093
0.40	0.40	25.03	10.00	0.40	4.51916	0.00169	0.00127
0.30	0.50	18.77	10.00	0.53	4.51454	0.00631	0.00054
0.20	0.60	12.51	10.00	0.80	4.51284	0.00801	0.00011
0.15	0.65	9.39	10.00	1.07	4.50909	0.01176	0.00092
0.10	0.70	6.26	10.00	1.60	4.50567	0.01518	0.00029
0.05	0.75	3.13	10.00	3.20	4.50435	0.01650	0.00072

Job Plot

	43 / g	87 / g	D_2O / mL	[43] / mM	[87] / mM
Solution X	0.0797	0.0000	15	10.02	0.00
Solution Y	0.0000	0.0606	25	0.00	10.00

Anion proton shift (average of 3 runs) – average of δH_a and δH_b

X / mL	Y / mL	$[87]_{tot}$ / mM	Mf of 87	δ	[43•87] / mM	Error / mM
0.70	0.10	1.25	0.12	7.34102	0.37	0.00
0.60	0.20	2.50	0.25	7.34230	0.69	0.02
0.50	0.30	3.75	0.37	7.34494	0.87	0.02
0.40	0.40	5.00	0.50	7.34799	0.89	0.02
0.30	0.50	6.25	0.62	7.34941	0.96	0.04
0.20	0.60	7.50	0.75	7.35312	0.66	0.17
0.10	0.70	8.75	0.87	7.35506	0.47	0.04
0.00	0.80	10.00	1.00	7.35815	0.00	0.00

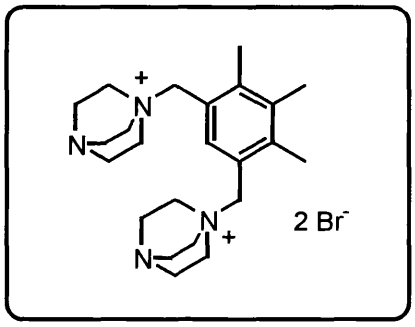
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•87] / mM	Error / mM
0.80	0.00	10.02	1.00	2.28200	0.00	0.00
0.70	0.10	8.77	0.88	2.28153	0.52	0.68
0.60	0.20	7.52	0.75	2.27928	2.56	0.28
0.50	0.30	6.26	0.63	2.27796	3.16	0.57
0.40	0.40	5.01	0.50	2.27715	3.04	0.49
0.30	0.50	3.76	0.38	2.27420	3.67	0.40
0.20	0.60	2.51	0.25	2.27351	2.66	0.16
0.10	0.70	1.25	0.13	2.27146	1.65	0.27

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•87] / mM	Error / mM
0.80	0.00	10.02	1.00	4.52085	0.00	0.00
0.70	0.10	8.77	0.88	4.51871	0.63	0.10
0.60	0.20	7.52	0.75	4.51541	1.37	0.15
0.50	0.30	6.26	0.63	4.51271	1.71	0.09
0.40	0.40	5.01	0.50	4.51036	1.76	0.07
0.30	0.50	3.76	0.38	4.50609	1.86	0.04
0.20	0.60	2.51	0.25	4.50399	1.42	0.02
0.10	0.70	1.25	0.13	4.50032	0.86	0.04

A.28 4,6-Bis(DABCO-N-methyl)-1,2,3-trimethylbenzene dibromide and dilithium 1,3-benzenedicarboxylate



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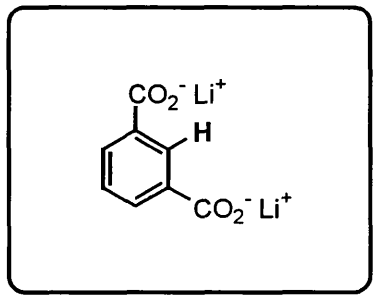


88

NMR Titration

	43 / g	88 / g	D_2O / mL	[43] / mM	[88] / mM
Solution X	0.2661	0.0179	10	50.17	10.06
Solution Y	0	0.0445	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[88] / mM	Ratio (43:88)	δ	Δδ	Error
0.80	0.00	50.17	10.06	4.99	7.99840	0.14745	0.00211
0.40	0.40	25.09	10.03	2.50	8.03589	0.10995	0.00203
0.30	0.50	18.81	10.02	1.88	8.04827	0.09757	0.00072
0.20	0.60	12.54	10.01	1.25	8.06820	0.07764	0.00228
0.15	0.65	9.41	10.01	0.94	8.08166	0.06418	0.00011
0.10	0.70	6.27	10.01	0.63	8.09577	0.05007	0.00216
0.05	0.75	3.14	10.00	0.31	8.11359	0.03226	0.00180
0.00	0.80	0.00	10.00	0.00	8.14585	0.00000	0.00182

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[88] / mM	Ratio (88:43)	δ	Δδ	Error
Cation reference		10.03	0.00	0.00	2.28268	0.00000	0.00054
0.80	0.00	50.17	10.06	0.20	2.25776	0.02492	0.00149
0.40	0.40	25.09	10.03	0.40	2.24368	0.03900	0.00172
0.30	0.50	18.81	10.02	0.53	2.23627	0.04641	0.00054
0.20	0.60	12.54	10.01	0.80	2.22873	0.05395	0.00184
0.15	0.65	9.41	10.01	1.06	2.22473	0.05795	0.00044
0.10	0.70	6.27	10.01	1.60	2.21703	0.06565	0.00183
0.05	0.75	3.14	10.00	3.19	2.20800	0.07468	0.00067

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[88] / mM	Ratio (88:43)	δ	Δδ	Error
Cation reference		10.03	0.00	0.00	4.52132	0.00000	0.00041
0.80	0.00	50.17	10.06	0.20	4.49974	0.02159	0.00147
0.40	0.40	25.09	10.03	0.40	4.47835	0.04298	0.00160
0.30	0.50	18.81	10.02	0.53	4.46853	0.05279	0.00064
0.20	0.60	12.54	10.01	0.80	4.45786	0.06346	0.00164
0.15	0.65	9.41	10.01	1.06	4.45214	0.06918	0.00039
0.10	0.70	6.27	10.01	1.60	4.44254	0.07878	0.00201
0.05	0.75	3.14	10.00	3.19	4.43100	0.09033	0.00075

Job Plot

	43 / g	88 / g	D_2O / mL	[43] / mM	[88] / mM
Solution X	0.0798	0.0000	15	10.03	0.00
Solution Y	0.0000	0.0445	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[88]_{tot}$ / mM	Mf of 88	δ	[43•88] / mM	Error / mM
0.70	0.10	1.25	0.12	8.06065	0.56	0.01
0.60	0.20	2.49	0.25	8.07187	0.97	0.00
0.50	0.30	3.74	0.37	8.08392	1.22	0.03
0.40	0.40	4.99	0.50	8.09480	1.33	0.02
0.30	0.50	6.24	0.62	8.10749	1.24	0.03
0.20	0.60	7.49	0.75	8.12100	0.94	0.00
0.10	0.70	8.75	0.87	8.13286	0.55	0.00
0.00	0.80	10.00	1.00	8.14451	0.00	0.00

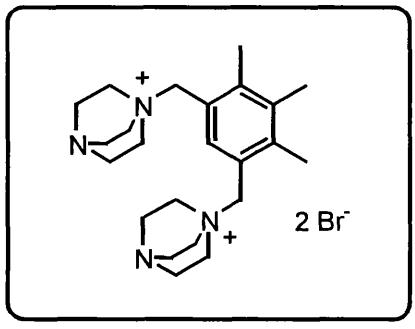
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•88] / mM	Error / mM
0.80	0.00	10.03	1.00	2.28268	0.00	0.00
0.70	0.10	8.78	0.88	2.27030	1.46	0.20
0.60	0.20	7.53	0.75	2.26050	2.24	0.07
0.50	0.30	6.28	0.63	2.24876	2.85	0.16
0.40	0.40	5.02	0.50	2.23679	3.09	0.02
0.30	0.50	3.77	0.38	2.22589	2.87	0.09
0.20	0.60	2.51	0.25	2.21610	2.24	0.04
0.10	0.70	1.26	0.13	2.20600	1.29	0.03

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•88] / mM	Error / mM
0.80	0.00	10.03	1.00	4.52132	0.00	0.00
0.70	0.10	8.78	0.88	4.50634	1.44	0.17
0.60	0.20	7.53	0.75	4.49368	2.28	0.05
0.50	0.30	6.28	0.63	4.47958	2.87	0.14
0.40	0.40	5.02	0.50	4.46500	3.10	0.02
0.30	0.50	3.77	0.38	4.45171	2.87	0.08
0.20	0.60	2.51	0.25	4.43968	2.25	0.03
0.10	0.70	1.26	0.13	4.42719	1.30	0.02

A.29 4,6-Bis(DABCO-N-methyl)-1,2,3-trimethylbenzene dibromide and disodium 1,3-benzenedicarboxylate



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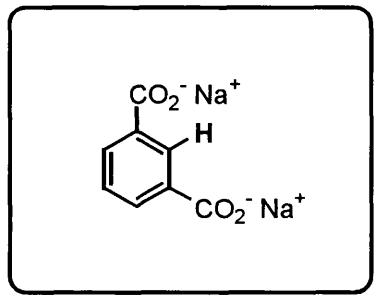


89

NMR Titration

	43 / g	89 / g	D_2O / mL	[43] / mM	[89] / mM
Solution X	0.2652	0.0210	10	50.00	10.00
Solution Y	0	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[89] / mM	Ratio (43:89)	δ	Δδ	Error
0.80	0.00	50.00	10.00	5.00	8.00075	0.14925	0.00213
0.40	0.40	25.00	10.00	2.50	8.03841	0.11160	0.00227
0.30	0.50	18.75	10.00	1.88	8.05252	0.09748	0.00230
0.20	0.60	12.50	10.00	1.25	8.07222	0.07779	0.00354
0.15	0.65	9.38	10.00	0.94	8.08372	0.06629	0.00300
0.10	0.70	6.25	10.00	0.63	8.09945	0.05056	0.00274
0.05	0.75	3.13	10.00	0.31	8.11933	0.03067	0.00291
0.00	0.80	0.00	10.00	0.00	8.15001	0.00000	0.00110

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[89] / mM	Ratio (89:43)	δ	Δδ	Error
Cation reference		10.04	0.00	0.00	2.28945	0.00000	0.00805
0.80	0.00	50.00	10.00	0.20	2.26215	0.02730	0.00171
0.40	0.40	25.00	10.00	0.40	2.24875	0.04070	0.00209
0.30	0.50	18.75	10.00	0.53	2.24251	0.04694	0.00230
0.20	0.60	12.50	10.00	0.80	2.23406	0.05539	0.00221
0.15	0.65	9.38	10.00	1.07	2.22861	0.06084	0.00220
0.10	0.70	6.25	10.00	1.60	2.22167	0.06778	0.00314
0.05	0.75	3.13	10.00	3.20	2.21354	0.07591	0.00267

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[89] / mM	Ratio (89:43)	δ	Δδ	Error
Cation reference		10.04	0.00	0.00	4.52177	0.00000	0.00153
0.80	0.00	50.00	10.00	0.20	4.50413	0.01764	0.00160
0.40	0.40	25.00	10.00	0.40	4.48363	0.03814	0.00185
0.30	0.50	18.75	10.00	0.53	4.47481	0.04696	0.00221
0.20	0.60	12.50	10.00	0.80	4.46342	0.05835	0.00207
0.15	0.65	9.38	10.00	1.07	4.45601	0.06576	0.00190
0.10	0.70	6.25	10.00	1.60	4.44703	0.07474	0.00286
0.05	0.75	3.13	10.00	3.20	4.43650	0.08527	0.00257

Job Plot

	43 / g	89 / g	D_2O / mL	[43] / mM	[89] / mM
Solution X	0.1326	0.0000	25	10.00	0.00
Solution Y	0.0000	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[89]_{tot}$ / mM	Mf of 89	δ	[43•89] / mM	Error / mM
0.70	0.10	1.25	0.12	8.06317	0.57	0.00
0.60	0.20	2.50	0.25	8.07370	0.99	0.02
0.50	0.30	3.75	0.37	8.08460	1.27	0.01
0.40	0.40	5.00	0.50	8.09633	1.38	0.03
0.30	0.50	6.25	0.62	8.10858	1.32	0.01
0.20	0.60	7.50	0.75	8.12186	1.06	0.02
0.10	0.70	8.75	0.87	8.13481	0.63	0.02
0.00	0.80	10.00	1.00	8.14845	0.00	0.00

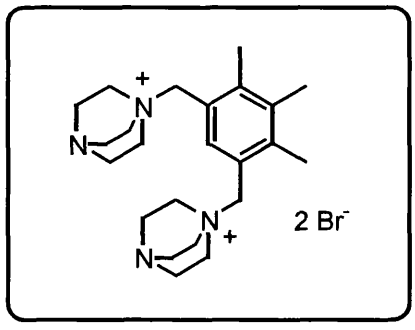
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•89] / mM	Error / mM
0.80	0.00	10.00	1.00	2.28945	0.00	0.00
0.70	0.10	8.75	0.88	2.27311	1.85	0.83
0.60	0.20	7.50	0.75	2.26250	2.61	0.53
0.50	0.30	6.25	0.63	2.25242	2.99	0.35
0.40	0.40	5.00	0.50	2.24172	3.08	0.14
0.30	0.50	3.75	0.38	2.23041	2.86	0.06
0.20	0.60	2.50	0.25	2.22051	2.23	0.02
0.10	0.70	1.25	0.13	2.21124	1.26	0.02

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•89] / mM	Error / mM
0.80	0.00	10.00	1.00	4.52177	0.00	0.00
0.70	0.10	8.75	0.88	4.50918	1.26	0.04
0.60	0.20	7.50	0.75	4.49620	2.18	0.05
0.50	0.30	6.25	0.63	4.48347	2.73	0.02
0.40	0.40	5.00	0.50	4.47006	2.95	0.08
0.30	0.50	3.75	0.38	4.45665	2.78	0.04
0.20	0.60	2.50	0.25	4.44447	2.20	0.04
0.10	0.70	1.25	0.13	4.43295	1.27	0.02

A.30 4,6-Bis(DABCO-N-methyl)-1,2,3-trimethylbenzene dibromide and dipotassium 1,3-benzenedicarboxylate



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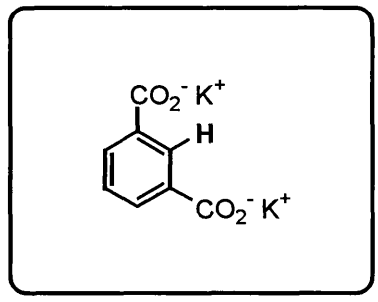


90

NMR Titration

	43 / g	90 / g	D_2O / mL	[43] / mM	[90] / mM
Solution X	0.2727	0.0248	10	51.41	10.23
Solution Y	0	0.0609	25	0.00	10.05

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[90] / mM	Ratio (43:90)	δ	$\Delta\delta$	Error
0.80	0.00	51.41	10.23	5.02	8.03736	0.15185	0.00549
0.40	0.40	25.71	10.14	2.53	8.07689	0.11232	0.00435
0.30	0.50	19.28	10.12	1.90	8.09382	0.09539	0.00601
0.20	0.60	12.85	10.10	1.27	8.11332	0.07589	0.00619
0.15	0.65	9.64	10.09	0.96	8.12515	0.06406	0.00547
0.10	0.70	6.43	10.08	0.64	8.13444	0.05478	0.00005
0.05	0.75	3.21	10.06	0.32	8.15415	0.03506	0.00023
0.00	0.80	0.00	10.05	0.00	8.18921	0.00000	0.00069

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[90] / mM	Ratio (90:43)	δ	Δδ	Error
Cation reference		10.07	0.00	0.00	2.30210	0.00000	0.00130
0.80	0.00	51.41	10.23	0.20	2.28148	0.02062	0.00368
0.40	0.40	25.71	10.14	0.39	2.27121	0.03089	0.00509
0.30	0.50	19.28	10.12	0.52	2.26444	0.03766	0.00439
0.20	0.60	12.85	10.10	0.79	2.25950	0.04260	0.00606
0.15	0.65	9.64	10.09	1.05	2.25262	0.04948	0.00442
0.10	0.70	6.43	10.08	1.57	2.24234	0.05976	0.00101
0.05	0.75	3.21	10.06	3.13	2.23567	0.06643	0.00019

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[90] / mM	Ratio (90:43)	δ	Δδ	Error
Cation reference		10.07	0.00	0.00	4.53968	0.00000	0.00105
0.80	0.00	51.41	10.23	0.20	4.52273	0.01695	0.00388
0.40	0.40	25.71	10.14	0.39	4.50539	0.03429	0.00505
0.30	0.50	19.28	10.12	0.52	4.49690	0.04278	0.00447
0.20	0.60	12.85	10.10	0.79	4.48862	0.05106	0.00599
0.15	0.65	9.64	10.09	1.05	4.48020	0.05948	0.00444
0.10	0.70	6.43	10.08	1.57	4.46786	0.07182	0.00002
0.05	0.75	3.21	10.06	3.13	4.45846	0.08122	0.00031

Job Plot

	43 / g	90 / g	D_2O / mL	[43] / mM	[90] / mM
Solution X	0.0801	0.0000	15	10.07	0.00
Solution Y	0.0000	0.0609	25	0.00	10.05

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[90]_{tot}$ / mM	Mf of 90	δ	[43•90] / mM	Error / mM
0.70	0.10	1.26	0.12	8.09382	0.60	0.00
0.60	0.20	2.51	0.25	8.10788	1.02	0.01
0.50	0.30	3.77	0.37	8.12155	1.26	0.00
0.40	0.40	5.02	0.50	8.13438	1.35	0.01
0.30	0.50	6.28	0.62	8.14735	1.28	0.01
0.20	0.60	7.54	0.75	8.16020	1.03	0.00
0.10	0.70	8.79	0.87	8.17359	0.60	0.01
0.00	0.80	10.05	1.00	8.18696	0.00	0.00

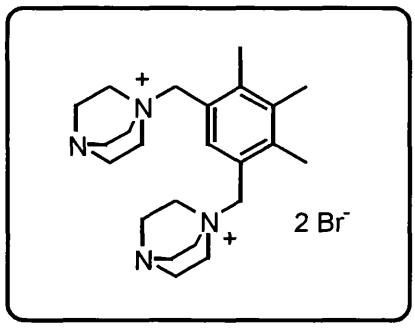
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•90] / mM	Error / mM
0.80	0.00	10.07	1.00	2.30210	0.00	0.00
0.70	0.10	8.81	0.88	2.29170	1.37	0.01
0.60	0.20	7.55	0.75	2.28136	2.33	0.02
0.50	0.30	6.30	0.63	2.27082	2.94	0.04
0.40	0.40	5.04	0.50	2.26029	3.14	0.06
0.30	0.50	3.78	0.38	2.24959	2.96	0.06
0.20	0.60	2.52	0.25	2.23948	2.35	0.05
0.10	0.70	1.26	0.13	2.22928	1.37	0.02

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•90] / mM	Error / mM
0.80	0.00	10.07	1.00	4.53968	0.00	0.00
0.70	0.10	8.81	0.88	4.52669	1.35	0.01
0.60	0.20	7.55	0.75	4.51397	2.29	0.03
0.50	0.30	6.30	0.63	4.50102	2.87	0.04
0.40	0.40	5.04	0.50	4.48814	3.07	0.04
0.30	0.50	3.78	0.38	4.47508	2.88	0.05
0.20	0.60	2.52	0.25	4.46258	2.29	0.03
0.10	0.70	1.26	0.13	4.45052	1.33	0.02

A.31 4,6-Bis(DABCO-N-methyl)-1,2,3-trimethylbenzene dibromide and calcium 1,3-benzenedicarboxylate



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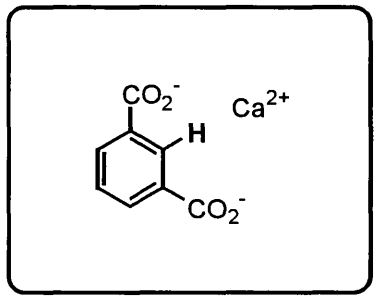


91

NMR Titration

	43 / g	91 / g	D_2O / mL	[43] / mM	[91] / mM
Solution X	0.2662	0.0207	10	50.19	10.14
Solution Y	0	0.0515	25	0.00	10.09

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[91] / mM	Ratio (43:91)	δ	$\Delta\delta$	Error
0.80	0.00	50.19	10.14	4.95	8.00848	0.15997	0.00334
0.40	0.40	25.09	10.11	2.48	8.05086	0.11759	0.00033
0.30	0.50	18.82	10.11	1.86	8.06724	0.10120	0.00230
0.20	0.60	12.55	10.10	1.24	8.08880	0.07965	0.00008
0.15	0.65	9.41	10.10	0.93	8.10079	0.06765	0.00192
0.10	0.70	6.27	10.09	0.62	8.11775	0.05070	0.00102
0.05	0.75	3.14	10.09	0.31	8.13738	0.03107	0.00268
0.00	0.80	0.00	10.09	0.00	8.16845	0.00000	0.00050

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[91] / mM	Ratio (91:43)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	2.27724	0.00000	0.00099
0.80	0.00	50.19	10.14	0.20	2.25379	0.02345	0.00271
0.40	0.40	25.09	10.11	0.40	2.24222	0.03502	0.00007
0.30	0.50	18.82	10.11	0.54	2.23739	0.03985	0.00214
0.20	0.60	12.55	10.10	0.80	2.23125	0.04600	0.00021
0.15	0.65	9.41	10.10	1.07	2.22610	0.05114	0.00186
0.10	0.70	6.27	10.09	1.61	2.22130	0.05595	0.00065
0.05	0.75	3.14	10.09	3.22	2.21330	0.06394	0.00130

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[91] / mM	Ratio (91:43)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	4.51641	0.00000	0.00095
0.80	0.00	50.19	10.14	0.20	4.49664	0.01977	0.00258
0.40	0.40	25.09	10.11	0.40	4.47860	0.03781	0.00015
0.30	0.50	18.82	10.11	0.54	4.47159	0.04482	0.00195
0.20	0.60	12.55	10.10	0.80	4.46250	0.05391	0.00021
0.15	0.65	9.41	10.10	1.07	4.45575	0.06066	0.00188
0.10	0.70	6.27	10.09	1.61	4.44908	0.06733	0.00080
0.05	0.75	3.14	10.09	3.22	4.43864	0.07777	0.00125

Job Plot

	43 / g	91 / g	D_2O / mL	[43] / mM	[91] / mM
Solution X	0.0796	0.0000	15	10.01	0.00
Solution Y	0.0000	0.0515	25	0.00	10.09

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[91]_{tot}$ / mM	Mf of 91	δ	[43•91] / mM	Error / mM
0.70	0.10	1.27	0.13	8.06915	0.60	0.00
0.60	0.20	2.54	0.25	8.08125	1.05	0.00
0.50	0.30	3.80	0.38	8.09861	1.26	0.03
0.40	0.40	5.06	0.50	8.11153	1.37	0.02
0.30	0.50	6.32	0.63	8.12662	1.26	0.01
0.20	0.60	7.58	0.75	8.13900	1.07	0.01
0.10	0.70	8.84	0.88	8.15346	0.64	0.01
0.00	0.80	10.09	1.00	8.16881	0.00	0.00

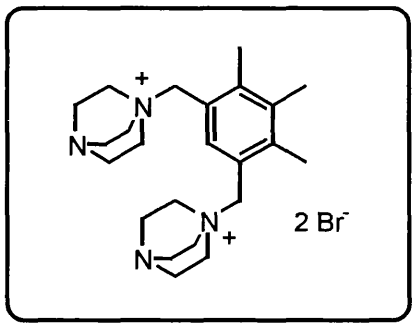
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•91] / mM	Error / mM
0.80	0.00	10.01	1.00	2.27724	0.00	0.00
0.70	0.10	8.75	0.87	2.26831	1.22	0.21
0.60	0.20	7.49	0.75	2.25815	2.23	0.07
0.50	0.30	6.23	0.62	2.25010	2.63	0.17
0.40	0.40	4.98	0.50	2.23980	2.90	0.08
0.30	0.50	3.73	0.37	2.23174	2.64	0.14
0.20	0.60	2.49	0.25	2.22145	2.16	0.06
0.10	0.70	1.24	0.12	2.21358	1.23	0.07

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•91] / mM	Error / mM
0.80	0.00	10.01	1.00	4.51641	0.00	0.00
0.70	0.10	8.75	0.87	4.50502	1.25	0.13
0.60	0.20	7.49	0.75	4.49281	2.23	0.06
0.50	0.30	6.23	0.62	4.48271	2.65	0.17
0.40	0.40	4.98	0.50	4.47008	2.91	0.06
0.30	0.50	3.73	0.37	4.45997	2.65	0.11
0.20	0.60	2.49	0.25	4.44767	2.15	0.06
0.10	0.70	1.24	0.12	4.43779	1.23	0.05

A.32 4,6-Bis(DABCO-N-methyl)-1,2,3-trimethylbenzene dibromide and disodium 1,4-benzenedicarboxylate



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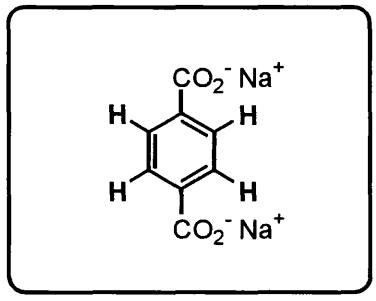


92

NMR Titration

	43 / g	92 / g	D_2O / mL	[43] / mM	[92] / mM
Solution X	0.2656	0.0210	10	50.08	10.00
Solution Y	0	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[92] / mM	Ratio (43:92)	δ	Δδ	Error
0.80	0.00	50.08	10.00	5.01	7.57250	0.16463	0.00086
0.40	0.40	25.04	10.00	2.51	7.61969	0.11744	0.00102
0.30	0.50	18.78	10.00	1.88	7.63743	0.09970	0.00127
0.20	0.60	12.52	10.00	1.25	7.66011	0.07702	0.00250
0.15	0.65	9.39	10.00	0.94	7.67318	0.06395	0.00209
0.10	0.70	6.26	10.00	0.63	7.68924	0.04789	0.00172
0.05	0.75	3.13	10.00	0.31	7.70927	0.02786	0.00207
0.00	0.80	0.00	10.00	0.00	7.73713	0.00000	0.00133

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[92] / mM	Ratio (92:43)	δ	Δδ	Error
Cation reference		10.02	0.00	0.00	2.28016	0.00000	0.00177
0.80	0.00	50.08	10.00	0.20	2.25341	0.02675	0.00088
0.40	0.40	25.04	10.00	0.40	2.23959	0.04057	0.00105
0.30	0.50	18.78	10.00	0.53	2.23457	0.04560	0.00101
0.20	0.60	12.52	10.00	0.80	2.22779	0.05238	0.00186
0.15	0.65	9.39	10.00	1.06	2.22245	0.05771	0.00120
0.10	0.70	6.26	10.00	1.60	2.21619	0.06397	0.00121
0.05	0.75	3.13	10.00	3.19	2.20919	0.07097	0.00084

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[43] / mM	[92] / mM	Ratio (92:43)	δ	Δδ	Error
Cation reference		10.02	0.00	0.00	4.51917	0.00000	0.00172
0.80	0.00	50.08	10.00	0.20	4.49425	0.02492	0.00079
0.40	0.40	25.04	10.00	0.40	4.47197	0.04720	0.00097
0.30	0.50	18.78	10.00	0.53	4.46391	0.05526	0.00094
0.20	0.60	12.52	10.00	0.80	4.45334	0.06583	0.00166
0.15	0.65	9.39	10.00	1.06	4.44561	0.07356	0.00112
0.10	0.70	6.26	10.00	1.60	4.43677	0.08240	0.00100
0.05	0.75	3.13	10.00	3.19	4.42653	0.09264	0.00066

Job Plot

	43 / g	92 / g	D_2O / mL	[43] / mM	[92] / mM
Solution X	0.0797	0.0000	15	10.02	0.00
Solution Y	0.0000	0.0525	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[92]_{tot}$ / mM	Mf of 92	δ	[43•92] / mM	Error / mM
0.70	0.10	1.25	0.12	7.65110	0.47	0.00
0.60	0.20	2.49	0.25	7.66263	0.81	0.00
0.50	0.30	3.74	0.37	7.67596	1.00	0.01
0.40	0.40	4.99	0.50	7.68931	1.06	0.01
0.30	0.50	6.24	0.62	7.70127	1.01	0.01
0.20	0.60	7.49	0.75	7.71371	0.81	0.03
0.10	0.70	8.74	0.87	7.72592	0.50	0.06
0.00	0.80	10.00	1.00	7.73941	0.00	0.00

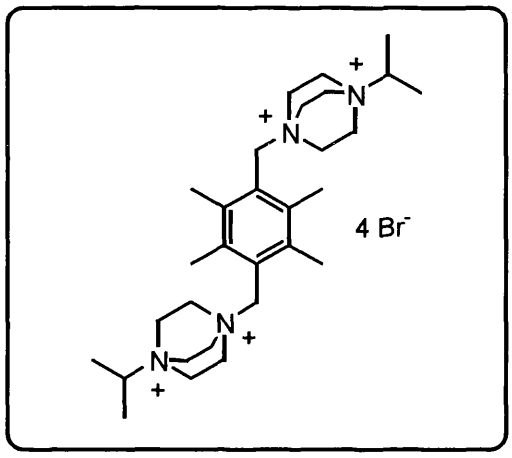
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•92] / mM	Error / mM
0.80	0.00	10.02	1.00	2.28016	0.00	0.00
0.70	0.10	8.77	0.88	2.26757	1.57	0.08
0.60	0.20	7.52	0.75	2.25641	2.54	0.02
0.50	0.30	6.27	0.63	2.24675	2.98	0.06
0.40	0.40	5.01	0.50	2.23737	3.06	0.10
0.30	0.50	3.76	0.38	2.22696	2.85	0.07
0.20	0.60	2.51	0.25	2.21752	2.24	0.03
0.10	0.70	1.25	0.13	2.20883	1.28	0.01

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[43]_{tot}$ / mM	Mf of 43	δ	[43•92] / mM	Error / mM
0.80	0.00	10.02	1.00	4.51917	0.00	0.00
0.70	0.10	8.77	0.88	4.50270	1.55	0.03
0.60	0.20	7.52	0.75	4.48824	2.50	0.00
0.50	0.30	6.27	0.63	4.47500	2.97	0.05
0.40	0.40	5.01	0.50	4.46219	3.07	0.07
0.30	0.50	3.76	0.38	4.44871	2.85	0.05
0.20	0.60	2.51	0.25	4.43620	2.23	0.02
0.10	0.70	1.25	0.13	4.42485	1.27	0.01

A.33 1,4-Bis(N'-isopropyl-DABCO-N-methyl)-2,3,5,6-tetramethylbenzene tetrabromide and tetrasodium 1,2,4,5-benzene-tetracarboxylate



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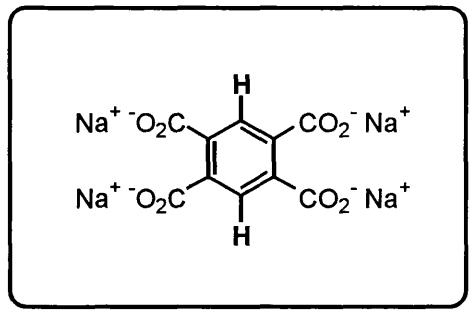


96

NMR Titration

	52 / g	96 / g	D_2O / mL	[52] / mM	[96] / mM
Solution X	0.4084	0.0349	10	51.67	10.20
Solution Y	0	0.0861	25	0.00	10.07

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[52] / mM	[96] / mM	Ratio (52:96)	δ	Δδ	Error
0.80	0.00	51.67	10.20	5.06	7.35866	0.00946	0.00330
0.40	0.40	25.84	10.14	2.55	7.33380	0.03432	0.00342
0.30	0.50	19.38	10.12	1.91	7.32737	0.04075	0.00272
0.20	0.60	12.92	10.10	1.28	7.32371	0.04441	0.00022
0.15	0.65	9.69	10.09	0.96	7.32514	0.04298	0.00138
0.10	0.70	6.46	10.08	0.64	7.32921	0.03891	0.00046
0.05	0.75	3.23	10.08	0.32	7.34254	0.02558	0.00058
0.00	0.80	0.00	10.07	0.00	7.36812	0.00000	0.00066

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[52] / mM	[96] / mM	Ratio (96:52)	δ	Δδ	Error
Cation reference		10.12	0.00	0.00	2.32672	0.00000	0.00243
0.80	0.00	51.67	10.20	0.20	2.31975	0.00697	0.00315
0.40	0.40	25.84	10.14	0.39	2.29959	0.02713	0.00352
0.30	0.50	19.38	10.12	0.52	2.29009	0.03663	0.00243
0.20	0.60	12.92	10.10	0.78	2.27881	0.04791	0.00059
0.15	0.65	9.69	10.09	1.04	2.27214	0.05458	0.00196
0.10	0.70	6.46	10.08	1.56	2.26392	0.06280	0.00066
0.05	0.75	3.23	10.08	3.12	2.25598	0.07074	0.00071

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[52] / mM	[96] / mM	Ratio (96:52)	δ	Δδ	Error
Cation reference		10.12	0.00	0.00	5.10993	0.00000	0.00171
0.80	0.00	51.67	10.20	0.20	5.10793	0.00200	0.00295
0.40	0.40	25.84	10.14	0.39	5.09535	0.01458	0.00308
0.30	0.50	19.38	10.12	0.52	5.08873	0.02120	0.00216
0.20	0.60	12.92	10.10	0.78	5.08027	0.02967	0.00054
0.15	0.65	9.69	10.09	1.04	5.07507	0.03486	0.00200
0.10	0.70	6.46	10.08	1.56	5.06739	0.04255	0.00104
0.05	0.75	3.23	10.08	3.12	5.05975	0.05018	0.00058

Job Plot

	52 / g	96 / g	D_2O / mL	[52] / mM	[96] / mM
Solution X	0.1200	0.0000	15	10.12	0.00
Solution Y	0.0000	0.0861	25	0.00	10.07

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[96]_{tot}$ / mM	Mf of 96	δ	[52•96] / mM	Error / mM
0.70	0.10	1.25	0.12	7.31700	1.20	0.07
0.60	0.20	2.51	0.25	7.30379	3.05	0.10
0.50	0.30	3.76	0.37	7.30301	4.63	0.14
0.40	0.40	5.02	0.50	7.30892	5.61	0.39
0.30	0.50	6.28	0.62	7.32273	5.35	0.35
0.20	0.60	7.54	0.75	7.33802	4.21	0.20
0.10	0.70	8.80	0.87	7.35261	2.46	0.29
0.00	0.80	10.07	1.00	7.36717	0.00	0.00

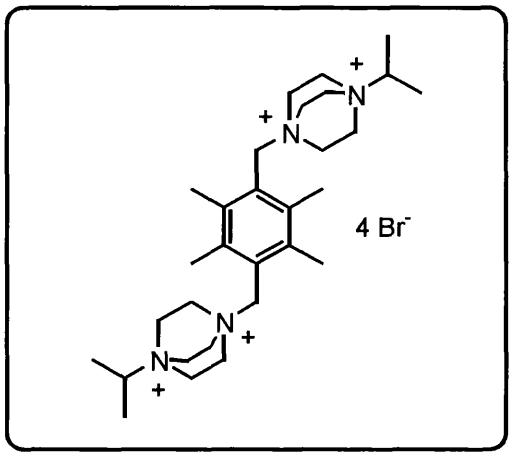
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[52]_{tot}$ / mM	Mf of 52	δ	[52•96] / mM	Error / mM
0.80	0.00	10.12	1.00	2.32672	0.00	0.00
0.70	0.10	8.86	0.88	2.30941	2.08	0.10
0.60	0.20	7.60	0.75	2.29430	3.34	0.05
0.50	0.30	6.34	0.63	2.28071	3.96	0.07
0.40	0.40	5.07	0.50	2.26848	4.01	0.21
0.30	0.50	3.81	0.38	2.25998	3.45	0.14
0.20	0.60	2.54	0.25	2.25523	2.46	0.08
0.10	0.70	1.27	0.13	2.25195	1.29	0.04

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[52]_{tot}$ / mM	Mf of 52	δ	[52•96] / mM	Error / mM
0.80	0.00	10.12	1.00	5.10993	0.00	0.00
0.70	0.10	8.86	0.88	5.10106	1.36	0.21
0.60	0.20	7.60	0.75	5.09205	2.35	0.04
0.50	0.30	6.34	0.63	5.08239	3.01	0.07
0.40	0.40	5.07	0.50	5.07158	3.36	0.24
0.30	0.50	3.81	0.38	5.06372	3.04	0.17
0.20	0.60	2.54	0.25	5.05875	2.24	0.09
0.10	0.70	1.27	0.13	5.05612	1.18	0.04

A.34 1,4-Bis(N'-isopropyl-DABCO-N-methyl)-2,3,5,6-tetramethylbenzene tetrabromide and tetrasodium 1,2,4,5-naphthalene-tetracarboxylate



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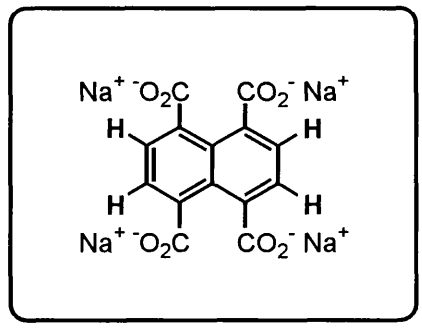


97

NMR Titration

	52 / g	97 / g	D_2O / mL	[52] / mM	[97] / mM
Solution X	0.4118	0.0391	10	52.10	9.97
Solution Y	0	0.0982	25	0.00	10.02

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[52] / mM	[97] / mM	Ratio (52:97)	δ	Δδ	Error
0.80	0.00	52.10	9.97	5.23	7.47770	0.07571	0.00166
0.40	0.40	26.05	9.99	2.61	7.47447	0.07894	0.00183
0.30	0.50	19.54	10.00	1.95	7.47768	0.07573	0.00210
0.20	0.60	13.03	10.01	1.30	7.48575	0.06766	0.00235
0.15	0.65	9.77	10.01	0.98	7.49021	0.06320	0.00082
0.10	0.70	6.51	10.01	0.65	7.50019	0.05322	0.00403
0.05	0.75	3.26	10.01	0.33	7.51869	0.03472	0.00202
0.00	0.80	0.00	10.02	0.00	7.55341	0.00000	0.00135

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[52] / mM	[97] / mM	Ratio (97:52)	δ	Δδ	Error
Cation reference		9.99	0.00	0.00	2.32538	0.00000	0.00210
0.80	0.00	52.10	9.97	0.19	2.30618	0.01919	0.00153
0.40	0.40	26.05	9.99	0.38	2.27655	0.04883	0.00136
0.30	0.50	19.54	10.00	0.51	2.26515	0.06023	0.00209
0.20	0.60	13.03	10.01	0.77	2.24998	0.07540	0.00155
0.15	0.65	9.77	10.01	1.02	2.23834	0.08704	0.00090
0.10	0.70	6.51	10.01	1.54	2.22618	0.09920	0.00266
0.05	0.75	3.26	10.01	3.08	2.21439	0.11099	0.00250

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[52] / mM	[97] / mM	Ratio (97:52)	δ	Δδ	Error
Cation reference		9.99	0.00	0.00	5.10884	0.00000	0.00207
0.80	0.00	52.10	9.97	0.19	5.08955	0.01929	0.00144
0.40	0.40	26.05	9.99	0.38	5.06310	0.04573	0.00153
0.30	0.50	19.54	10.00	0.51	5.05172	0.05712	0.00187
0.20	0.60	13.03	10.01	0.77	5.03558	0.07326	0.00142
0.15	0.65	9.77	10.01	1.02	5.02263	0.08621	0.00095
0.10	0.70	6.51	10.01	1.54	5.00751	0.10133	0.00365
0.05	0.75	3.26	10.01	3.08	4.99299	0.11585	0.00222

Job Plot

	52 / g	97 / g	D_2O / mL	[52] / mM	[97] / mM
Solution X	0.1185	0.0000	15	9.99	0.00
Solution Y	0.0000	0.0982	25	0.00	10.02

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[97]_{tot}$ / mM	Mf of 97	δ	[52•97] / mM	Error / mM
0.70	0.10	1.25	0.13	7.46441	1.31	0.03
0.60	0.20	2.51	0.25	7.46705	2.54	0.08
0.50	0.30	3.76	0.38	7.47434	3.48	0.09
0.40	0.40	5.01	0.50	7.48739	3.88	0.09
0.30	0.50	6.27	0.63	7.50522	3.54	0.13
0.20	0.60	7.52	0.75	7.52337	2.66	0.09
0.10	0.70	8.77	0.88	7.53897	1.51	0.09
0.00	0.80	10.02	1.00	7.55371	0.00	0.00

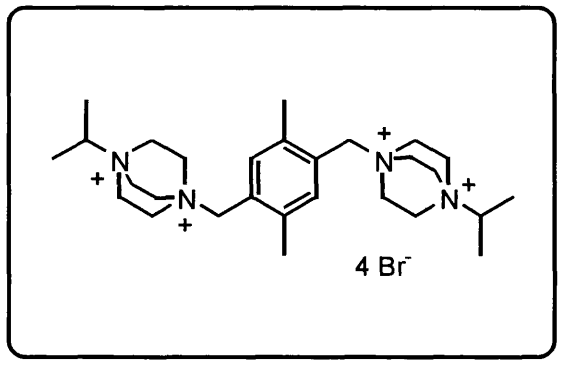
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[52]_{tot}$ / mM	Mf of 52	δ	[52•97] / mM	Error / mM
0.80	0.00	9.99	1.00	2.32538	0.00	0.00
0.70	0.10	8.74	0.87	2.29812	2.10	0.07
0.60	0.20	7.49	0.75	2.27591	3.27	0.04
0.50	0.30	6.24	0.62	2.25325	3.97	0.02
0.40	0.40	4.99	0.50	2.23315	4.06	0.03
0.30	0.50	3.74	0.37	2.22093	3.45	0.08
0.20	0.60	2.49	0.25	2.21290	2.47	0.05
0.10	0.70	1.25	0.12	2.20654	1.31	0.03

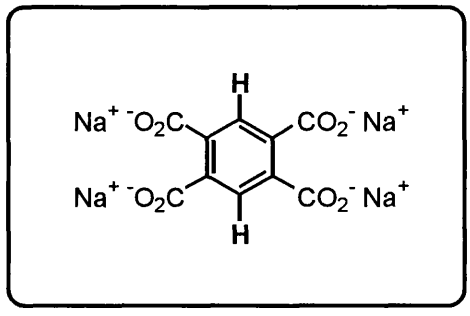
Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[52]_{tot}$ / mM	Mf of 52	δ	[52•97] / mM	Error / mM
0.80	0.00	9.99	1.00	5.10884	0.00	0.00
0.70	0.10	8.74	0.87	5.08935	1.40	0.10
0.60	0.20	7.49	0.75	5.06919	2.44	0.00
0.50	0.30	6.24	0.62	5.04477	3.28	0.01
0.40	0.40	4.99	0.50	5.01978	3.65	0.02
0.30	0.50	3.74	0.37	5.00272	3.26	0.06
0.20	0.60	2.49	0.25	4.99205	2.39	0.04
0.10	0.70	1.25	0.12	4.98323	1.29	0.03

A.35 2,5-Bis(N'-isopropyl-DABCO-N-methyl)-1,4-dimethylbenzene tetrabromide and tetrasodium 1,2,4,5-benzene-tetracarboxylate



53



96

NMR Titration

	53 / g	96 / g	D_2O / mL	[53] / mM	[96] / mM
Solution X	0.3832	0.0343	10	50.27	10.03
Solution Y	0	0.0860	25	0.00	10.06

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[53] / mM	[96] / mM	Ratio (53:96)	δ	Δδ	Error
0.80	0.00	50.27	10.03	5.01	7.36828	0.00881	0.00704
0.40	0.40	25.13	10.04	2.50	7.32731	0.03216	0.00276
0.30	0.50	18.85	10.05	1.88	7.31862	0.04085	0.00318
0.20	0.60	12.57	10.05	1.25	7.31432	0.04515	0.00194
0.15	0.65	9.42	10.05	0.94	7.31281	0.04666	0.00178
0.10	0.70	6.28	10.05	0.63	7.31991	0.03956	0.00091
0.05	0.75	3.14	10.05	0.31	7.32147	0.03800	0.00068
0.00	0.80	0.00	10.06	0.00	7.35947	0.00000	0.00064

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[53] / mM	[96] / mM	Ratio (96:53)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	2.35028	0.00000	0.00062
0.80	0.00	50.27	10.03	0.20	2.34882	0.00147	0.00468
0.40	0.40	25.13	10.04	0.40	2.32848	0.02181	0.00170
0.30	0.50	18.85	10.05	0.53	2.31904	0.03124	0.00231
0.20	0.60	12.57	10.05	0.80	2.30587	0.04441	0.00177
0.15	0.65	9.42	10.05	1.07	2.29382	0.05647	0.00209
0.10	0.70	6.28	10.05	1.60	2.28386	0.06642	0.00210
0.05	0.75	3.14	10.05	3.20	2.27420	0.07608	0.00059

Job Plot

	53 / g	96 / g	D_2O / mL	[53] / mM	[96] / mM
Solution X	0.1144	0.0000	15	10.00	0.00
Solution Y	0.0000	0.0860	25	0.00	10.06

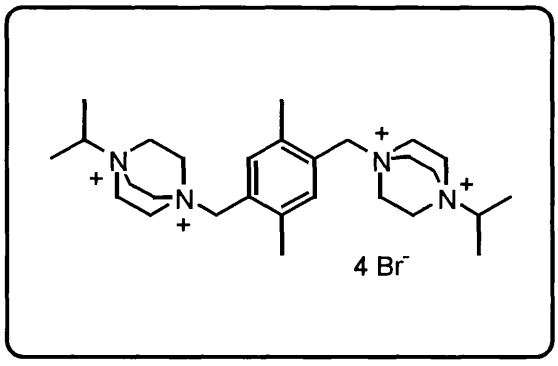
Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[96]_{tot}$ / mM	Mf of 96	δ	[53•96] / mM	Error / mM
0.70	0.10	1.26	0.13	7.34930	0.19	0.02
0.60	0.20	2.52	0.25	7.30823	2.03	0.01
0.50	0.30	3.78	0.38	7.29879	3.61	0.02
0.40	0.40	5.04	0.50	7.30261	4.51	0.06
0.30	0.50	6.30	0.63	7.31503	4.38	0.01
0.20	0.60	7.55	0.75	7.33229	3.17	0.03
0.10	0.70	8.80	0.88	7.34795	1.49	0.07
0.00	0.80	10.06	1.00	7.35855	0.00	0.00

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[53]_{tot}$ / mM	Mf of 53	δ	[53•96] / mM	Error / mM
0.80	0.00	10.00	1.00	2.35028	0.00	0.00
0.70	0.10	8.75	0.87	2.33794	1.24	0.03
0.60	0.20	7.49	0.75	2.32190	2.44	0.00
0.50	0.30	6.24	0.62	2.30601	3.17	0.01
0.40	0.40	4.99	0.50	2.29022	3.43	0.01
0.30	0.50	3.74	0.37	2.27689	3.14	0.01
0.20	0.60	2.49	0.25	2.27183	2.24	0.01
0.10	0.70	1.24	0.12	2.26820	1.17	0.01

A.36 2,5-Bis(N'-isopropyl-DABCO-N-methyl)-1,4-dimethylbenzene tetrabromide and tetrasodium 1,2,4,5-naphthalene-tetracarboxylate



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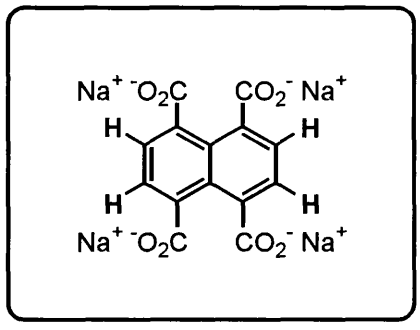


97

NMR Titration

	53 / g	97 / g	D_2O / mL	[53] / mM	[97] / mM
Solution X	0.3839	0.0395	10	50.36	10.07
Solution Y	0	0.0981	25	0.00	10.01

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[53] / mM	[97] / mM	Ratio (53:97)	δ	Δδ	Error
0.80	0.00	50.36	10.07	5.00	7.51546	0.03963	0.00176
0.40	0.40	25.18	10.04	2.51	7.50795	0.04714	0.00155
0.30	0.50	18.88	10.03	1.88	7.50781	0.04728	0.00111
0.20	0.60	12.59	10.02	1.26	7.50976	0.04533	0.00110
0.15	0.65	9.44	10.02	0.94	7.51317	0.04192	0.00115
0.10	0.70	6.29	10.01	0.63	7.52033	0.03476	0.00166
0.05	0.75	3.15	10.01	0.31	7.53365	0.02144	0.00094
0.00	0.80	0.00	10.01	0.00	7.55509	0.00000	0.00067

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[53] / mM	[97] / mM	Ratio (97:53)	δ	Δδ	Error
Cation reference		10.06	0.00	0.00	2.36128	0.00000	0.00079
0.80	0.00	50.36	10.07	0.20	2.34909	0.01219	0.00152
0.40	0.40	25.18	10.04	0.40	2.32219	0.03909	0.00158
0.30	0.50	18.88	10.03	0.53	2.30987	0.05141	0.00130
0.20	0.60	12.59	10.02	0.80	2.29052	0.07076	0.00188
0.15	0.65	9.44	10.02	1.06	2.27731	0.08397	0.00100
0.10	0.70	6.29	10.01	1.59	2.26351	0.09777	0.00017
0.05	0.75	3.15	10.01	3.18	2.25010	0.11118	0.00124

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[53] / mM	[97] / mM	Ratio (97:53)	δ	Δδ	Error
Cation reference		10.06	0.00	0.00	4.77006	0.00000	0.00027
0.80	0.00	50.36	10.07	0.20	4.75117	0.01889	0.00145
0.40	0.40	25.18	10.04	0.40	4.70980	0.06026	0.00163
0.30	0.50	18.88	10.03	0.53	4.68990	0.08016	0.00141
0.20	0.60	12.59	10.02	0.80	4.65908	0.11098	0.00279
0.15	0.65	9.44	10.02	1.06	4.63616	0.13390	0.00080
0.10	0.70	6.29	10.01	1.59	4.61093	0.15913	0.00022
0.05	0.75	3.15	10.01	3.18	4.58537	0.18469	0.00093

Job Plot

	53 / g	97 / g	D_2O / mL	[53] / mM	[97] / mM
Solution X	0.1150	0.0000	15	10.06	0.00
Solution Y	0.0000	0.0981	25	0.00	10.01

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[97]_{tot}$ / mM	Mf of 97	δ	[53•97] / mM	Error / mM
0.70	0.10	1.25	0.12	7.50356	1.13	0.01
0.60	0.20	2.49	0.25	7.49900	2.45	0.04
0.50	0.30	3.74	0.37	7.50069	3.57	0.03
0.40	0.40	4.99	0.50	7.50798	4.14	0.05
0.30	0.50	6.24	0.62	7.52061	3.84	0.04
0.20	0.60	7.50	0.75	7.53396	2.90	0.00
0.10	0.70	8.75	0.87	7.54587	1.61	0.01
0.00	0.80	10.01	1.00	7.55669	0.00	0.00

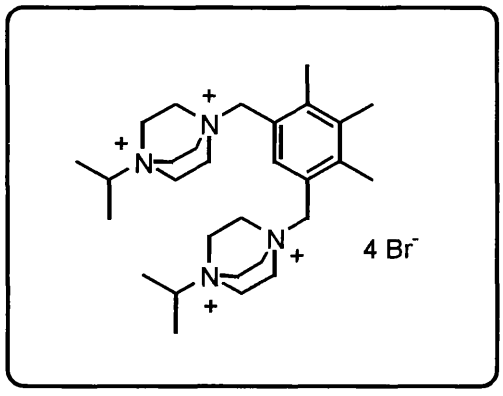
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[53]_{tot}$ / mM	Mf of 53	δ	[53•97] / mM	Error / mM
0.80	0.00	10.06	1.00	2.36128	0.00	0.00
0.70	0.10	8.81	0.88	2.34221	1.40	0.02
0.60	0.20	7.55	0.75	2.32150	2.50	0.00
0.50	0.30	6.30	0.63	2.29779	3.32	0.00
0.40	0.40	5.04	0.50	2.27471	3.63	0.01
0.30	0.50	3.78	0.38	2.25917	3.21	0.00
0.20	0.60	2.52	0.25	2.25008	2.33	0.00
0.10	0.70	1.26	0.13	2.24350	1.24	0.01

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[53]_{tot}$ / mM	Mf of 53	δ	[53•97] / mM	Error / mM
0.80	0.00	10.06	1.00	4.77006	0.00	0.00
0.70	0.10	8.81	0.88	4.74123	1.24	0.02
0.60	0.20	7.55	0.75	4.70798	2.29	0.03
0.50	0.30	6.30	0.63	4.67182	3.02	0.00
0.40	0.40	5.04	0.50	4.62907	3.47	0.01
0.30	0.50	3.78	0.38	4.60112	3.12	0.00
0.20	0.60	2.52	0.25	4.58429	2.29	0.00
0.10	0.70	1.26	0.13	4.57168	1.22	0.00

A.37 4,6-Bis(N'-isopropyl-DABCO-N-methyl)-1,2,3-trimethylbenzene tetrabromide and tetrasodium 1,2,4,5-benzene-tetracarboxylate



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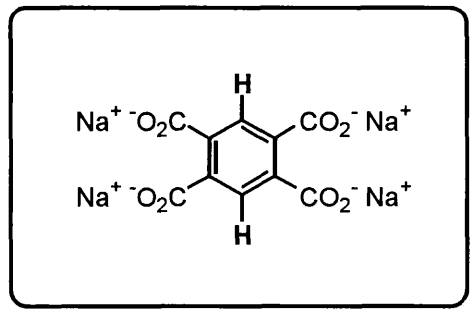


96

NMR Titration

	54 / g	96 / g	D_2O / mL	[54] / mM	[96] / mM
Solution X	0.3889	0.0342	10	50.09	10.00
Solution Y	0	0.0856	25	0.00	10.01

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[54] / mM	[96] / mM	Ratio (54:96)	δ	Δδ	Error
0.80	0.00	50.09	10.00	5.01	7.37418	0.01007	0.00255
0.40	0.40	25.05	10.00	2.50	7.35863	0.00547	0.00485
0.30	0.50	18.78	10.00	1.88	7.35405	0.01005	0.00092
0.20	0.60	12.52	10.01	1.25	7.35305	0.01106	0.00246
0.15	0.65	9.39	10.01	0.94	7.35433	0.00977	0.00110
0.10	0.70	6.26	10.01	0.63	7.35246	0.01165	0.00066
0.05	0.75	3.13	10.01	0.31	7.35641	0.00769	0.00205
0.00	0.80	0.00	10.01	0.00	7.36410	0.00000	0.00008

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[54] / mM	[96] / mM	Ratio (96:54)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	2.32381	0.00000	0.00075
0.80	0.00	50.09	10.00	0.20	2.32087	0.00294	0.00261
0.40	0.40	25.05	10.00	0.40	2.30933	0.01448	0.00481
0.30	0.50	18.78	10.00	0.53	2.30211	0.02171	0.00113
0.20	0.60	12.52	10.01	0.80	2.29443	0.02939	0.00247
0.15	0.65	9.39	10.01	1.07	2.29002	0.03379	0.00129
0.10	0.70	6.26	10.01	1.60	2.28081	0.04300	0.00033
0.05	0.75	3.13	10.01	3.20	2.27638	0.04744	0.00150

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[54] / mM	[96] / mM	Ratio (96:54)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	4.85564	0.00000	0.00048
0.80	0.00	50.09	10.00	0.20	4.85179	0.00385	0.00254
0.40	0.40	25.05	10.00	0.40	4.82683	0.02880	0.00462
0.30	0.50	18.78	10.00	0.53	4.81333	0.04230	0.00113
0.20	0.60	12.52	10.01	0.80	4.79553	0.06011	0.00261
0.15	0.65	9.39	10.01	1.07	4.78433	0.07130	0.00146
0.10	0.70	6.26	10.01	1.60	4.76764	0.08800	0.00076
0.05	0.75	3.13	10.01	3.20	4.75793	0.09771	0.00138

Job Plot

	54 / g	96 / g	D_2O / mL	[54] / mM	[96] / mM
Solution X	0.1166	0.0000	15	10.01	0.00
Solution Y	0.0000	0.0856	25	0.00	10.01

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[96]_{tot}$ / mM	Mf of 96	δ	[54•96] / mM	Error / mM
0.70	0.10	1.25	0.12	7.37227	-0.56	0.17
0.60	0.20	2.50	0.25	7.36321	0.68	0.26
0.50	0.30	3.75	0.37	7.35872	2.35	0.07
0.40	0.40	5.00	0.50	7.35869	3.15	0.75
0.30	0.50	6.26	0.62	7.35801	4.27	0.88
0.20	0.60	7.51	0.75	7.35889	4.60	0.15
0.10	0.70	8.76	0.87	7.36299	2.53	0.95
0.00	0.80	10.01	1.00	7.36665	0.00	0.00

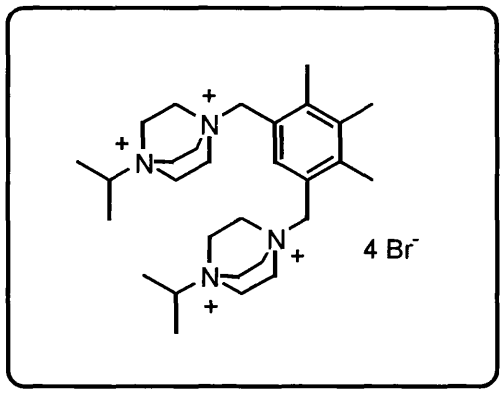
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[54]_{tot}$ / mM	Mf of 54	δ	[54•96] / mM	Error / mM
0.80	0.00	10.01	1.00	2.32381	0.00	0.00
0.70	0.10	8.76	0.88	2.31723	1.09	0.19
0.60	0.20	7.51	0.75	2.30926	2.07	0.28
0.50	0.30	6.26	0.63	2.29944	2.89	0.01
0.40	0.40	5.01	0.50	2.28951	3.25	0.17
0.30	0.50	3.76	0.38	2.28161	3.00	0.13
0.20	0.60	2.50	0.25	2.27700	2.22	0.04
0.10	0.70	1.25	0.13	2.27427	1.17	0.06

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[54]_{tot}$ / mM	Mf of 54	δ	[54•96] / mM	Error / mM
0.80	0.00	10.01	1.00	4.85564	0.00	0.00
0.70	0.10	8.76	0.88	4.84093	1.17	0.11
0.60	0.20	7.51	0.75	4.82431	2.15	0.13
0.50	0.30	6.26	0.63	4.80288	3.01	0.01
0.40	0.40	5.01	0.50	4.78041	3.44	0.08
0.30	0.50	3.76	0.38	4.66525	6.52	0.06
0.20	0.60	2.50	0.25	4.77290	1.89	0.02
0.10	0.70	1.25	0.13	4.75298	1.17	0.03

A.38 4,6-Bis(N'-isopropyl-DABCO-N-methyl)-1,2,3-trimethylbenzene tetrabromide and tetrasodium 1,2,4,5-naphthalene-tetracarboxylate



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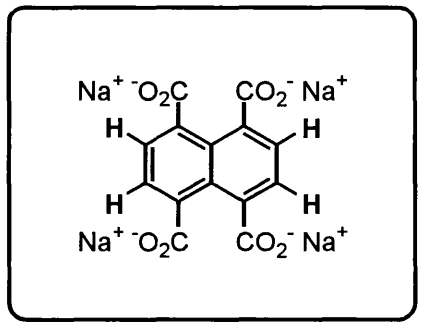


97

NMR Titration

	54 / g	97 / g	D_2O / mL	[54] / mM	[97] / mM
Solution X	0.3900	0.0392	10	50.23	10.00
Solution Y	0.0000	0.0980	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[54] / mM	[97] / mM	Ratio (54:97)	δ	Δδ	Error
0.80	0.00	50.23	10.00	5.03	7.50459	0.04948	0.00124
0.40	0.40	25.12	10.00	2.51	7.50222	0.05184	0.00048
0.30	0.50	18.84	10.00	1.88	7.50339	0.05068	0.00192
0.20	0.60	12.56	10.00	1.26	7.50642	0.04765	0.00053
0.15	0.65	9.42	10.00	0.94	7.51171	0.04235	0.00076
0.10	0.70	6.28	10.00	0.63	7.51775	0.03632	0.00150
0.05	0.75	3.14	10.00	0.31	7.53059	0.02348	0.00095
0.00	0.80	0.00	10.00	0.00	7.55407	0.00000	0.00158

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[54] / mM	[97] / mM	Ratio (97:54)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	2.32515	0.00000	0.00224
0.80	0.00	50.23	10.00	0.20	2.31863	0.00652	0.00122
0.40	0.40	25.12	10.00	0.40	2.30050	0.02465	0.00046
0.30	0.50	18.84	10.00	0.53	2.28971	0.03544	0.00122
0.20	0.60	12.56	10.00	0.80	2.27663	0.04852	0.00079
0.15	0.65	9.42	10.00	1.06	2.26761	0.05754	0.00050
0.10	0.70	6.28	10.00	1.59	2.25608	0.06907	0.00072
0.05	0.75	3.14	10.00	3.18	2.24954	0.07561	0.00088

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[54] / mM	[97] / mM	Ratio (97:54)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	4.85684	0.00000	0.00201
0.80	0.00	50.23	10.00	0.20	4.82519	0.03165	0.00115
0.40	0.40	25.12	10.00	0.40	4.77272	0.08412	0.00060
0.30	0.50	18.84	10.00	0.53	4.74486	0.11198	0.00091
0.20	0.60	12.56	10.00	0.80	4.70497	0.15187	0.00140
0.15	0.65	9.42	10.00	1.06	4.67208	0.18476	0.00030
0.10	0.70	6.28	10.00	1.59	4.64909	0.20775	0.00094
0.05	0.75	3.14	10.00	3.18	4.62911	0.22773	0.00077

Job Plot

	54 / g	97 / g	D_2O / mL	[54] / mM	[97] / mM
Solution X	0.1165	0.0000	15	10.00	0.00
Solution Y	0.0000	0.0980	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[97]_{tot}$ / mM	Mf of 97	δ	[54•97] / mM	Error / mM
0.70	0.10	1.25	0.12	7.50872	0.11	0.00
0.60	0.20	2.50	0.25	7.50553	0.24	0.00
0.50	0.30	3.75	0.37	7.50592	0.36	0.00
0.40	0.40	5.00	0.50	7.51136	0.42	0.01
0.30	0.50	6.25	0.62	7.52230	0.39	0.01
0.20	0.60	7.50	0.75	7.53256	0.32	0.00
0.10	0.70	8.75	0.87	7.54366	0.18	0.02
0.00	0.80	10.00	1.00	7.55373	0.00	0.00

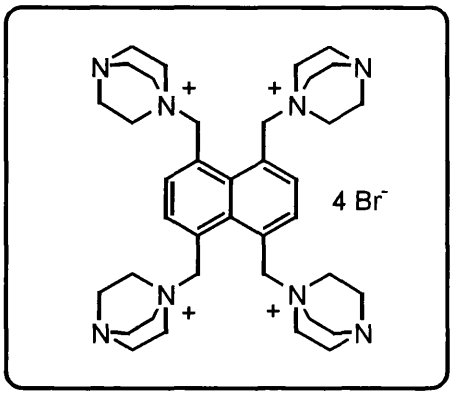
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[54]_{tot}$ / mM	Mf of 54	δ	[54•97] / mM	Error / mM
0.80	0.00	10.00	1.00	2.32515	0.00	0.00
0.70	0.10	8.75	0.88	2.31204	1.38	0.12
0.60	0.20	7.50	0.75	2.29830	2.42	0.02
0.50	0.30	6.25	0.63	2.28088	3.33	0.03
0.40	0.40	5.00	0.50	2.26440	3.66	0.09
0.30	0.50	3.75	0.38	2.25429	3.20	0.06
0.20	0.60	2.50	0.25	2.24766	2.33	0.03
0.10	0.70	1.25	0.13	2.24338	1.23	0.02

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[54]_{tot}$ / mM	Mf of 54	δ	[54•97] / mM	Error / mM
0.80	0.00	10.00	1.00	4.85684	0.00	0.00
0.70	0.10	8.75	0.88	4.81752	1.44	0.04
0.60	0.20	7.50	0.75	4.77296	2.64	0.00
0.50	0.30	6.25	0.63	4.71878	3.62	0.03
0.40	0.40	5.00	0.50	4.67192	3.87	0.00
0.30	0.50	3.75	0.38	4.63978	3.41	0.02
0.20	0.60	2.50	0.25	4.62553	2.42	0.01
0.10	0.70	1.25	0.13	4.61607	1.26	0.01

A.39 1,4,5,8-Tetrakis(DABCO-N-methyl)naphthalene tetrabromide and trisodium 1,3,5-benzenetricarboxylate



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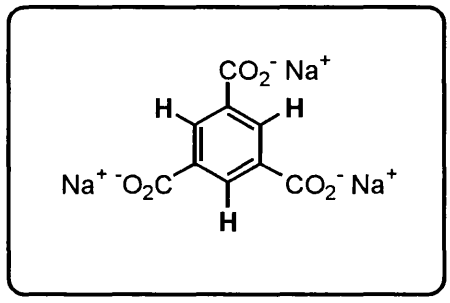


95

NMR Titration

	55 / g	95 / g	D_2O / mL	[55] / mM	[95] / mM
Solution X	0.2610	0.0138	5	55.03	10.00
Solution Y	0	0.0690	25	0.00	10.00

Anion proton shift (average of 2 runs)

X / mL	Y / mL	[55] / mM	[95] / mM	Ratio (55:95)	δ	Δδ	Error
0.80	0.00	55.03	10.00	5.50487	8.37236	0.11650	0.00046
0.40	0.40	27.52	10.00	2.75244	8.35390	0.09803	0.00012
0.30	0.50	20.64	10.00	2.06433	8.34681	0.09094	0.00021
0.20	0.60	13.76	10.00	1.37622	8.33786	0.08199	0.00006
0.15	0.65	10.32	10.00	1.03216	8.33086	0.07500	0.00049
0.10	0.70	6.88	10.00	0.68811	8.32135	0.06548	0.00002
0.05	0.75	3.44	10.00	0.34405	8.30319	0.04732	0.00008
0.00	0.80	0.00	10.00	0.00000	8.25587	0.00000	0.00005

Cation Benzyl proton shift (average of 2 runs)

X / mL	Y / mL	[55] / mM	[95] / mM	Ratio (95:55)	δ	Δδ	Error
Cation reference		10.06	0.00	0.00	5.21643	0.00000	0.00049
0.80	0.00	55.03	10.00	0.18	5.22481	0.00838	0.00052
0.40	0.40	27.52	10.00	0.36	5.19970	0.01673	0.00004
0.30	0.50	20.64	10.00	0.48	5.18741	0.02902	0.00005
0.20	0.60	13.76	10.00	0.73	5.16964	0.04679	0.00007
0.15	0.65	10.32	10.00	0.97	5.15475	0.06168	0.00035
0.10	0.70	6.88	10.00	1.45	5.13602	0.08040	0.00013
0.05	0.75	3.44	10.00	2.91	5.10832	0.10811	0.00047

Job Plot

	55 / g	95 / g	D_2O / mL	[55] / mM	[95] / mM
Solution X	0.0954	0.0000	10	10.06	0.00
Solution Y	0.0000	0.0690	25	0.00	10.00

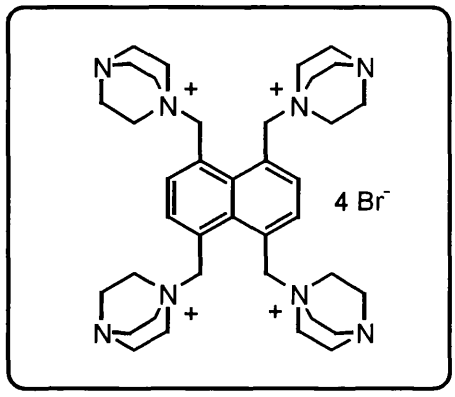
Anion proton shift (average of 2 runs)

X / mL	Y / mL	$[95]_{tot}$ / mM	Mf of 95	δ	[55•95] / mM	Error / mM
0.70	0.10	1.24	0.12	8.34599	0.91	0.01
0.60	0.20	2.49	0.25	8.34192	1.74	0.01
0.50	0.30	3.73	0.37	8.33662	2.45	0.01
0.40	0.40	4.98	0.50	8.32693	2.89	0.02
0.30	0.50	6.23	0.62	8.31277	2.90	0.00
0.20	0.60	7.49	0.75	8.29584	2.45	0.03
0.10	0.70	8.74	0.87	8.27804	1.61	0.03
0.00	0.80	10.00	1.00	8.25532	0.00	0.00

Cation Benzyl proton shift (average of 2 runs)

X / mL	Y / mL	$[55]_{tot}$ / mM	Mf of 55	δ	[55•95] / mM	Error / mM
0.80	0.00	10.06	1.00	5.21643	0.00	0.00
0.70	0.10	8.81	0.88	5.20229	0.63	0.01
0.60	0.20	7.55	0.75	5.18750	1.10	0.01
0.50	0.30	6.30	0.63	5.16924	1.50	0.01
0.40	0.40	5.04	0.50	5.14549	1.80	0.00
0.30	0.50	3.79	0.38	5.12043	1.83	0.00
0.20	0.60	2.53	0.25	5.10170	1.46	0.01
0.10	0.70	1.26	0.13	5.08610	0.83	0.01

A.40 1,4,5,8-Tetrakis(DABCO-N-methyl)naphthalene tetrabromide and tetrasodium 1,2,4,5-benzene-tetracarboxylate



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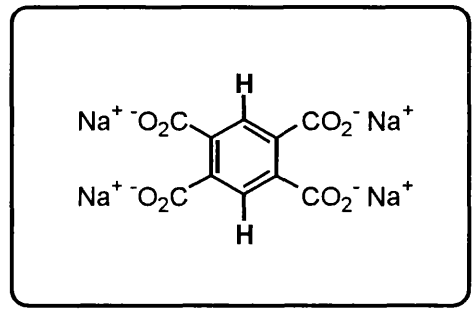


96

NMR Titration

	55 / g	96 / g	D_2O / mL	[55] / mM	[96] / mM
Solution X	0.2401	0.0171	5	50.12	9.90
Solution Y	0	0.0855	25	0.00	10.00

Anion proton shift (average of 2 runs)

X / mL	Y / mL	[55] / mM	[96] / mM	Ratio (55:96)	δ	Δδ	Error
0.80	0.00	50.12	9.90	5.06359	7.48059	0.11276	0.00076
0.40	0.40	25.06	9.95	2.51920	7.46774	0.09991	0.00057
0.30	0.50	18.80	9.96	1.88705	7.46234	0.09451	0.00029
0.20	0.60	12.53	9.97	1.25648	7.45279	0.08496	0.00010
0.15	0.65	9.40	9.98	0.94177	7.44418	0.07635	0.00021
0.10	0.70	6.27	9.99	0.62746	7.43002	0.06219	0.00019
0.05	0.75	3.13	9.99	0.31354	7.40687	0.03904	0.00019
0.00	0.80	0.00	10.00	0.00000	7.36783	0.00000	0.00061

Cation Benzyl proton shift (average of 2 runs)

X / mL	Y / mL	[55] / mM	[96] / mM	Ratio (96:55)	δ	Δδ	Error
Cation reference		10.04	0.00	0.00	5.21397	0.00000	0.00008
0.80	0.00	50.12	9.90	0.20	5.22880	0.01483	0.00058
0.40	0.40	25.06	9.95	0.40	5.20936	0.00461	0.00007
0.30	0.50	18.80	9.96	0.53	5.20082	0.01315	0.00017
0.20	0.60	12.53	9.97	0.80	5.18745	0.02652	0.00004
0.15	0.65	9.40	9.98	1.06	5.17777	0.03620	0.00007
0.10	0.70	6.27	9.99	1.59	5.16572	0.04825	0.00048
0.05	0.75	3.13	9.99	3.19	5.15479	0.05918	0.00020

Job Plot

	55 / g	96 / g	D_2O / mL	[55] / mM	[96] / mM
Solution X	0.0952	0.0000	10	10.04	0.00
Solution Y	0.0000	0.0855	25	0.00	10.00

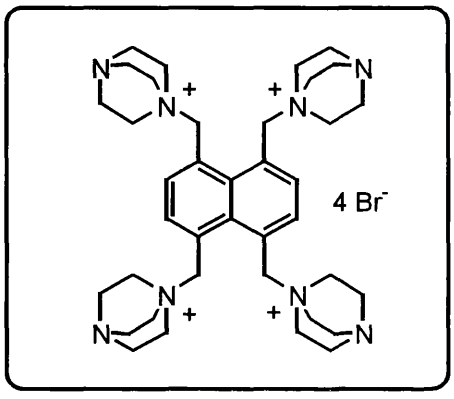
Anion proton shift (average of 2 runs)

X / mL	Y / mL	$[96]_{tot}$ / mM	Mf of 96	δ	[55•96] / mM	Error / mM
0.70	0.10	1.25	0.12	7.47196	1.11	0.00
0.60	0.20	2.49	0.25	7.46585	2.09	0.01
0.50	0.30	3.74	0.37	7.45798	2.88	0.00
0.40	0.40	4.99	0.50	7.44585	3.33	0.01
0.30	0.50	6.24	0.62	7.42631	3.13	0.01
0.20	0.60	7.49	0.75	7.40578	2.45	0.02
0.10	0.70	8.74	0.87	7.38702	1.47	0.02
0.00	0.80	10.00	1.00	7.36718	0.00	0.00

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[55]_{tot}$ / mM	Mf of 55	δ	[55•96] / mM	Error / mM
0.80	0.00	10.04	1.00	5.21397	0.00	0.00
0.70	0.10	8.79	0.88	5.20535	0.54	0.00
0.60	0.20	7.53	0.75	5.19585	0.98	0.00
0.50	0.30	6.28	0.63	5.18352	1.38	0.00
0.40	0.40	5.03	0.50	5.16975	1.60	0.03
0.30	0.50	3.77	0.38	5.15835	1.51	0.01
0.20	0.60	2.52	0.25	5.15169	1.13	0.01
0.10	0.70	1.26	0.13	5.14557	0.62	0.04

A.41 1,4,5,8-Tetrakis(DABCO-N-methyl)naphthalene tetrabromide and tetrasodium 1,2,4,5-naphthalene-tetracarboxylate



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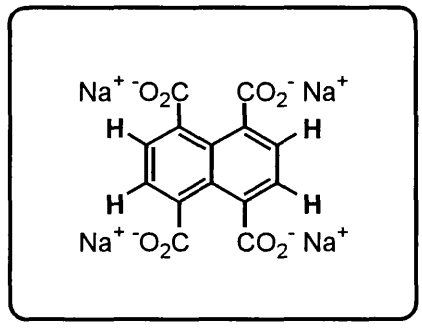


97

NMR Titration

	55 / g	97 / g	D_2O / mL	[55] / mM	[97] / mM
Solution X	0.4743	0.0392	10	50.00	10.00
Solution Y	0	0.0980	25	0.00	10.00

Anion proton shift (average of 2 runs)

X / mL	Y / mL	[55] / mM	[97] / mM	Ratio (55:97)	δ	Δδ	Error
0.80	0.00	50.00	10.00	5.00	7.63069	0.08345	0.01249
0.40	0.40	25.00	10.00	2.50	7.61355	0.06630	0.00636
0.30	0.50	18.75	10.00	1.88	7.60783	0.06059	0.00643
0.20	0.60	12.50	10.00	1.25	7.60036	0.05312	0.00435
0.15	0.65	9.38	10.00	0.94	7.59224	0.04500	0.00496
0.10	0.70	6.25	10.00	0.63	7.58069	0.03345	0.00145
0.05	0.75	3.13	10.00	0.31	7.56913	0.02188	0.00158
0.00	0.80	0.00	10.00	0.00	7.54724	0.00000	0.00536

Cation Benzyl proton shift (average of 2 runs)

X / mL	Y / mL	[55] / mM	[97] / mM	Ratio (97:55)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	5.21215	0.00000	0.00060
0.80	0.00	50.00	10.00	0.20	5.19923	0.01292	0.00345
0.40	0.40	25.00	10.00	0.40	5.17008	0.04207	0.00119
0.30	0.50	18.75	10.00	0.53	5.15521	0.05694	0.00228
0.20	0.60	12.50	10.00	0.80	5.13216	0.07999	0.00145
0.15	0.65	9.38	10.00	1.07	5.11475	0.09740	0.00263
0.10	0.70	6.25	10.00	1.60	5.09211	0.12004	0.00064
0.05	0.75	3.13	10.00	3.20	5.07463	0.13752	0.00003

Job Plot

	55 / g	97 / g	D_2O / mL	[55] / mM	[97] / mM
Solution X	0.2371	0.0000	25	10.00	0.00
Solution Y	0.0000	0.0980	25	0.00	10.00

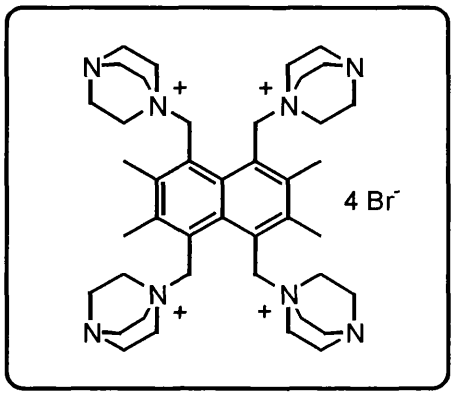
Anion proton shift (average of 2 runs)

X / mL	Y / mL	$[97]_{tot}$ / mM	Mf of 97	δ	[55•97] / mM	Error / mM
0.70	0.10	1.25	0.12	7.62856	1.09	0.01
0.60	0.20	2.50	0.25	7.62000	1.93	0.00
0.50	0.30	3.75	0.37	7.61043	2.46	0.05
0.40	0.40	5.00	0.50	7.60184	2.77	0.02
0.30	0.50	6.25	0.62	7.58549	2.24	0.23
0.20	0.60	7.50	0.75	7.57602	1.83	0.02
0.10	0.70	8.75	0.87	7.56432	0.91	0.04
0.00	0.80	10.00	1.00	7.55567	0.00	0.00

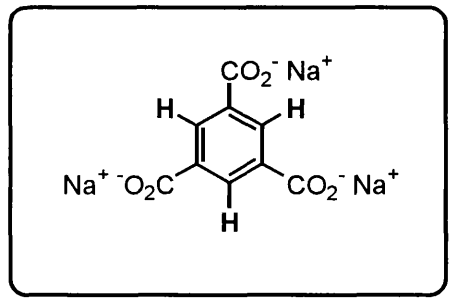
Cation Benzyl proton shift (average of 2 runs)

X / mL	Y / mL	$[55]_{tot}$ / mM	Mf of 55	δ	[55•97] / mM	Error / mM
0.80	0.00	10.00	1.00	5.21215	0.00	0.00
0.70	0.10	8.75	0.88	5.19306	0.98	0.02
0.60	0.20	7.50	0.75	5.17180	1.77	0.02
0.50	0.30	6.25	0.63	5.14326	2.52	0.09
0.40	0.40	5.00	0.50	5.11452	2.85	0.03
0.30	0.50	3.75	0.38	5.09072	2.66	0.11
0.20	0.60	2.50	0.25	5.08350	1.88	0.01
0.10	0.70	1.25	0.13	5.08000	0.97	0.00

A.42 1,4,5,8-Tetrakis(DABCO-N-methyl)-2,3,6,7-tetramethylnaphthalene tetrabromide and trisodium 1,3,5-benzenetricarboxylate



56



95

NMR Titration

	56 / g	95 / g	D_2O / mL	[56] / mM	[95] / mM
Solution X	0.5038	0.0278	10	50.15	10.07
Solution Y	0	0.0691	25	0.00	10.01

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[56] / mM	[95] / mM	Ratio (56:95)	δ	$\Delta\delta$	Error
0.80	0.00	50.15	10.07	4.98	8.35629	0.09879	0.00187
0.40	0.40	25.07	10.04	2.50	8.33852	0.08102	0.00229
0.30	0.50	18.80	10.03	1.87	8.33269	0.07520	0.00355
0.20	0.60	12.54	10.03	1.25	8.32288	0.06538	0.00267
0.15	0.65	9.40	10.02	0.94	8.31510	0.05760	0.00181
0.10	0.70	6.27	10.02	0.63	8.30552	0.04802	0.00147
0.05	0.75	3.13	10.01	0.31	8.28948	0.03198	0.00082
0.00	0.80	0.00	10.01	0.00	8.25750	0.00000	0.00221

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[56] / mM	[95] / mM	Ratio (95:56)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	2.57488	0.00000	0.00344
0.80	0.00	50.15	10.07	0.20	2.57657	0.00169	0.00201
0.40	0.40	25.07	10.04	0.40	2.54937	0.02551	0.00274
0.30	0.50	18.80	10.03	0.53	2.53636	0.03852	0.00302
0.20	0.60	12.54	10.03	0.80	2.51458	0.06030	0.00258
0.15	0.65	9.40	10.02	1.07	2.49819	0.07669	0.00179
0.10	0.70	6.27	10.02	1.60	2.47626	0.09862	0.00131
0.05	0.75	3.13	10.01	3.20	2.44658	0.12830	0.00063

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[56] / mM	[95] / mM	Ratio (95:56)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	5.20747	0.00000	0.00362
0.80	0.00	50.15	10.07	0.20	5.20916	0.00169	0.00216
0.40	0.40	25.07	10.04	0.40	5.19201	0.01546	0.00242
0.30	0.50	18.80	10.03	0.53	5.18408	0.02339	0.00289
0.20	0.60	12.54	10.03	0.80	5.17097	0.03650	0.00256
0.15	0.65	9.40	10.02	1.07	5.16084	0.04663	0.00183
0.10	0.70	6.27	10.02	1.60	5.14763	0.05984	0.00127
0.05	0.75	3.13	10.01	3.20	5.13053	0.07694	0.00067

Job Plot

	56 / g	95 / g	D_2O / mL	[56] / mM	[95] / mM
Solution X	0.1508	0.0000	15	10.01	0.00
Solution Y	0.0000	0.0691	25	0.00	10.01

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[95]_{tot}$ / mM	Mf of 95	δ	[56•95] / mM	Error / mM
0.70	0.10	1.25	0.13	8.33857	0.92	0.02
0.60	0.20	2.50	0.25	8.33158	1.68	0.04
0.50	0.30	3.76	0.38	8.32421	2.26	0.06
0.40	0.40	5.01	0.50	8.31393	2.52	0.05
0.30	0.50	6.26	0.63	8.30204	2.44	0.05
0.20	0.60	7.51	0.75	8.28850	1.95	0.06
0.10	0.70	8.76	0.88	8.27549	1.19	0.12
0.00	0.80	10.01	1.00	8.26127	0.00	0.00

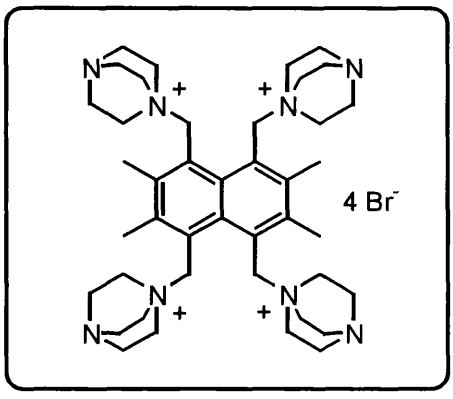
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[56]_{tot}$ / mM	Mf of 56	δ	[56•95] / mM	Error / mM
0.80	0.00	10.01	1.00	2.57488	0.00	0.00
0.70	0.10	8.76	0.87	2.56080	0.63	0.03
0.60	0.20	7.50	0.75	2.54305	1.23	0.03
0.50	0.30	6.25	0.62	2.52126	1.72	0.00
0.40	0.40	5.00	0.50	2.49599	2.02	0.03
0.30	0.50	3.75	0.37	2.46961	2.03	0.01
0.20	0.60	2.50	0.25	2.44606	1.65	0.01
0.10	0.70	1.25	0.12	2.42732	0.95	0.02

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[56]_{tot}$ / mM	Mf of 56	δ	[56•95] / mM	Error / mM
0.80	0.00	10.01	1.00	5.20747	0.00	0.00
0.70	0.10	8.76	0.87	5.19907	0.63	0.08
0.60	0.20	7.50	0.75	5.18828	1.24	0.06
0.50	0.30	6.25	0.62	5.17522	1.73	0.02
0.40	0.40	5.00	0.50	5.15974	2.05	0.05
0.30	0.50	3.75	0.37	5.14392	2.05	0.02
0.20	0.60	2.50	0.25	5.13067	1.65	0.01
0.10	0.70	1.25	0.12	5.12027	0.94	0.04

A.43 1,4,5,8-Tetrakis(DABCO-N-methyl)-2,3,6,7-tetramethylnaphthalene tetrabromide and tetrasodium 1,2,4,5-benzene-tetracarboxylate



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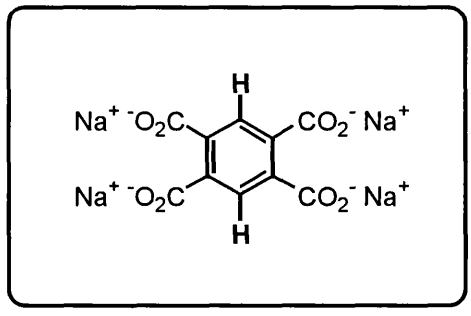


96

NMR Titration

	56 / g	96 / g	D_2O / mL	[56] / mM	[96] / mM
Solution X	0.5041	0.0343	10	50.18	10.03
Solution Y	0	0.0855	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[56] / mM	[96] / mM	Ratio (56:96)	δ	Δδ	Error
0.80	0.00	50.18	10.03	5.00	7.46475	0.08809	0.00123
0.40	0.40	25.09	10.01	2.51	7.45152	0.07485	0.00033
0.30	0.50	18.82	10.01	1.88	7.44687	0.07021	0.00012
0.20	0.60	12.54	10.00	1.25	7.43945	0.06279	0.00027
0.15	0.65	9.41	10.00	0.94	7.43243	0.05576	0.00010
0.10	0.70	6.27	10.00	0.63	7.42206	0.04539	0.00016
0.05	0.75	3.14	10.00	0.31	7.40477	0.02810	0.00083
0.00	0.80	0.00	10.00	0.00	7.37666	0.00000	0.00043

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[56] / mM	[96] / mM	Ratio (96:56)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	2.57326	0.00000	0.00269
0.80	0.00	50.18	10.03	0.20	2.58967	0.01641	0.00054
0.40	0.40	25.09	10.01	0.40	2.57027	0.00299	0.00018
0.30	0.50	18.82	10.01	0.53	2.56222	0.01104	0.00018
0.20	0.60	12.54	10.00	0.80	2.55018	0.02308	0.00021
0.15	0.65	9.41	10.00	1.06	2.54139	0.03187	0.00021
0.10	0.70	6.27	10.00	1.59	2.53085	0.04241	0.00031
0.05	0.75	3.14	10.00	3.19	2.51952	0.05374	0.00055

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[56] / mM	[96] / mM	Ratio (96:56)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	5.20581	0.00000	0.00252
0.80	0.00	50.18	10.03	0.20	5.22191	0.01610	0.00112
0.40	0.40	25.09	10.01	0.40	5.21185	0.00604	0.00020
0.30	0.50	18.82	10.01	0.53	5.20846	0.00265	0.00018
0.20	0.60	12.54	10.00	0.80	5.20355	0.00226	0.00027
0.15	0.65	9.41	10.00	1.06	5.20004	0.00577	0.00011
0.10	0.70	6.27	10.00	1.59	5.19560	0.01021	0.00027
0.05	0.75	3.14	10.00	3.19	5.19107	0.01474	0.00050

Job Plot

	56 / g	96 / g	D_2O / mL	[56] / mM	[96] / mM
Solution X	0.1508	0.0000	15	10.01	0.00
Solution Y	0.0000	0.0855	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[96]_{tot}$ / mM	Mf of 96	δ	[56•96] / mM	Error / mM
0.70	0.10	1.25	0.12	7.46052	1.13	0.03
0.60	0.20	2.50	0.25	7.45140	2.02	0.07
0.50	0.30	3.75	0.37	7.44303	2.71	0.09
0.40	0.40	5.00	0.50	7.43216	3.05	0.11
0.30	0.50	6.25	0.62	7.41687	2.83	0.10
0.20	0.60	7.50	0.75	7.40136	2.19	0.07
0.10	0.70	8.75	0.87	7.38693	1.26	0.05
0.00	0.80	10.00	1.00	7.37296	0.00	0.00

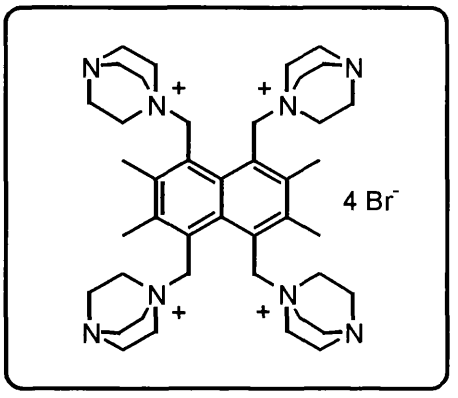
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[56]_{tot}$ / mM	Mf of 56	δ	[56•96] / mM	Error / mM
0.80	0.00	10.01	1.00	2.57326	0.00	0.00
0.70	0.10	8.76	0.88	2.56527	0.40	0.01
0.60	0.20	7.51	0.75	2.55528	0.77	0.03
0.50	0.30	6.26	0.63	2.54372	1.05	0.03
0.40	0.40	5.01	0.50	2.53142	1.19	0.03
0.30	0.50	3.75	0.38	2.52155	1.10	0.02
0.20	0.60	2.50	0.25	2.51450	0.83	0.01
0.10	0.70	1.25	0.13	2.50894	0.46	0.01

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[56]_{tot}$ / mM	Mf of 56	δ	[56•96] / mM	Error / mM
0.80	0.00	10.01	1.00	5.20581	0.00	0.00
0.70	0.10	8.76	0.88	5.20335	0.39	0.08
0.60	0.20	7.51	0.75	5.20024	0.76	0.09
0.50	0.30	6.26	0.63	5.19632	1.08	0.10
0.40	0.40	5.01	0.50	5.19226	1.24	0.08
0.30	0.50	3.75	0.38	5.18862	1.18	0.06
0.20	0.60	2.50	0.25	5.18657	0.88	0.05
0.10	0.70	1.25	0.13	5.18190	0.55	0.01

A.44 1,4,5,8-Tetrakis(DABCO-N-methyl)-2,3,6,7-tetramethylnaphthalene tetrabromide and tetrasodium 1,2,4,5-naphthalene-tetracarboxylate



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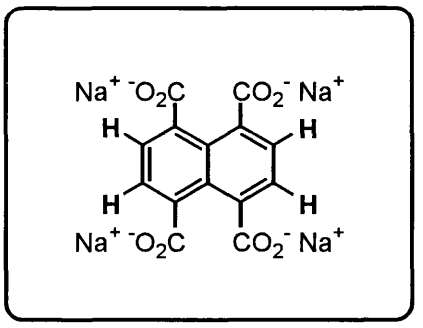


97

NMR Titration

	56 / g	97 / g	D_2O / mL	[56] / mM	[97] / mM
Solution X	0.5359	0.0403	10	53.34	10.28
Solution Y	0	0.0991	25	0.00	10.11

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[56] / mM	[97] / mM	Ratio (56:97)	δ	Δδ	Error
0.80	0.00	53.34	10.28	5.19	7.65184	0.07228	0.00065
0.40	0.40	26.67	10.19	2.62	7.63543	0.05587	0.00124
0.30	0.50	20.00	10.17	1.97	7.62996	0.05040	0.00144
0.20	0.60	13.34	10.15	1.31	7.62299	0.04343	0.00073
0.15	0.65	10.00	10.14	0.99	7.61708	0.03753	0.00140
0.10	0.70	6.67	10.13	0.66	7.60956	0.03001	0.00151
0.05	0.75	3.33	10.12	0.33	7.59788	0.01832	0.00152
0.00	0.80	0.00	10.11	0.00	7.57956	0.00000	0.00175

Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	[56] / mM	[97] / mM	Ratio (97:56)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	2.59534	0.00000	0.00119
0.80	0.00	53.34	10.28	0.19	2.59400	0.00133	0.00092
0.40	0.40	26.67	10.19	0.38	2.56456	0.03077	0.00147
0.30	0.50	20.00	10.17	0.51	2.55134	0.04399	0.00184
0.20	0.60	13.34	10.15	0.76	2.53199	0.06335	0.00174
0.15	0.65	10.00	10.14	1.01	2.51756	0.07778	0.00163
0.10	0.70	6.67	10.13	1.52	2.49959	0.09575	0.00221
0.05	0.75	3.33	10.12	3.04	2.47814	0.11720	0.00153

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[56] / mM	[97] / mM	Ratio (97:56)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	5.22643	0.00000	0.00111
0.80	0.00	53.34	10.28	0.19	5.22359	0.00284	0.00097
0.40	0.40	26.67	10.19	0.38	5.20354	0.02289	0.00134
0.30	0.50	20.00	10.17	0.51	5.19457	0.03186	0.00164
0.20	0.60	13.34	10.15	0.76	5.18217	0.04426	0.00056
0.15	0.65	10.00	10.14	1.01	5.17219	0.05424	0.00147
0.10	0.70	6.67	10.13	1.52	5.15999	0.06644	0.00223
0.05	0.75	3.33	10.12	3.04	5.14539	0.08104	0.00131

Job Plot

	56 / g	97 / g	D_2O / mL	[56] / mM	[97] / mM
Solution X	0.1509	0.0000	15	10.01	0.00
Solution Y	0.0000	0.0991	25	0.00	10.11

Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[97]_{tot}$ / mM	Mf of 97	δ	[56•97] / mM	Error / mM
0.70	0.10	1.27	0.13	7.64610	0.98	0.01
0.60	0.20	2.55	0.25	7.63749	1.68	0.02
0.50	0.30	3.81	0.38	7.62984	2.16	0.02
0.40	0.40	5.08	0.50	7.62034	2.29	0.05
0.30	0.50	6.34	0.63	7.61016	2.06	0.04
0.20	0.60	7.60	0.75	7.60040	1.55	0.05
0.10	0.70	8.86	0.88	7.59173	0.86	0.01
0.00	0.80	10.11	1.00	7.58380	0.00	0.00

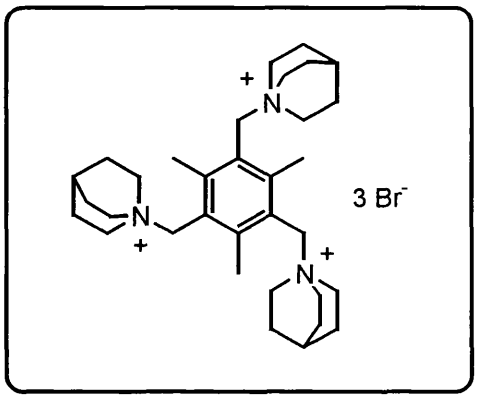
Cation Methyl proton shift (average of 3 runs)

X / mL	Y / mL	$[56]_{tot}$ / mM	Mf of 56	δ	[56•97] / mM	Error / mM
0.80	0.00	10.01	1.00	2.59534	0.00	0.00
0.70	0.10	8.75	0.87	2.57561	1.19	0.00
0.60	0.20	7.49	0.75	2.55459	2.10	0.03
0.50	0.30	6.24	0.62	2.53223	2.71	0.02
0.40	0.40	4.98	0.50	2.51010	2.92	0.04
0.30	0.50	3.73	0.37	2.49245	2.64	0.03
0.20	0.60	2.49	0.25	2.47902	1.99	0.02
0.10	0.70	1.24	0.12	2.46771	1.09	0.01

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[56]_{tot}$ / mM	Mf of 56	δ	[56•97] / mM	Error / mM
0.80	0.00	10.01	1.00	5.22643	0.00	0.00
0.70	0.10	8.75	0.87	5.21294	1.21	0.01
0.60	0.20	7.49	0.75	5.19837	2.16	0.02
0.50	0.30	6.24	0.62	5.18334	2.76	0.02
0.40	0.40	4.98	0.50	5.16803	2.99	0.05
0.30	0.50	3.73	0.37	5.15635	2.68	0.03
0.20	0.60	2.49	0.25	5.14710	2.02	0.03
0.10	0.70	1.24	0.12	5.13923	1.11	0.09

A.45 2,4,6-Tris(quinuclidine-N-methyl)-1,3,5-trimethylbenzene tribromide and disodium DL-malate



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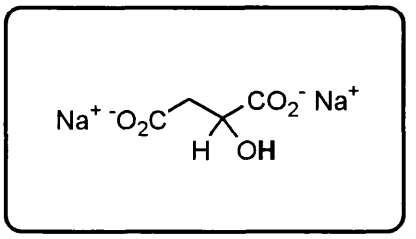


99

NMR Titration

	45 / g	99 / g	D_2O / mL	[45] / mM	[99] / mM
Solution X	0.3663	0.0196	10	50.01	10.00
Solution Y	0	0.0490	25	0.00	10.00

Anion proton shift (average of 2 runs)

X / mL	Y / mL	[45] / mM	[99] / mM	Ratio (45:99)	δ	Δδ	Error
0.80	0.00	50.01	10.00	5.00	4.14184	0.02166	0.00057
0.40	0.40	25.00	10.00	2.50	4.14527	0.01822	0.00014
0.30	0.50	18.75	10.00	1.88	4.14662	0.01688	0.00017
0.20	0.60	12.50	10.00	1.25	4.14873	0.01477	0.00050
0.15	0.65	9.38	10.00	0.94	4.15064	0.01286	0.00026
0.10	0.70	6.25	10.00	0.63	4.15274	0.01076	0.00003
0.05	0.75	3.13	10.00	0.31	4.15643	0.00707	0.00018
0.00	0.80	0.00	10.00	0.00	4.16350	0.00000	0.00294

Cation Methyl proton shift (average of 2 runs)

X / mL	Y / mL	[45] / mM	[99] / mM	Ratio (99:45)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	2.49548	0.00000	0.00060
0.80	0.00	50.01	10.00	0.20	2.50719	0.01172	0.00123
0.40	0.40	25.00	10.00	0.40	2.49880	0.00332	0.00124
0.30	0.50	18.75	10.00	0.53	2.49589	0.00042	0.00065
0.20	0.60	12.50	10.00	0.80	2.49355	0.00193	0.00070
0.15	0.65	9.38	10.00	1.07	2.49166	0.00381	0.00092
0.10	0.70	6.25	10.00	1.60	2.49128	0.00419	0.00089
0.05	0.75	3.13	10.00	3.20	2.49085	0.00463	0.00021

Cation Benzyl proton shift (average of 2 runs)

X / mL	Y / mL	[45] / mM	[99] / mM	Ratio (99:45)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	4.61066	0.00000	0.00041
0.80	0.00	50.01	10.00	0.20	4.61759	0.00693	0.00115
0.40	0.40	25.00	10.00	0.40	4.61160	0.00094	0.00118
0.30	0.50	18.75	10.00	0.53	4.60972	0.00094	0.00071
0.20	0.60	12.50	10.00	0.80	4.60863	0.00203	0.00064
0.15	0.65	9.38	10.00	1.07	4.60822	0.00244	0.00129
0.10	0.70	6.25	10.00	1.60	4.60871	0.00195	0.00091
0.05	0.75	3.13	10.00	3.20	4.61132	0.00066	0.00047

Job Plot

	45 / g	99 / g	D_2O / mL	[45] / mM	[99] / mM
Solution X	0.1099	0.0000	15	10.00	0.00
Solution Y	0.0000	0.0490	25	0.00	10.00

Anion proton shift (average of 2 runs)

X / mL	Y / mL	$[99]_{tot}$ / mM	Mf of 99	δ	[45•99] / mM	Error / mM
0.70	0.10	1.25	0.12	4.14750	0.84	0.02
0.60	0.20	2.50	0.25	4.15010	1.39	0.02
0.50	0.30	3.75	0.37	4.14992	2.11	0.05
0.40	0.40	5.00	0.50	4.15227	2.30	0.05
0.30	0.50	6.25	0.62	4.15327	2.60	0.07
0.20	0.60	7.50	0.75	4.15648	2.06	0.61
0.10	0.70	8.75	0.87	4.15961	1.20	1.07
0.00	0.80	10.00	1.00	4.16273	0.00	0.00

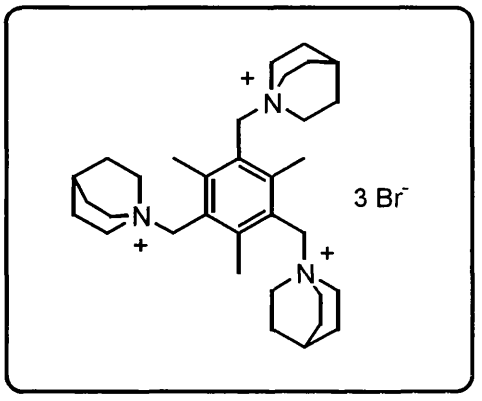
Cation Methyl proton shift (average of 2 runs)

X / mL	Y / mL	$[45]_{tot}$ / mM	Mf of 45	δ	[45•99] / mM	Error / mM
0.80	0.00	10.00	1.00	2.49548	0.00	0.00
0.70	0.10	8.75	0.88	2.49280	0.09	0.01
0.60	0.20	7.50	0.75	2.49074	0.14	0.01
0.50	0.30	6.25	0.63	2.48897	0.16	0.00
0.40	0.40	5.00	0.50	2.48981	0.11	0.00
0.30	0.50	3.75	0.38	2.48849	0.11	0.00
0.20	0.60	2.50	0.25	2.49035	0.05	0.02
0.10	0.70	1.25	0.13	2.49625	0.00	0.00

Cation Benzyl proton shift (average of 2 runs)

X / mL	Y / mL	$[45]_{tot}$ / mM	Mf of 45	δ	[45•99] / mM	Error / mM
0.80	0.00	10.00	1.00	4.61066	0.00	0.00
0.70	0.10	8.75	0.88	4.60865	2.65	0.61
0.60	0.20	7.50	0.75	4.60704	4.08	0.06
0.50	0.30	6.25	0.63	4.60633	4.07	0.39
0.40	0.40	5.00	0.50	4.60783	2.13	0.16
0.30	0.50	3.75	0.38	4.60832	1.32	0.00
0.20	0.60	2.50	0.25	4.61258	-0.72	0.55
0.10	0.70	1.25	0.13	4.61500	-0.82	0.76

A.46 2,4,6-Tris(quinuclidine-N-methyl)-1,3,5-trimethylbenzene tribromide and trisodium DL-isocitrate



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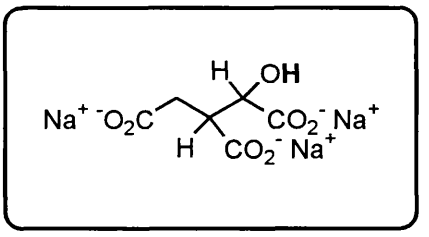


98

NMR Titration

	45 / g	98 / g	D_2O / mL	[45] / mM	[98] / mM
Solution X	0.3663	0.0308	10	50.01	9.99
Solution Y	0	0.0771	25	0.00	10.00

Anion proton shift (average of 3 runs)

X / mL	Y / mL	[45] / mM	[98] / mM	Ratio (45:98)	δ	Δδ	Error
0.80	0.00	50.01	9.99	5.01	3.83499	0.02442	0.00189
0.40	0.40	25.00	9.99	2.50	3.83612	0.02329	0.00037
0.30	0.50	18.75	9.99	1.88	3.83740	0.02201	0.00054
0.20	0.60	12.50	10.00	1.25	3.84186	0.01754	0.00154
0.15	0.65	9.38	10.00	0.94	3.84591	0.01350	0.00267
0.10	0.70	6.25	10.00	0.63	3.84923	0.01017	0.00353
0.05	0.75	3.13	10.00	0.31	3.85222	0.00719	0.00225
0.00	0.80	0.00	10.00	0.00	3.85941	0.00000	0.00162

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	[45] / mM	[98] / mM	Ratio (98:45)	δ	Δδ	Error
Cation reference		10.00	0.00	0.00	4.60681	0.00000	0.00082
0.80	0.00	50.01	9.99	0.20	4.61776	0.01094	0.00145
0.40	0.40	25.00	9.99	0.40	4.61167	0.00486	0.00051
0.30	0.50	18.75	9.99	0.53	4.61058	0.00376	0.00027
0.20	0.60	12.50	10.00	0.80	4.61128	0.00446	0.00143
0.15	0.65	9.38	10.00	1.07	4.61286	0.00605	0.00235
0.10	0.70	6.25	10.00	1.60	4.61430	0.00749	0.00315
0.05	0.75	3.13	10.00	3.20	4.61682	0.01000	0.00199

Job Plot

	45 / g	98 / g	D_2O / mL	[45] / mM	[98] / mM
Solution X	0.1099	0.0000	15	10.00	0.00
Solution Y	0.0000	0.0771	25	0.00	10.00

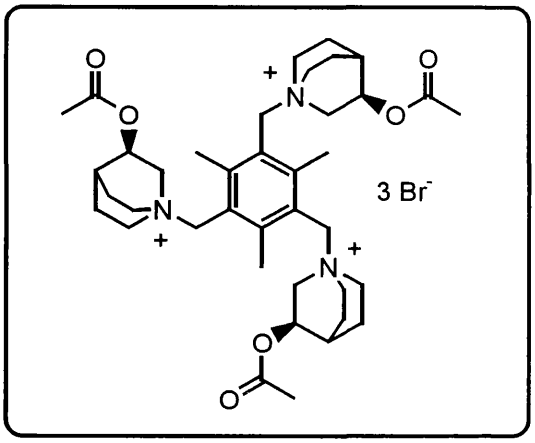
Anion proton shift (average of 3 runs)

X / mL	Y / mL	$[98]_{tot}$ / mM	Mf of 98	δ	[45•98] / mM	Error / mM
0.70	0.10	1.25	0.12	3.82000	1.94	0.01
0.60	0.20	2.50	0.25	3.83840	1.93	0.57
0.50	0.30	3.75	0.37	3.83939	2.74	0.37
0.40	0.40	5.00	0.50	3.84241	3.01	0.33
0.30	0.50	6.25	0.62	3.84578	2.88	0.22
0.20	0.60	7.50	0.75	3.84896	2.45	0.12
0.10	0.70	8.75	0.87	3.85247	1.56	0.06
0.00	0.80	10.00	1.00	3.85669	0.00	0.00

Cation Benzyl proton shift (average of 3 runs)

X / mL	Y / mL	$[45]_{tot}$ / mM	Mf of 45	δ	[45•98] / mM	Error / mM
0.80	0.00	10.00	1.00	4.60681	0.00	0.00
0.70	0.10	8.75	0.88	4.60880	1.71	2.86
0.60	0.20	7.50	0.75	4.60953	2.00	2.17
0.50	0.30	6.25	0.63	4.60969	1.77	0.81
0.40	0.40	5.00	0.50	4.61083	1.97	0.38
0.30	0.50	3.75	0.38	4.61268	2.16	0.10
0.20	0.60	2.50	0.25	4.61579	2.20	0.29
0.10	0.70	1.25	0.13	4.61700	1.25	0.00

A.47 2,4,6-Tris((R)-(+)-3-acetoxyquinuclidine-N-methyl)-1,3,5-trimethylbenzene tribromide and disodium D-malate



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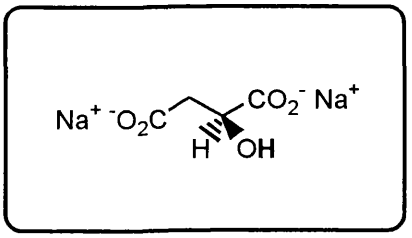


100

NMR Titration

	46 / g	100 / g	D_2O / mL	[46] / mM	[100] / mM
Solution X	0.2269	0.0114	5	50.04	11.63
Solution Y	0	0.0203	10	0.00	10.35

Anion proton shift (average of 2 runs)

X / mL	Y / mL	[46] / mM	[100] / mM	Ratio (46:100)	δ	Δδ	Error
0.80	0.00	50.04	11.63	4.30	4.12681	0.02995	0.00753
0.40	0.40	25.02	10.99	2.28	4.13788	0.01888	0.00973
0.30	0.50	18.77	10.83	1.73	4.13830	0.01845	0.00699
0.20	0.60	12.51	10.67	1.17	4.14233	0.01443	0.00774
0.15	0.65	9.38	10.59	0.89	4.14476	0.01200	0.00621
0.10	0.70	6.26	10.51	0.60	4.14831	0.00845	0.00799
0.05	0.75	3.13	10.43	0.30	4.15128	0.00548	0.00624
0.00	0.80	0.00	10.35	0.00	4.15676	0.00000	0.00773

Cation Benzyl proton shift (average of 2 runs)

X / mL	Y / mL	[46] / mM	[100] / mM	Ratio (100:46)	δ	Δδ	Error
Cation reference		10.02	0.00	0.00	4.87590	0.00000	0.00794
0.80	0.00	50.04	11.63	0.23	4.88040	0.00450	0.00791
0.40	0.40	25.02	10.99	0.44	4.87775	0.00185	0.00716
0.30	0.50	18.77	10.83	0.58	4.87741	0.00151	0.00696
0.20	0.60	12.51	10.67	0.85	4.87605	0.00015	0.00820
0.15	0.65	9.38	10.59	1.13	4.87619	0.00029	0.00611
0.10	0.70	6.26	10.51	1.68	4.87727	0.00137	0.00807
0.05	0.75	3.13	10.43	3.34	4.87571	0.00019	0.00802

Job Plot

	46 / g	100 / g	D_2O / mL	[46] / mM	[100] / mM
Solution X	0.0908	0.0000	10	10.02	0.00
Solution Y	0.0000	0.0203	10	0.00	10.35

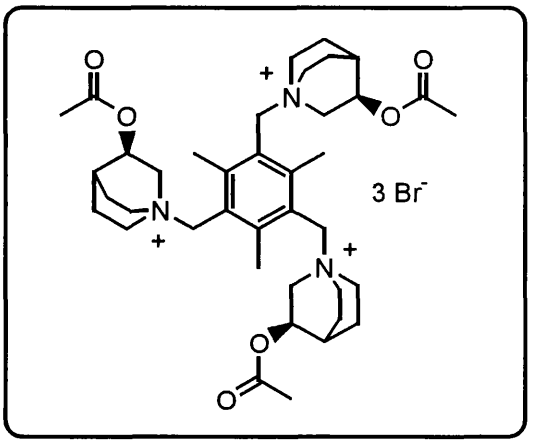
Anion proton shift (average of 2 runs)

X / mL	Y / mL	$[100]_{tot}$ / mM	Mf of 100	δ	[46•100] / mM	Error / mM
0.70	0.10	1.33	0.13	4.14136	0.48	0.09
0.60	0.20	2.65	0.26	4.14288	0.86	0.12
0.50	0.30	3.96	0.38	4.14255	1.31	0.08
0.40	0.40	5.26	0.51	4.14478	1.47	0.05
0.30	0.50	6.55	0.63	4.14982	1.09	0.36
0.20	0.60	7.83	0.76	4.15127	1.04	0.05
0.10	0.70	9.10	0.88	4.15466	0.51	0.34
0.00	0.80	10.35	1.00	4.15715	0.00	0.00

Cation Benzyl proton shift (average of 2 runs)

X / mL	Y / mL	$[46]_{tot}$ / mM	Mf of 46	δ	[46•100] / mM	Error / mM
0.80	0.00	10.02	1.00	4.87590	0.00	0.00
0.70	0.10	8.73	0.87	4.87483	1.35	0.89
0.60	0.20	7.45	0.74	4.87398	2.07	0.03
0.50	0.30	6.18	0.62	4.87394	1.75	1.45
0.40	0.40	4.92	0.49	4.87395	1.39	0.68
0.30	0.50	3.68	0.37	4.87670	-0.43	0.33
0.20	0.60	2.44	0.24	4.87617	-0.10	0.22
0.10	0.70	1.22	0.12	4.87618	-0.05	0.12

A.48 2,4,6-Tris((R)-(+)-3-acetoxyquinuclidine-N-methyl)-1,3,5-trimethylbenzene tribromide and disodium L-malate



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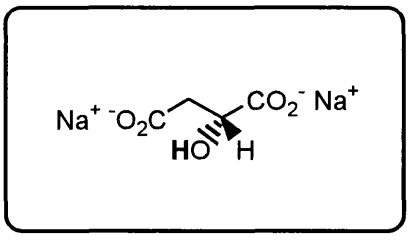

101

NMR Titration

	46 / g	101 / g	D_2O / mL	[46] / mM	[101] / mM
Solution X	0.2267	0.0098	5	50.01	9.95
Solution Y	0	0.0199	10	0.00	10.15

Anion proton shift (average of 2 runs)

X / mL	Y / mL	[46] / mM	[101] / mM	Ratio (46:101)	δ	Δδ	Error
0.80	0.00	50.01	9.95	5.03	4.12702	0.02922	0.00661
0.40	0.40	25.00	10.05	2.49	4.13448	0.02176	0.00739
0.30	0.50	18.75	10.07	1.86	4.13848	0.01776	0.00687
0.20	0.60	12.50	10.10	1.24	4.14127	0.01497	0.00700
0.15	0.65	9.38	10.11	0.93	4.14539	0.01084	0.00737
0.10	0.70	6.25	10.12	0.62	4.14644	0.00980	0.00705
0.05	0.75	3.13	10.14	0.31	4.15211	0.00413	0.00731
0.00	0.80	0.00	10.15	0.00	4.15624	0.00000	0.00699

Cation Benzyl proton shift (average of 2 runs)

X / mL	Y / mL	[46] / mM	[101] / mM	Ratio (101:46)	δ	Δδ	Error
Cation reference		10.01	0.00	0.00	4.87471	0.00000	0.00814
0.80	0.00	50.01	9.95	0.20	4.88182	0.00710	0.00753
0.40	0.40	25.00	10.05	0.40	4.87751	0.00280	0.00843
0.30	0.50	18.75	10.07	0.54	4.87736	0.00264	0.00778
0.20	0.60	12.50	10.10	0.81	4.87477	0.00005	0.00730
0.15	0.65	9.38	10.11	1.08	4.87592	0.00121	0.00770
0.10	0.70	6.25	10.12	1.62	4.87490	0.00019	0.00803
0.05	0.75	3.13	10.14	3.24	4.87304	0.00167	0.01363

Job Plot

	46 / g	101 / g	D_2O / mL	[46] / mM	[101] / mM
Solution X	0.0908	0.0000	10	10.01	0.00
Solution Y	0.0000	0.0199	10	0.00	10.12

Anion proton shift (average of 2 runs)

X / mL	Y / mL	$[101]_{tot}$ / mM	Mf of 101	δ	[46•101] / mM	Error / mM
0.70	0.10	1.28	0.13	4.14146	0.43	0.10
0.60	0.20	2.55	0.25	4.14181	0.84	0.16
0.50	0.30	3.82	0.38	4.14259	1.18	0.50
0.40	0.40	5.09	0.50	4.14368	1.42	0.01
0.30	0.50	6.35	0.63	4.14954	0.81	0.28
0.20	0.60	7.61	0.75	4.15028	0.82	0.19
0.10	0.70	8.87	0.88	4.15209	0.54	0.19
0.00	0.80	10.12	1.00	4.15441	0.00	0.00

Cation Benzyl proton shift (average of 2 runs)

X / mL	Y / mL	$[46]_{tot}$ / mM	Mf of 46	δ	[46•101] / mM	Error / mM
0.80	0.00	10.01	1.00	4.87471	0.00	0.00
0.70	0.10	8.75	0.87	4.87522	-0.51	0.33
0.60	0.20	7.49	0.75	4.87383	0.76	0.18
0.50	0.30	6.23	0.62	4.87609	-0.99	0.17
0.40	0.40	4.98	0.50	4.87241	1.32	0.40
0.30	0.50	3.73	0.37	4.87481	-0.04	0.03
0.20	0.60	2.48	0.25	4.87700	-0.65	0.57
0.10	0.70	1.24	0.12	4.87800	-0.47	0.29