# Supramolecular Chemistry at the Polymer-Oil Interface



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This dissertation is submitted for the degree of Doctor of Philosophy.

#### Declaration

This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the Preface and specified in the text.

It is not substantially the same as any that I have submitted, or, is being concurrently submitted for a degree or diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text. I further state that no substantial part of my dissertation has already been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text

It does not exceed the prescribed word limit for the relevant Degree Committee.

Christopher Leslie Truscott

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#### Abstract

The movement away from metals towards polymers for automobile bearing coatings opens a new area for the possible modification of these coatings. This project, done in collaboration with Castrol, was to understand adsorption of small molecules at the surface of these polymers and work towards engineering host-guest interactions at the surface to provide binding of specific molecules.

Initially, the commercial polyamide-imide was characterised via Nuclear Magnetic Resonance (NMR), Infrared (IR) and Ultra-Violet/Visible (UV-Vis) spectroscopies to understand the nature of the functional groups and structures present. This revealed that the imidisation reaction was incomplete so the functionality within the polymer could change and thus alter how molecules interact with it. This reaction was then investigated via IR and NMR spectroscopy and it was shown that the degree of imidisation varied with temperature.

Then the characterised polyamide-imide was used to study the adsorption of alkylphenols, a class of molecules that have structures and functionality like that of common additives used in engine oils. Additionally, the adsorption of water was studied as it is a common contaminant. These two systems were studied via solution depletion isotherms and neutron reflectivity measurements. The isotherms confirmed the adsorption of the molecules whilst neutron reflection was used to characterise the layers. For alkylphenol, a rather sparsely packed layer of the molecules and solvent existed at the surface with their alkyl tails extending into the solvent. For water; the molecules diffuse into the polyamideimide. It can be partially removed by washing the surface with dry dodecane; however, some water remains in the polymer layer.

A viologen-cucurbit[8]uril binding site was chosen as the supramolecular surface interaction. The binding unit was incorporated into the polyamide-imide. The synthesis of the binding site polymer was achieved in two stages; the reproduction of the commercial polymer and the synthesis of a polymer containing 100% viologen with and without threaded cucurbit[8]uril. Whilst the synthesis appeared successful, neutron reflectivity measurements showed that, when in contact with a solution containing a second guest, no adsorption was seen on the polymer containing cucurbit[8]uril.

In order to study the supramolecular interaction in non-polar solvent, a series of rotaxanes were synthesised with viologen-cucurbit[8]uril cores and bulky stopper groups to prevent unthreading of the cucurbituril as well as enhancing the solubility of the system. The two components were linked via an amidisation reaction between an acid chloride and an amine. Due to the low solubility of the products confirmation of synthesis was only possible in one case.

As well as using a viologen-cucurbit[8]uril binding site, binding in cucurbiturils via halogen bonding was investigated as common halogen bonding species show good solubility in non-polar solvents. Initially co-crystals of 2,5-diiodo-1,3,4,6tetrafluorobenzene with tertiary amides were studied. With N,N-dimethylformamide, a 1:2 co-crystal was seen but the structure with N-methyl-2-pyrrolidone had a stoichiometry of 1:1. In both structures the oxygen of the amide is involved in a halogen bonding; however, for N-methyl-2-pyrrolidone it is bifurcated leading to the formation of chains. A 50-50 mixture of pyridine and formic acid was found to solubilize both halogen bond donors and cucurbit[n]uril. Over the course of these experiments the structure of the co-crystals of two halogen bond donors, 2,5-diiodo-1,3,4,6-tetrafluorobenzene and 2,4,6-triiodo-1,3,5trifluorobenzene, with pyridine were determined. Crystals of the cucurbituriladducts weren't of sufficient quality to determine the structure. The presence of binding solution was confirmed by <sup>1</sup>H and <sup>19</sup>F NMR experiments on the methyliodide-cucurbit[6]uril and trans-diiodooctrafluoroazobenzene-cucurbit[8]uril systems.

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LIST OF SCHEMES

### Chapter 1

### **General Introduction**

#### **1.1** Bearings and Their Surface Science

Bearings are machine components that constrain motion of a part to the desired direction and reduce the friction between the fixed and moving parts of the system. Bearings can be divided up by the type of motion they are involved in: rotary, linear or thrust, and how they are constructed: plain, rolling element, fluid or magnetic. Rotary bearings involve circular motion such as in axles. Linear bearings constrain motion in a single translational direction, such as machine tables and thrust bearings constrain systems with rotary motion and a force in the axial direction, such as a marine propeller axle. In this thesis, we will focus on rotary bearings which are common in automobile engines, and are of interest to our industrial sponsor [1].

The simplest form of the rotary bearing is a plain bearing consisting of a shaft rotating in a hole. A subset of plain bearings is used for watchmaking and other precision systems; the surface of the bearing is an ultrahard, glassy material such as sapphire, which gives them their name: jewel bearings. Rolling-element bearings work by having a rolling element between the moving and stationary parts; these rolling elements can be spheres or cylinders. In some cases, the moving and stationary components can be separated and supported by a fluid, such as in air bearings, or a magnetic field. The schematics of these bearing types are given in the Figure 1.1.



Figure 1.1: Schematics of common bearing designs.

As there is often contact between the moving and stationary elements, friction will affect the efficiency and the lifetime of the bearing. The lubrication of these systems is the subject of significant work in the literature [2–4]. If the fluid film between the two surfaces is thick enough to support the applied load, then the bearing is said to operate in the hydrodynamic regime. As the load increases, the surfaces move closer together, the contact area can elastically deform and lubrication becomes dependent on the ability to form a fluid film. This is called elastohydrodynamic lubrication. If the load increases further, surface asperities are brought into contact with each other and the friction is determined by the direct interaction of the two surfaces. This is boundary lubrication.

The transition between these regimes can be seen if the friction coefficient is plotted as a function of Hersey number (Equation 1.1).

Hersey Number = 
$$\frac{\eta N}{P}$$
 (1.1)

Where  $\eta$  is the fluid viscosity, N is the speed and P is the applied load. These graphs are called Stribeck or Stribeck-Hersey Curves [5]. A Stribeck curve is illustrated in Figure 1.2. At low Hersey numbers the boundary lubrication dominates as direct surface-surface contact takes place. At high Hersey numbers a large lubricant film thickness is present. This is the hydrodynamic lubrication regime. Between the two there is a mixed region where both factors play a role.

The possibility of boundary lubrication, where there is contact between the



Figure 1.2: A cartoon of the Stribeck curve showing the three lubrication regimes.

asperities of the two substrates, means that the choice of bearing surface is important. The compositions of commercial bearings are often confidential but tend to be two-layer: a hard under-layer to support the load (such as steel or aluminium) and a softer top-layer to reduce the friction and prevent wear [6]. This soft layer can embed potentially damaging particulates broken off by high wear, preventing them from gouging the bearing surfaces. Softer layers can be metallic (bronze or lead alloys) or, more increasingly, organic in nature (graphite/graphite alloys or polymers). These layers can be complex with inorganic particles, such as aluminium or molybdenum disulfide, embedded into the polymeric matrices. These matrices include polytetrafluoroethene (PTFE) or Nylon [7].

The presence and chemistry of films of adsorbed molecules can help to reduce friction and prevent surface wear. So, surface active components are added to lubricants to control boundary film lubrication [8].

In this thesis, we will focus on the case of boundary film lubrication for bearing materials where the nature and construction of the bearing itself and any hydrodynamic effects of the lubricant can be ignored and the focus is on the surface behaviour alone. Initially, two different surfaces were chosen: (i) lead, an older, soft bearing surface material, and (ii) polyamide-imide, a new polymeric material of growing commercial interest. In this way, we intended to capture the key mechanism of action of the two main classes of materials. However, after an extensive series of initial experimental studies (not presented here due to the lack of space), we determined that the lead samples were readily corroded by the additives of interest instead of showing simple surface adsorption. In addition, it became apparent that it was not possible to produce a surface with suitable roughness for neutron reflection (NR), one of our principal methods of analysis. When deposited on usual substrates, such as silicon or sapphire, the metal would de-wet and form separated islands or drops. Hence the focus of the work is the polyamide-imide surface. It was important that the continuous phase used suitably mirrors those seen in commercial situations. For petroleum products, a base oil is used as the continuous phase. These oils are classified into five groups, generally with more refined components in higher groups [9], as outline in Table 1.1.

Group	Manufacture	% Saturates	% sulfur	Viscosity Index
1	Solvent	> 00	> 0.03 80	$90 > W_{\text{insertise}} < 190$
1	Refining	> 90		$> 90 > 0.05  80 \ge VIS$
2	Partial	$\geq 90$	< 0.03	$80 \ge \text{Viscosity} \le 120$
2	Hydrocracking			
9	Full	$\geq 90$	< 0.03	Viscosity $> 120$
5	Hydrocracking			
Δ	S	mthetic oil ma	de of poly-	v-olefins
т	0,	infinetie on ma	ac or poly-c	a olemis.
5 Other oils not covered by the other groups			ther groups.	

Table 1.1: The Base Oil Groups.

After discussions with our commercial colleagues, we decided to use dodecane as the continuous phase in most cases. This is good match for the saturated nature of most of the base oils of interest. It is reasonably straightforward to obtain at reasonable purity. In addition, studies of non-covalent interactions in alkanes are rare, providing some additional novelty to this aspect of our study, as discussed below.

Specific compounds are added to lubricants to help with friction (friction modifiers [8]) and wear (anti-wear additives). The most significant anti-wear additives are zinc dialkyldithiophosphates and zinc dithiophosphates (generally referred to as ZDDPs) [10]. Under the pressure and temperature of tribological contacts, they decompose to form glassy inorganic phosphate sacrificial films on metal components that prevent contact of surface asperities [11]. However, due to increasing pressure on the use of sulphur and damage to catalytic converters, alternatives are much in demand.

Organic friction modifiers have similar structures to surfactants with a hy-

drophobic tail and hydrophilic head group [12]. As a result they tend to partition to the surface where they are believed to act. The hydrophobic tail is often an alkyl backbone, sometimes incorporating alkene groups, alkyl rings and branches. These hydrophobic parts provide solubility in the oil phase. The hydrophilic head group includes polar functional groups like carboxylic acids or phenols. This group is thought to partition to the more polar metal surface due to being partly ionic as well as the presence of hydroxide or other polar groups on the surface.

There are broadly two accepted mechanisms for lubrication by small organic molecule friction modifiers known as the monolayer and thick film models [8]. In the monolayer model, the organic molecules are physically or chemically adsorbed to both of the surfaces that are in contact and the low shear strength derives from the weak van der Waals interaction of the hydrophobic tails on either surface. In the boundary layer regime, these monolayers prevent surfacesurface contacts and so reduce the coefficient of friction [13–15]. The lubrication properties of these layers are dependent on the length of the hydrophobic tail [16] and the functional group of the hydrophilic head [17]. In some cases, the organic layer is shown to be much thicker, 10 — 100s nm [18–21]. These thicker layers are also considered to operate by preventing surface-surface contact in the boundary layer regime.

Larger, high molecular weight polymeric friction modifiers work by this latter mechanism, forming thick layers at the surface. The presence of sufficiently clustered functional groups that strongly adsorb to the surface and a mediumto-high molecular weight are necessary for the formation of this layer [22–25].

A molecular view of damage during boundary lubrication operation is shown in Figure 1.3. A component is adsorbed to the surface. Under shear this layer can be damaged and some of the molecules removed. This leaves gaps in the layer that can be replenished from the molecules in solution or, if not replaced fast enough, may allow harmful compounds to adsorb leading to damage to the surface. The action of these layers is dependent on the strength of their interaction with the surface. This project focuses on understanding and then controlling these interactions.


Figure 1.3: Schematic of damage to an organic layer during boundary lubrication operation.

The interactions between an adsorbate molecule and the surface can be broadly divided into two groups: if the interaction is strong and a chemical bond is formed then the molecule has undergone chemisorption. If the interaction is weak then the molecule has been physisorbed. Chemisorption is common in engine systems as molecules often coordinate to the metal atoms that constitute engineering surfaces, such as the adsorption of fatty acids [26] and amines [27] at iron oxide surfaces

## **1.2** Non-Covalent Interactions

In this work, we will mainly address physisorbed systems as this allows for the replenishment of the surface organic layer, should it be removed. Noncovalent interactions can be used to direct the assembly of molecules and are ideal candidates for mediating the physisorption of molecules at surfaces. The principal non-covalent interactions are now outlined.

#### 1.2.1 Van der Waals Forces

Van der Waals forces are the set of non-covalent interactions that involve dipoles [28]. All molecules interact with other molecules via van der Waals forces. Often thought of as transient dipoles arising from the distribution of electron density in molecules, it is more correctly a quantum mechanical effect that depends on

the dielectric properties of the molecules. Dipoles can be permanent, caused by the distribution of electron density in the covalent bonds of the molecule. The Keesom Force is the interaction between the permanent dipoles of molecules [29], the Debye Force concerns the interaction between a permanent dipole and a transient dipole in another molecule. The interactions between two transient dipoles in separate molecules are known as the London Dispersion Forces [30]. Whilst an individual van der Waals interaction is weak, they are sufficiently universal that they can overcome other stronger, but more specific, non-covalent interactions.

#### 1.2.2 Hydrogen Bonding

Hydrogen bonding is the electrostatic interaction between an area of low-electron density on a hydrogen atom and an electron-rich atom, often oxygen or nitrogen.

The species with the hydrogen is called the donor whilst the part of the molecule it is interacting with is called the acceptor. This is illustrated in Figure 1.4. Hydrogen bonds are broken down into three categories; strong, moderate and weak [31]. A summary of the structural and energetic characteristics for these three groups can be found in Table 1.2.



Figure 1.4: The hydrogen bond between a donor and an acceptor.

Strong hydrogen bonds typically involve electron deficient donors  $(-^+OH)$  or acceptors with excess electrons  $(-O^-)$ ; these interactions are referred to as ionic hydrogen bonds. Moderate hydrogen bonds are formed between neutral donors and acceptors. The majority of hydrogen bonds are in this category and so are referred to as *normal* hydrogen bonds. Weak hydrogen bonding occurs when there is little difference in electronegativity between the donor and hydrogen or when the acceptor is bonding via  $\pi$  electrons.

#### 1.2.3 Halogen Bonding

Halogen bonding is a relatively new non-covalent interaction. This interesting interaction is reported to involve a low electron density region, called a  $\sigma$ -hole, on a halogen (usually bromine or iodine) interacting with an electron-rich ele-

	Strong	Moderate	Weak	
Interaction	Covalent	Mostly	Electrostatic	
Interaction		Electrostatic		
Bond Lengths	$\mathrm{A-H}\approx\mathrm{H}{\cdots}\mathrm{B}$	$A\!-\!H\!<\!H\!\cdots\!B$	$A\!-\!H\ll H\!\cdots\!B$	
H····B $(\mathring{A})$	1.2 - 1.5	1.5 - 2.2	2.2 - 3.2	
A····B $(\mathring{A})$	2.2 - 2.5	2.5 - 3.2	3.2 - 4.0	
Bond Angle (°)	175 - 180	130 - 180	90 - 150	
Bond Energy	14 40	4 15	< 1	
$(\text{kcal mol}^{-1})$	14 - 40	4 - 10	< 4	
Examples	Gas-phase dimers	Acids	Gas-phase dimers	
	with strong acids	Alcohols	with weak acids	
	or strong bases	Phenols	ols or weak bases	
	Acid Salts	Hydrates	Minor Components	
	Proton Sponges	All biological	of 3-center bonds	
	Pseudohydrates	molecules	$C-H\cdots O/N$ bonds	
	HF complexes		$\rm O/N{-}H{\cdots}\pi$ bonds	

Table 1.2: Summary of Strong, Moderate and Weak Hydogen Bonding. Adapted from [31]

ment (such as oxygen, nitrogen, sulfur or halide anions) [32, 33]. The  $\sigma$ -holes are believed to arise due to covalent bonds on polarisable atoms [34] and hence appear for a range of elements. Therefore, halogen bonding is a subset of more general  $\sigma$ -hole bonding, with examples such as the bonding in sulfide structures [34].

Halogen bonding has been used to assemble monolayers on the surface of graphite. The assembly of 1,4-dibromo-2,3,5,6-tetrafluorobenzene and 1,4-dibromo-2,3,5,6-tetrafluorobenzene with 4,4'-bipyridine was observed via monolayer x-ray diffraction and analysed with Density Functional Theory calculations [35–37].

#### 1.2.4 $\pi - \pi$ Interactions

The delocalisation of electrons in  $\pi$ -systems can convey stability to molecules. This delocalisation also generates differences in electron density across a molecule and so a potential electrostatic interaction between the electron-rich parts of one  $\pi$ -system and the electron-poor parts of another [38]; this interaction is called  $\pi$ - $\pi$  stacking. Variations in electron density also allow  $\pi$ -systems to interact with ions; both cation- $\pi$  [39] and anion- $\pi$  [40] interactions have been reported. These  $\pi$ -systems can also act as acceptors for hydrogen bonds and interact with other polar molecules [41].

#### **1.2.5** Hydrophobic Interactions

The formation of aggregates of non-polar molecules in aqueous solvents with the exclusion of water molecules is called the hydrophobic effect [42]. It has been suggested that the presence of solutes causes the organisation of water molecules in order to maximise the inter-water molecule hydrogen bonding. As the solutes aggregate then these constrained water molecules are released and so this is considered an entropic effect. This is outlined in Figure 1.5.



Figure 1.5: A cartoon illustrating the hydrophobic effect.

# **1.3 Host-Guest Interactions**

One application of non-covalent interactions is the formation of multi-molecular complexes. One form of multi-molecular complex is the host-guest complex. Here, one molecule (the guest) is contained within another (the host). The host can have a pre-formed cavity (known as cavitand) or a cavity formed by the

#### 1.3. HOST-GUEST INTERACTIONS

assembly of separate molecules (known as capsules); these systems are shown in Figure 1.6a with an example of a pre-formed cavity complex in Figure 1.6b. The driving forces for complexation are varied with guests bound via non-covalent interactions e.g. hydrogen bonding, halogen bonding. In addition, the hydrophobic effect can be important as ordered, high energy solvent is released from the host's interior [43].



with a pre-formed cavity (top) and a capsule (bottom).

(b) Example of a pre-formed cavity complex - I<sub>2</sub> complexed in cucurbit[6]uril.

Figure 1.6: Two forms of host-guest interactions (a) and an example of a performed cavity complex (b).

#### 1.3.1 Cucurbit[n]uril

The class of host chosen for this work was the pumpkin-shaped synthetic receptor, cucurbit[n]uril. The general reaction scheme for the formation of cucurbit[n]uril from glycoluril (1) and formaldehyde (2) is shown in Scheme 1.1.

In 1905 Behrend *et al* observed the formation of a precipitate from the acidic condensation of glycoluril with an excess of formaldehyde [44]. When dissolved in hot concentrated sulphuric acid, diluted with water, filtered and then re-boiled a crystalline precipitate was formed. It had the formula  $C_{10}H_{11}N_7O_4 \cdot 2H_2O$ .

This work was revisited by Freeman *et al* in 1981 who mangaged to re-create the precipitate observed by Behrend [45]. They determined the crystal structure of the calcium bisulfate complex and observed the cyclic hexamer; cucurbit[6]uril. The rounded shape of the molecule lead them to coin the term cucurbituril from the name for the family containing the pumpkin, cucurbitaceae.



Scheme 1.1: General reaction scheme for the formation of cucurbit[n]uril.

Further homologues of cucurbit[n]uril were discovered in 2000 when Kim isolated cucurbit[5]uril, cucurbit[7]uril and cucurbit[8]uril [46]. Additionally, electrospray ionisation mass spectroscopy revealed the existance of cucurbit[9]uril, cucurbit[10]uril and cucurbit[11]uril; however, they couldn't be isolated.

A patent filed by Day, Arnold and Blanch for the synthesis of cucurbit[n]uril provided evidence via <sup>13</sup>C NMR spectroscopy for the existance of homologues up to n = 13 [47]. The patent principally focused on the effect of the conditions and templating molecules on the ratio of each homologue formed.

Snushall *et al* investigated the synthesis of cucurbit[n]uril and provided evidence, via <sup>13</sup>C NMR spectroscopy, for the existence of homologues up to n = 16 [48]. They isolated cucurbit[10]uril as complex containing cucurbit[5]uril; a new type of supramolecular construct named a gyroscane [49]. Uncomplexed cucurbit[10]uril could be isolated by displacement of the cucurbit[5]uril with a pair of second guests then consecutive removal of those guests by washing [50].

#### 1.3.2 Host-Guest Chemistry of Cucurbit[8]uril

Cucurbit[8]uril has been chosen as the host for this project because, due to the size of its cavity, it can contain two guests [46]. This means that one guest can be used to bind the cucurbit[8]uril to the surface leaving room for a second guest to bind from solution.

#### 1.3. HOST-GUEST INTERACTIONS

The host-guest chemistry of cucurbit[n]uril is dominated by two factors: firstly, interactions with the carbonyl lined portal and secondly, the packing within the cucurbit[n]urils cavity [51]. For the former, this means that cationic guests are favoured over neutral guests and anionic guests tend to be excluded. For the latter, the more closely the volume of the guest and the cavity matches, the stronger the binding as van der Waals forces are maximised; however, if the guest's volume exceeds that of the cavity, the guest cannot bind. A good example of these factors is the binding of primary alkyl ammonium ions in cucurbit[6]uril as shown in Figure 1.7 [52–54]. As the length of the alkyl chain increases the binding constant increases as well. The binding constants peak at butyl and pentyl chains and then decrease as the length of the chain exceeds the length of the cavity.



(a) General structure of a n carbon alkyl ammonium ion.



(b) Variation of binding coefficient with the carbon number for alkyl ammonium ions. Data taken from [52–54].

Figure 1.7: Example of the structures and binding constants for ammonium cation guests in cucurbit[6]uril.

As the size of the cavity in the cucurbit[n]uril increases, the size selectivity for the guest changes. Consider the three isomers of diaminobenzene (*ortho*, *meta* and *para*); for cucurbit[6]uril, only the *para*-isomer is complexed whilst for cucurbit[7]uril all three can be complexed [55]. This change in size is particularly pronounced for cucurbit[8]uril, as the size of the cavity allows the inclusion of two guests.

Two distinct behaviours have been observed for the inclusion of two guests into cucurbit[8]uril: homo- and hetero- dimers [51]. Guests that form homodimers tend to be mono-cationic, such as 4-arylpyridinum cations (Figure 1.8), and are arranged in the cavity to maximise the distance between the two positive charges [56]. For dicationic guests, homodimerization is dependent on the



(a) X-ray Crystal Structure showing the arrangement of two 4-(4-methoxyphenyl)-1-methylpyridinium in cucurbit[8]uril.

(c) The arrangement of two aryl Nmethylpyridiniums in a Cucurbit[8]uril

Figure 1.8: An example of the molecular structure, arrangement and crystal structure of systems that show homodimerisation.

distance between the positive charges. For example, with viologen-based guests homodimerization doesn't occur, but if the viologen is reduced then a homodimer does form. Equally, if the positive charges are suitably far apart, e.g. (E)-diaminostilbene dihydrochloride [57] or the protonated 2,6-bis(4,5-dihydro-1H-imidazol-2-yl)naphthalene [46], homodimerization can occur.

The inclusion of a positively charged guest in the cucurbit[8]uril can allow for the binding of a second, electron-rich guest in the cucurbit[8]uril via a charge transfer interaction. This was first observed for methylviologen and either 2,6dihydroxynaphthalene or 1,4-dihydroxybenzene (two molecules that don't bind with cucurbit[8]uril on their own). The charge transfer interaction was confirmed by the presence of the charge-transfer absorption in the solution UV-Vis spectrum and changes in the <sup>1</sup>H chemical shifts of the aromatic protons of the second guests [58].

#### 1.3.3 Halogen Bonding and Cucurbit[n]urils

Whilst the most common guest binding mechanism is an electrostatic interaction between a cation and the electron-rich carbonyl portal, halogen bonding has also been reported.



Figure 1.9: The crystal structure of the diiodine-cucurbit[6]uril complex. The cucurbit[6]uril has been cut away to better show the diiodine inside. The oxygen at the bottom belongs to a halogen bonded water molecule.

El-Sheshtawy *et al* reported the crystal structures of the complexes of cucurbit[6]uril and molecular dibromine and diiodine. The structure for the diiodine complex can be seen in Figure 1.9. Both dihalogens form one halogen bond with a carbonyl at the top portal and a second with a water molecule at the bottom one. The binding constant for diiodine in aqueous solution was found to be 1.4  $\pm 0.2 \times 10^6$  M<sup>-1</sup> which is high for a neutral, hydrophobic molecule.

Only the dihalogens have been observed as halogen bonded inclusion complexes.

Zhang *et al* observed a halogen bonded exclusion complex: a aryl iodide interacting with a carbonyl of a cucurbit[6]uril. The cucurbit[6]urils form a chain held together by coordination to sodium ions. The complex can be seen in Figure 1.10.

There are several examples of halogen bonding involving the cucubituril's building block, glycoluril. For example, the glycoluril derivative (**3**), shown in Figure 1.11a forms halogen bonded chains via bromine-oxygen contacts between the molecules [59].



Figure 1.10: The crystal structure of the exclusion complex showing the sodium ions holding the cucurbiturils together. The short contact corresponding to the halogen bonding interaction is marked with a black line.

This interaction is shown in Figure 1.11c.

A glycoluril dimer based molecule (4), whose structure is shown in 1.11b, shows similiar bromine-oxygen contacts via the carbonyl of the glycoluril. These contacts form chains of the molecules [60]. These few examples suggest the potential of halogen bonding for guest binding in cucurbit[n]uril. This coupled with the relatively high solubility of halogen bond donors compared with ionic species in non-polar solvents means that halogen donors could be a good choice for guests in these solvents.



(a) A glycoluril based de- (b) A glycoluril dimer based molecole. trivative.



(c) Crystal structure of  ${\bf 3}$  showing the halogen bonds, indicated in black, connecting the molecules. Ester groups have been removed for clarity.



(d) Crystal structure of **4** showing the halogen bonds, indicated in black, connecting the molecules.

Figure 1.11: Examples of halogen bonding involving glycoluril derivatives.

# Chapter 2

# Theory and Experimental Procedures

During this chapter, the experimental procedures and, where necessary, the theory for those techniques used in this project will be set out. The project consisted of diverse, but interlocking, experimental work and so a range of techniques were explored. The characterisation of the commercial polymer required chemical characterisation techniques such as Infrared (IR) Spectroscopy and Nuclear Magnetic Resonance (NMR) Spectroscopy as well as more polymerspecific techniques such as Gel Permeation Chromatography (GPC). Following this, surface physical chemistry techniques such as solution depletion isotherms and neutron reflection were used to characterise the adsorption of alkylphenols and water at the polyamide-imide surface. A mixture of both these groups of techniques was used when the viologen-cucurbit<sup>[8]</sup>uril binding unit was incorporated into a polymer surface and the adsorption of a functionalised polymer was studied. Studies of the viologen-cucurbit[8]uril binding unit in the form of a rotaxane required synthetic characterisation techniques as well as NMR techniques designed for host-guest experiments. Exploring the possibility of halogen bonding as a guest binding mechanism for cucurbiturils had two main experimental directions: (i) solid state structural analysis via single crystal x-ray analysis and (ii) solution state NMR analysis.

#### **General Solubility Testing** 2.1

A known quantity of the molecule or polymer was added to 1 mL of solvent. It was then agitated and allowed to stand. If the solid material was still evident after an hour then the molecule was deemed insoluble. This process is outlined in Figure 2.1.



Figure 2.1: The procedure for testing the general solubility of a molecule or polymer in a solvent.

# 2.2 Fourier Transform Infrared (FT-IR) Spectroscopy

Molecules have characteristic IR absorptions determined by their structure. These absorptions correspond to transitions between vibrational modes of the molecule. The number of vibrational modes is dictated by the number of atoms (N) present: linear molecules have 3N-5 and non-linear molecules have 3N-6. For a vibrational mode to be infrared active, there must be a change in dipole moment during the vibration.

Absorption spectroscopy seeks to determine the wavelength-dependent absorption of a sample. One way to do this is to measure the absorption of monochromatic light, then vary the wavelength to build up a spectrum. FT-IR spectroscopy works by illuminating the sample with a beam containing multiple wavelengths and recording the degree of absorption of this beam. The set of wavelengths is then varied to build up an interferogram. This then undergoes a Fourier Transform to produce the spectrum. This technique has several advantages: a lower signal-to-noise ratio, higher throughput, and higher wavelength resolution.

#### 2.2.1 The FT-IR Spectrometer

A Perkin-Elmer Spectrum 100 spectrometer was used to collect the FT-IR spectra (Figure 2.2b). A multiwavelength beam can be encoded as an interferogram using a modified Michael-Morley Interferometer (marked in Figure 2.2a). A movable mirror allows for wavelength selection. The beam passes through a Jacquinot or J-stop; an aperture that restricts the maximum divergence of the beam to that one comparable with the resolution. The beam can then pass through a wavelength filter, although in these experiments no filter was used. The beam is then transverses the sample environment. The different sample accessories used are discussed in more depth below. A liquid nitrogen-cooled Mercury-Cadmium-Tellerium detector was used to measure the attenuation of the beam by the sample.



(a) Schematic of the IR spectrometer used.



(b) The Perkin-Elmer Spectrum 100 Spectrometer.

Figure 2.2: The IR Spectrometer used.

#### 2.2.2Attenuated Total Reflection (ATR)

For powder samples, a Golden Gate ATR accessory was used to collect their IR spectra. ATR-FTIR spectroscopy is a surface-sensitive technique. If an IR beam is brought into a ATR crystal at a suitable angle, it will undergo total internal reflection at the crystal interfaces and so will be transported along the crystal as shown in Figure 2.3a. When the beam is reflected at an interface, an evanescent wave extends beyond the interface. If a sample is brought into contact with the interface, an absorption spectrum of the sample can be collected.



Figure 2.3: The ATR accessory and its operation.

#### 2.2.3 The Liquid FT-IR Cell

For liquid samples, a Pike liquid cell assembly was used. As outlined in Figure 2.4, a 1 mm PTFE spacer between two  $CaF_2$  windows provides a sample container. The system is sealed via a pair of PTFE gaskets and a syringe plate in a screw-secured container. The sample solution is then added to the cell via a syringe. A cell containing clean solvent was used as a background for IR spectroscopy experiments. When in operation, the cell was washed between samples with clean solvent to prevent cross-contamination between samples.



Figure 2.4: A schematic of the Pike Liquid Cell used.

# 2.2.4 Determination of the Concentration of Water in Dodecane

For the solution depletion isotherm (Section 2.6) of water adsorbing onto the surface of the polyamide-imide powder from dodecane, the concentration of water was determined by IR spectroscopy. The IR spectra of samples with increasing water content in 10 % steps from dry to saturated dodecane were recorded. The water peak absorptions were plotted against concentration to allow an unknown concentration to be determined from a given absorption.

# 2.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear spin angular momentum (known as Nuclear Spin or Spin) is a property possessed by all nuclei. These magnetic dipole moments will interact with an applied magentic field  $(B_0)$ . For a bulk sample, this can be expressed as a bulk magnetisation vector (**M**) which will point along  $B_0$  (the first state in Figure 2.5). The application of radio frequency energy will lead to the bulk magnetisation not being aligned with the applied field any more (the perturbation step in Figure 2.5). This difference in direction of the two vectors leads to torque on **M** and so it precesses about  $B_0$ . The frequency of the precession is given by  $\omega_0 = \gamma B_0$  in rad  $s^{-1}$ , where  $\gamma$  is the gyromagnetic ratio, an isotope specific quantity. This precession can be measured by the induction of a current in radiofrequency coil in the xy-plane. If the perturbating frequency is turned off, the current induced by the precession of **M** will decay as it returns to its equilibrium position. This is called free induction decay (FID). The Fourier Transform of this signal gives the NMR spectrum.



Figure 2.5: Alignment of the bulk magnetisation (**M**) with the applied magnetic field  $(B_0)$ , perturbation by a radio frequency pulse, then precession of **M** about  $B_0$  and relaxation back to the equilibrium position.

The relaxation of the bulk magnetisation to the equilibrium position principally occurs via two mechanisms: (i) spin-lattice and (ii) spin-spin relaxation. During spin-lattice relaxation energy is exchanged with the surroundings whilst in spinspin relaxation energy is exchanged with other nuclear spins.

#### 2.3.1 Two-Dimensional NMR Spectroscopy

By varying the radio frequency pulse sequence it is possible to measure the interaction between nuclei. FIDs have a time scale that depends on the their decay; in addition, it is possible to produce a synthetic timescale by varying the delay between pulses. This gives a second dimension to spectra. A general scheme for a 2D NMR experiment is shown in Figure 2.6. There is a period where the magnetisation of the sample is prepared. The sample is then given a period of evolution  $(t_1)$  then the state to be measured is prepared (mixing). The FID signal is then measured over  $t_2$ . The 2D NMR techniques used in this project are outlined below.



Figure 2.6: The general scheme of a 2D NMR experiment showing the preparation, evolution, mixing and FID stages.

#### Correlation Spectroscopy (COSY)

The COSY experiment is a homonuclear experiment that allows the identification of spins that are scalar coupled. This allows for the tracing of the coupling network of a molecule. A schematic of the pulse sequence used is shown in Figure 2.7. The experiment works by rotating one spin and then letting the magnetisation evolve under the offset of spin one and any coupling it is involved in over  $t_1$ . The resulting magnetisation is tested again by rotation and collection of the FID.

#### Heteronuclear Single-Quantum Correlation (HSQC)

A HSQC experiment records the one-bond correlations between two different elements. The experimental pulse sequence is outlined in Figure 2.8. An antiphase state is set-up for spin 1. It is then transferred to spin 2 and the state of



Figure 2.7: Schematic of the pulse sequence used for a typical COSY experiment.





Figure 2.8: Schematic of the pulse sequence for a HSQC experiment. Filled and unfilled boxes represent rotations of 90  $^{\circ}$  and 180  $^{\circ}$  respectively.

#### Heteronuclear Multiple-Bond Correlation (HMBC)

Like a HSQC experiment, HMBC experiments show through bond correlations between NMR-active nuclei; however, they are longer range (greater than a bond) correlations. In order to see these longer range correlations the short range, single bond couplings need to be suppressed and this can be done via a modified HSQC pulse sequence as shown in Figure 2.9. A correctly sized time delay ( $\tau_1$ ) following a pulse for the first spin will give rise to anti-phase magnetisation for one bond coupled systems. This is then converted to multiplequantum coherence by a 90 ° pulse for spin 2. Once the FID is collected for this experiment, the pulse sequence is repeated with, after  $\tau_1$ , the pulse for spin 2 rotated in the opposite direction. When these two experiments are summed, the single bond correlations cancel out and they are removed from the resulting spectrum.



Figure 2.9: Schematic of the pulse sequence for a HMBC experiment. Filled and unfilled boxes represent rotations of 90  $^{\circ}$  and 180  $^{\circ}$  respectively.

#### 2.3.2 Sample Preparation for NMR Experiments

Solution NMR samples were prepared by dissolving the sample in 0.75 to 1 mL of deuterated solvent. The solutions were then pipetted into a quartz 8 inch 5mm borosilicate glass tube (Wilmad 528 PP). A list of the solvents used can be seen in Table 2.1.

Table 2.1: Manufacturer, purity and method of determination.

Solvent	Manufacturer	Purity / %	Method
DMSO	Sigma Aldrich	99.9	MS
$D_2O$	Sigma Aldrich	99.9	MS

#### 2.3.3 The NMR Instruments

The spectra were collected by the NMR service at the Department of Chemistry at the University of Cambridge.  $^{1}$ H and  $^{13}$ C spectra was collected on a 500 MHz

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DCH Cryoprobe spectrometer.  $^{19}{\rm F}$  spectra was collected using a 400 MHz QNP Cryoprobe spectrometer.

# 2.4 Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography is a form of size exclusion chromatography. For polymers, the hydrodynamic radius of the polymer in solution  $(R_{hyd})$  can be related to the number of repeat units (N) present and so its molecular weight.

$$\frac{1}{R_{hyd}} = \frac{1}{N^2} \langle \sum_{i \neq j} \frac{1}{r_{ij}} \rangle \tag{2.1}$$

For GPC the stationary phase used is a gel with a distribution of different pore sizes as shown in Figure 2.10. The polymer sample is added at t = 0 followed by a constant pressure of clean solvent. The polymers' motion through the column is slowed by adsorption into the pores of the gel. Smaller polymers can fit into



Figure 2.10: A schematic of a GPC experiment.

more pores and so move slowly than larger polymers (as shown in Figure 2.10). Large polymers will be expelled quickly. The time period this occurs over is determined by the polydispersity of the polymer. If the exclusion time of a polymer of known molecular weight is known then the molecular weight of an unknown polymer can be estimated.

#### 2.4.1The Gel Permeation Chromatograph

The instrument consisted of a Varian PLgel 5  $\mu$  Mixed-C column connected in series with a Shimadzu SPDM20A prominence diode array detector, Wyatt Optilab DSP interferometric refractometer, and a Wyatt Dawn DSP laser photometer. The instrument was based in the Melville Laboratory for Polymer Synthesis in the Department of Chemistry at the University of Cambridge. The moving phase used was a Lithium Chloride solution in Dimethylformamide. Polymer exiting the column was detected by UV-Vis spectroscopy. The molecular weight was determined via calibration with polystyrene.

#### 2.5Brunauer-Emmett-Teller (BET) Analysis

To determine the surface area of the powders used in solution depletion isotherms BET surface area analysis was used. This analysis involves measuring the adsorption of a gas of a known molecular area (usually nitrogen). An outline of BET theory can be found in section 2.6.2.

In surface area analysis, the powder sample is purged and degassed to remove contaminant adsorbates such as carbon dioxide and water. The sample is then cooled, under vacuum, to cryogenic temperatures. Then, a known volume of gas is added to the sample and a measurement of the equilibrium pressure allows for the amount adsorbed to be measured. If the gas only adsorbs as a monolayer then a Langmuir analysis can be applied, if the gas forms multilayers then BET analysis is used to calculate the amount adsorbed that corresponds to a monolayer. As the molecular area of the adsorbate is known then the surface area of powder can be calculated. If the analysis is continued and the gas condenses into the pores of the material, it is possible to fit a pore distribution to the adsorption and desorption curves.

#### 2.5.1 The BET Instrument

BET analysis of the polyamide-imide powders was conducted by Dr Zlatko Saracevic (Department of Chemical Engineering and Bio-technology, University of Cambridge) using a micromeritics Tristar 3000 (The Cambridge Centre for Medical Materials, University of Cambridge). The analysis was done using nitrogen.

## 2.6 Solution Depletion Isotherms

Solution depletion isotherms give information on the amount and nature of interaction between an additive and the substrate. Starting with a known concentration of the additive in solution ([Additive]<sub>Start</sub>), a mass of substrate is added and the two mixed until equilibrium is reached. The solid is separated via centrifugation or filtration, the supernaturant is removed and the concentration of additive, ([Additive]<sub>Final</sub>), is determined by a spectroscopic technique. This methodology is outlined in Figure 2.11.

It is assumed that any change in concentration is due to adsorption of the additive on the surface of the substrate. This assumption is valid whilst the surface area of the substrate present is greater than the surface area of the sample container. The sample container had a surface area of 0.01 m<sup>2</sup> and a typical substrate surface area was 4 m<sup>2</sup>; so the container corresponds to 0.26 % of the total surface area present.

The number of the moles of additive on the surface can be calculated from these concentrations.

Surface Moles = 
$$([Additive]_{Start} - [Additive]_{Final}) \times V_{Solution}$$
 (2.2)

The value for the surface moles is more typically given in terms of molecules per  $m^2$  so an average area per molecule can be determined.

#### Procedure for Solution Depletion Isotherms with Polyamide-imide Powder

A stock solution of the additive in dodecane was produced. The stock solution was diluted with dodecane to make a series of concentrations covering the range



Figure 2.11: Methodology for room temperature solution depletion isotherms.

of the isotherm, each was a volume of 8 mL. Polyamide-imide powder was added to each sample and the mixture was shaken for 16 hours. The powder was then separated by centrifuging at 10000 rpm for 20 minutes. The supernaturant was removed and the concentration determined via a spectroscopic technique.

#### 2.6.1 Inert Atmosphere Solution Depletion Isotherms

In the case of water, the possibility of atmospheric water affecting the concentration of water in dodecane meant that the isotherms and water solutions were conducted under a nitrogen atmosphere. The polyamide-imide powder was equilibriated under a nitrogen flow. The water solutions were produced directly under nitrogen. The solution was then added to the powder and stirred, via a magentic stirrer, for 2 hours until equilibrium was reached. A sample for IR spectroscopy was extracted via syringe and filter. A IR liquid cell (shown in 2.2.3) was used to collect the IR spectrum.

#### 2.6.2 Isotherm Models

#### The Langmuir Adsorption Model

The adsorption model proposed by Langmuir [61–63] is based on the following assumptions:

- The surface is homogeneous and can be divided into a set of equivalent sites.
- Molecules are immobile once adsorbed.
- Each surface site can only contain one molecule.
- There are no interactions between adsorbed molecules.

The underlying reaction is summarised in equation 2.3. A chemical reaction between a free adsorbate  $(A_{\rm free})$  and an empty surface site (S) yields an adsorbed molecule  $(A_{\rm abs})$ . This reaction has the equilibrium constant  $K_{\rm eq}$ 

$$A_{\rm free} + S \stackrel{K_{\rm eq}}{=} A_{\rm ads}$$
 (2.3)

By defining the fraction of surface sites as  $\Theta_A = \frac{[A_{ads}]}{[S_0]}$  and the partial pressure of free A over the surface as  $p_A$  the Langmuir Adsorption Isotherm can be derived.

$$\Theta_{\rm A} = \frac{\rm K_{eq} p_{\rm A}}{1 + \rm K_{eq} p_{\rm A}}$$
(2.4)

A set of Langmuir isotherms can be seen in Figure 2.12. The general shape of the isotherm is a curve up to a plateau, at which the surface is saturated. The rate of saturation reflects the size of  $K_{eq}$ . Large values of  $K_{eq}$  saturate quickly reflecting a strong thermodynamic driving force for adsorption, whilst small values of  $K_{eq}$  saturate more slowly.



Figure 2.12: Langmuir Isotherms for different values of  $K_{eq}$ .

#### The Brunauer-Emmett-Teller Isotherm

Outlined by Brunauer, Emmett and Teller in 1938, BET theory deals with the adsorption of multilayers at surfaces [64]. BET theory builds on the fundamen-

tals outlined by Langmuir. It has the following assumptions:

- Molecules adsorb in layers infinitally on the surface.
- There are no interactions between adsorbed layers.
- Langmuir theory can be applied to the adsorption of each layer.

The total volume adsorbed,  $V_{total}$ , can be calculated using: (i) volume of a full monolayer,  $V_M$ ; (ii) the equilibrium pressure of gas in contact with the surface, P and (iii) the saturation pressure of adsorbate,  $P_0$ . A constant, c, is particular to each adsorbate and represents the energetics of adsorption.

$$V_{total} = \frac{V_M c(\frac{P}{P_0})}{(1 - (\frac{P}{P_0}))(1 + (c - 1)(\frac{P}{P_0}))}$$
(2.5)

This constant is related to  $\Delta H_{ads}$ , the adsorbate-surface interactions, and  $\Delta H_{liq}$ , the adsorbate-adsorbate interactions.

$$c = \exp(\frac{\Delta H_{ads} - \Delta H_{liq}}{RT})$$
(2.6)

Three versions of the BET isotherm can be seen in Figure 2.13 with three adsorption energies;  $E_{ads}$ ,  $2E_{ads}$  and  $3E_{ads}$ . The volume corresponding to a monolayer (V<sub>m</sub>) is marked on the graph. In all cases the adsorption continues beyond a single monolayer; however, the speed of monolayer formation depends on the adsorption energy. High energy means fast saturation, whilst low energy means slow saturation.

#### 2.6.3 Concentration Determination Methods

#### The Beer-Lambert Law

This law describes how absorbance varies with the thickness and concentration of the sample. The combined Beer-Lambert law fuses Beer's Law, that absorbance is proportional to the concentration of the sample (c), and Lambert's Law, that absorbance is proportional to the thickness, l, of the sample. The combined law is shown below.

$$A = \epsilon lc \tag{2.7}$$

where  $\epsilon$  is the molar extinction coefficient.



Figure 2.13: Three BET isotherms with  $E_{ads}$  (black),  $2E_{ads}$  (blue) and  $3E_{ads}$  (red). The dashed line indicates the volume of one monolayer.

# 2.7 Ultraviolet-Visible (UV-Vis) Spectroscopy

A Ultraviolet-Visible spectrum reflects the absorption of energy for transitions between electronic energy levels of a molecule. The transitions are between filled bonding or non-bonding orbitals, and unfilled non-bonding or anti-bonding orbitals.

#### 2.7.1 The UV-Vis Spectrometer

A Perkin-Elmer Lambda 25 spectrometer was used to measure UV-Vis spectra. The optical set-up of the spectrometer is shown in Figure 2.14. The instrument uses two lamps: a halogen lamp for the visible spectral range, and a deuterium lamp for the UV spectral range. When operating in the visible range, a mirror reflects the halogen lamp into the source mirror. When operating in the UV range it is rotated to allow light from the deuterium lamp into the source mirror. After the source mirror the beam is pre-filtered via a filter wheel to prepare for monochromation. The filter changes via rotation to alter the wavelengths filtered during operation. There is a slit prior to the monochromator to cut down the beam width.



Figure 2.14: The optics set-up used in the Perkin-Elmer Lambda 25 Spectrometer.

Monochromation is achieved via a holographic concave grating with 1053 lines/mm in the centre. To select the desired wavelength, the monochromator is rotated so that the wavelength is reflected through the exit slit. This slit limits the beam to be near-monochromatic. For the Lambda 25 instrument, the spectral bandpass caused by the monochromator and slit is 1 nm. A spherical mirror focuses the beam onto a beam splitter to produce a sample and reference beam. These two beams are reflected through the sample and reference cells. The beams are then focused onto photodiode detectors via a convex lens.

#### 2.7.2 Polyamide-imide Tumbled Dodecane Background

Polyamide-imide powder (0.5 to 2.5 g in 0.5 intervals) was tumbled overnight in Dodecane (8 mL). The powder was separated by centrifuging for 20 minutes at 10000 rpm. The supernaturant was removed and the UV-Vis spectrum over the wavelength range 200 to 900 nm was recorded using a Perkin Elmer Lambda25 UV-Vis Spectrometer five times.

# 2.7.3 Determination of the Concentration of Alkylphenols in Dodecane

In order to determine the concentration of a solution by UV-Vis spectroscopy, the extinction coefficient was determined by measuring a range of concentrations. A stock solution was made of the additive in dodecane was made then diluted to the desired sample concentration. The UV-Vis spectrum of each sample was collected over a wavelength range of 200 to 900 nm five times on a Perkin Elmer Lambda25 UV-Vis Spectrometer using a 1 cm quartz cell. An average of the five runs was taken. A summary of the additive stock solutions and the sampled concentration ranges can be found in Table 2.2.

Table 2.2: Summary of stock solutions used for UV-Vis spectroscopy calibration.

Additive	Mass	Moles	Volume of	Maximum	Minimum
	Used / g	used	Dodecane / mL	Conc. / M	Conc. / M
Phenol	0.0235	$2.5\times 10^{-4}$	50	$5  imes 10^{-3}$	$1 \times 10^{-5}$
4-Octyl Phenol	0.0516	$2.5 \times 10^{-4}$	50	$5 \times 10^{-3}$	$1 \times 10^{-5}$
4-Nonyl Phenol	0.0551	$2.5\times 10^{-4}$	50	$5 \times 10^{-3}$	$1 \times 10^{-5}$

### 2.8 Neutron Reflection

The modulus of the wave vector (k) and energy (E) of an incident neutron of wavelength  $\lambda$  is given below.

$$k = \frac{2\pi}{\lambda} \tag{2.8} \qquad E = \frac{\hbar}{2m_n}k \tag{2.9}$$

Modulus of the wave vector.

Energy of the neutron.

When a neutron enters a material it will be subject to a potential, V, which comprises the net effect of the interactions between that neutron and any scatterers in the medium. This potential is proportional to the difference in scattering length densities  $(\Delta N_b)$  of the two materials either side of the interface. The scattering length density  $(N_b)$  of a material is a volume-normalised weighted sum of the coherent scattering lengths (b) of the atoms present.

$$V = \frac{h^2}{2\pi m_n} \Delta N_b \qquad (2.10) \qquad \qquad N_b = \frac{\sum_i n_i b_i}{Volume} \qquad (2.11)$$

Scattering Length Density

When the neutron hits an interface only the normal component of the wave vector  $(k_{i\perp})$  is altered by the barrier potential, and it is the normal component of the kinetic energy that determines if the neutron can overcome the barrier.

$$E_{i\perp} = \frac{(hk_i \sin\theta_i)^2}{8\pi^2 m_n} \tag{2.12}$$

If the energy is smaller than the potential then there is total reflection from the surface. When the kinetic energy is equal to the potential it is possible to calculate a critical value of q  $(q_c)$  below which no neutrons pass through the interface and the beam is entirely reflected.

$$E_{i\perp} = V$$

$$\frac{(hk_i \sin\theta_i)^2}{8\pi^2 m_n} = \frac{h^2}{2\pi m_n} \Delta N_b$$

$$2k_i \sin\theta_i = \sqrt{16\pi\Delta N_b}$$
using  $q = 2k_i \sin\theta_i$ 

$$q_c = \sqrt{16\pi\Delta N_b}$$
(2.13)

If the interaction is elastic the momentum is conserved and therefore  $\theta_i = \theta_r$ . This is specular reflection. If the kinetic energy is larger than the potential

#### 2.8. NEUTRON REFLECTION

barrier then the neutron is either reflected or can be transmitted into the bulk of the material. If it is transmitted then  $E_{i\perp}$  is reduced by the potential and so the beam  $(k_t)$  must change direction: it is refracted. This change in the normal wave vector is below.

$$k_{t\perp}^2 = k_{i\perp}^2 - 4\pi N_b \tag{2.14}$$

The refractive index (n) is the ratio of the transmitted and incident beams.

$$n^2 = \frac{k_t^2}{k_i^2} \tag{2.15}$$

A wave vector can be expressed in terms of its perpendicular and parallel components.

$$k^2 = k_{\parallel}^2 + k_{\perp}^2 \tag{2.16}$$

As the potential only varies normal to the surface then the parallel components of the incident and transmitted beams must be the same. This allows for the refractive index to be rewritten in terms of these components.

$$n^{2} = \frac{k_{i\parallel}^{2} + k_{i\perp}^{2} - 4\pi N_{b}}{k_{i}^{2}}$$
$$= 1 - \frac{4\pi N_{b}}{k_{i}^{2}}$$
using  $k_{i}^{2} = \frac{4\pi^{2}}{\lambda^{2}}$  $n^{2} = 1 - \frac{\lambda^{2} N_{b}}{\pi}$  (2.17)

The refractive index also contains a term associated with the absorption properties of the material; however, for this analysis we will assume it is small. The ratio of transmission to the total incident beam is called transmittance (t) and the ratio of reflection to the total incident beam is the reflectance (r). These are the Fresnel Coefficients.

$$t = \frac{2k_{i\perp}}{k_{i\perp} + k_{t\perp}} \qquad (2.18) \qquad \qquad r = \frac{k_{i\perp} - k_{t\perp}}{k_{i\perp} + k_{t\perp}} \qquad (2.19)$$

The reflectivity is the square of the reflectance and is the measured quantity in a reflection experiment. The Fresnel reflectivity is outlined below.

$$R = r^{2} = \left[\frac{q - (q^{2} - q_{c}^{2})^{\frac{1}{2}}}{q + (q^{2} - q_{c}^{2})^{\frac{1}{2}}}\right]^{2}$$
(2.20)

If  $q \gg q_c$  then the simplified reflectivity is shown below.

$$R(q) = \frac{16\pi^2}{q^4} |N_b(q)|^2$$
(2.21)

where  $N_b(q)$  is a function dependent on the variation of the scattering length density in the z-direction.

$$N_b(q) = \int_{-\infty}^{\infty} exp(iqz) \frac{dN_b}{dz} dz$$
(2.22)

For both rough and diffuse surfaces, the system is represented as a smooth transition from one Scattering Length Density  $(N_{b,0})$  to another  $(N_{b,1})$  over a given lengthscale  $(\sigma)$ . This model is shown in Figure 2.15. The effect of this is to reduce the specular reflectivity by a factor which reflects the distance over which the scattering length density varies.

$$R \approx \left(\frac{16\pi^2}{q^4} N_b^2\right) e^{-q_z^2 \sigma^2}$$
(2.23)



Figure 2.15: A rough and a diffuse surface with the respective scattering length density profiles.

For a two interface system composed of three layers (Figure 2.16) with three different refractive indices  $(n_1, n_2 \text{ and } n_3 \text{ and so scattering length densities: } N_{b1}$ ,  $N_{b2}$  and  $N_{b3}$ ) when an incident beam strikes the top interface and providing  $q < q_c$  there are reflected (red) and transmitted (blue) waves formed. This transmitted beam will then strike the lower interface and a second set of reflected and transmitted waves are generated. These reflected waves will constructively or destructively interfere with each other depending on phase difference between them. This phase difference is caused by the path difference which depends on the thickness of the layer, d.



Figure 2.16: Reflection from a two interface system.

Working through the reflectivity calculations it is possible to show that this causes an oscillation in the reflectivity.

$$Rq^{4} = \left[ (N_{b3} - N_{b1})^{2} + (N_{b2} - N_{b2})^{2} + 2(N_{b3} - N_{b1})(N_{b2} - N_{b3})\cos(qd) \right]$$
(2.24)

For an m-layer system, the reflection coefficient for each interface is calculated separately. It starts with the interface between the substrate (mth) and bottom, (m+1)th, layer. Starting with a general expression for the j, j+1 interface below.

$$r_{j,j+1} = \frac{n_j \sin\theta - n_{j+1} \sin\theta_{j+1}}{n_j \sin\theta + n_{j+1} \sin\theta_{j+1}}$$
(2.25)

For the m-1,m interface a phase factor,  $\beta_m$ , is included as a optic path term involving the refractive index  $(n_m)$  and thickness  $(d_m)$  for the mth layer.

$$r_{m-1,m} = \frac{r_{m-1,m} - r_{m,m+1}e^{2i\beta_m}}{r_{m-1,m} + r_{m,m+1}e^{2i\beta_m}}$$

where:

$$\beta_m = \frac{2\pi}{\lambda} n_m d_m \sin\theta$$

In order to generalise to m layers, it is possible to use the matrix method. Starting with the matrix Cm, the sample is then represented by the product of these matrices.

#### 2.8.1 The Sample Cell Set-up

Neutron Reflection experiments were carried out on silicon blocks spin coated with the sample polymer. The silicon wafers used were  $50 \ge 100 \ge 10$  mm blocks (n-type, < 111 > orientation, Crystan).

Prior to spin coating the wafers were cleaned by immersion in concentrated Nitric Acid (ACS Reagent Grade, 70%, Sigma Aldrich) for 2 hours then by washing and immersion in distilled water overnight. The wafers were then dried and cleaned via UV-Ozone exposure for 20 minutes using a UV-Ozone Procleaner (Windsor Scientific) or UVOCS UV-Ozone Cleaning System (ISIS facility, Rutherford-Appleton Laboratary).

The wafers were spin coated using a SCS 6800 Series Spin coater. For spin coating, the polymers were prepared as 5 wt% solutions in dimethylformamide. The spin coating cycles consisted of two stages: first, a short, slow rotation to remove excess solution from the surface then a faster, longer rotation to thin the surface layer to the desired thickness. It was shown, via neutron reflection, that DMF remained in the polymer layer. For later samples, the layer was cured at 100 °C at 1 mbar; no detectable solvent remained in the layer.



Figure 2.17: Schematic of the Neutron Reflection Cell

A schematic of the sample cell used can be seen in Figure 2.17. The polymer coated wafer was placed on top of a polytetrafluoroethylene trough. This was then sandwiched between two steel plates and the trough sealed against the silicon wafer by screws connecting the two plates. A rubber mat between the plate and the wafer distributed the pressure over the crystal evenly. The trough could then be filled via pipette with the sample solution and sealed with a screw fitting and a bung. The sample system was then attached to the instrument via a magnetic mount allowing for easy removal and remounting of the sample
without major adverse effects for the sample's alignment.

The orientation of the cell with respect to the reflectometer can be seen in the insert in Figure 2.19. The neutron beam is brought in through the silicon wafer, reflected at the polymer-liquid interface, and exits back through the silicon wafer.

## 2.8.2 The Neutron Reflectometers

The two neutron reflectometers used in this project were based at the ISIS spallation source at the Rutherford-Appleton Laboratory.

At the ISIS facility,  $H^-$  ions are accelerated in a linear accelerator (the blue line in Figure 2.18). These are then passed into a synchrotron via a gold foil that strips the electrons off the hydride ions to produce a medium-energy proton beam. Once in the synchrotron these protons are accelerated further (the red line). At a frequency of 50 Hz, the beam is diverted to a water-cooled heavy metal target. It is this impact that generates the neutrons for the instruments (the purple line).



Figure 2.18: A Diagram of the Accelerators and Target at the ISIS facility.

#### INTER

INTER is a reflectometer based at the second target station at ISIS [65, 66]. A schematic of the INTER instrument is shown in Figure 2.19. After emerging from the the target, the beam of neutrons passes through a grooved composite  $D_2O$ /methane moderator to maximise the number of long wavelength neutrons present. A guide directs the pulse to the chopper set-up. The first, T<sup>0</sup> chopper, removes high energy neutrons and gamma rays. This chopper defines t = 0 for the time-of-flight measurement. The second counter-rotating chopper defined the wavelength distribution for the instrument. The pulse is then guided to a set of coarse jaws to cut the beamwidth and then a set of slits to produce finer collimation of the beam. A pair of glass scintillator monitors are used to determine the incident wavelength distribution. The beam is then brought into contact with the sample and the reflected beam is detected by a low-background <sup>3</sup>He gas detector.



Figure 2.19: Schematic of the INTER Instrument from moderator to detector.

#### SURF

The SURF instrument is a reflectometer based on Target Station 1 at ISIS [67]. The design of the instrument is very similar to that of INTER. After being produced at the target, the neutrons are passed through a liquid hydrogen

moderator to, again, maximise the number of lower energy neutrons. A nimonic chopper removes high energy neutrons and gamma radiation from the pulse and a double disc chopper selects the wavelength range. Coarse jaws give a degree of collimation before the wavelength distribution is measured by a low efficiency scintillator monitor. A set of slits defines the beam size and it then illuminates the sample. The reflected beam is brought back through a set of slits to minimise the background. The beam is then detected by a  ${}^{3}He$  gas detector.

#### 2.8.3 The Analysis of Neutron Reflectivity Data

The neutron reflectivity profiles generated by these experiments were analysed using RasCAL; a Matlab program written for the analysis of multi-contrast neutron reflectivity experiments (Version 1.1, A. Hughes, ISIS Neutron Source, Rutherford Appleton Laboratory). RasCAL utilises an Abeles Matrix Formalism in which each material in the system is modelled as a slab characterised by its scattering length density, thickness and roughness. The system is then a series of these slabs layered on top of each other. From this, a model reflectivity profile can be calculated. This model is then compared to the experimental data and the parameters systematically changed until the model as closely matches the experimental data as possible. The model is then checked to avoid unphysical systems such as roughness being greater than thickness. Simultaneous fitting of multiple contrasts allows for constraint of the fit [68, 69]. Generally, the model was kept as simple as possible to avoid over-modelling the data. However, in some cases a more complicated SLD model was used based on a gaussian distribution of a component. This continuously changing SLD profile was divided into multiple thin layers with a defined SLD; this process is shown in Figure 2.20.



Figure 2.20: The conversion of a smooth variation in the SLD into a series of thin layers so the system can be modelled.

## 2.9 Single Crystal X-ray Diffraction

Diffraction from a three-dimensional array of atoms is called Bragg Diffraction. Similar to the scattering of waves by a diffraction grating, Bragg Diffraction is the scattering of waves by planes of atoms within the crystal. The condition for constructive interference is given by Bragg's Law.

$$m\lambda = 2dsin(\theta) \tag{2.26}$$

 $\lambda$  is the wavelength of the scattered wave, d is the spacing between atomic planes,  $\theta$  is the angle of the diffracted wave, and m is an integer. Thus, by collecting the pattern of scattered waves as a function of  $\theta$  from a single crystal, it is possible to determine the internal structure of the crystal.

## 2.9.1 The Crystallisation Techniques



(a) Set-up for Slow Evaporation of the (b) Set-up for Non-Solvent Diffusion. Sample.

Figure 2.21: Different Crystallisation Methologies.

Two techniques were used to prepare samples for x-ray diffraction. In all cases, the components were dissolved in the minimum of solvent. The samples were vortexed or sonicated until no more solid could be seen. The first method involved placing the solution in a topless vial inside a larger container with a hole in the top. This allowed for a slow evaporation of the solvent; this set-up is shown in Figure 2.21a. The second method involved the diffusion of a second non-solvent into the sample. Again, the crystallisation mixture was placed in a vial in a larger container; a small amount of non-solvent was added to the larger container and the system was sealed. This set-up is shown in Figure 2.21b.

## 2.9.2 The Single Crystal X-ray Diffractometer

Diffraction patterns were collected and analysed by Dr Andrew Bond at the Department of Chemistry in the University of Cambridge. The diffractometer used was a NONIUS FR590 single crystal X-ray diffractometer and the patterns were collected at 77 K. Further information on the crystal structures can be found in appendices A.1, A.2 and A.3.

## 48 CHAPTER 2. THEORY AND EXPERIMENTAL PROCEDURES

# Chapter 3

# Characterisation of the Commercial Polyamide-imide Polymer

## 3.1 Introduction

The class of commercial polyamide-imide polymer chosen as the baseline polymer is Torlon PAI produced by Solvay Speciality Polymers. Combining thermal stability, good wear resistance with a tolerance of organic solvents makes this polymer an excellent choice for automobile engine bearing applications [70]. The exact formulation of the polyamide-imide is tailored to its specific application (high-strength, resistance to wear etc). Here, we focus on the basic polymaideimide, Torlon LM. The molecular structure of the polymer (5) is shown in Figure 3.1. Further more, there are examples of analysis [71] and applications of Torlon polymers for hollow fibre membranes [72] and nanosilica-polymer composites [73] in the literature.



Figure 3.1: The structure of the repeat unit of polyamide-imide Torlon LM.

In this chapter, we discuss the characteristics of the commercial polymer as well as demonstrating the effect of temperature on the chemistry of the polyamideimide. As outlined in the scheme below, the synthesis of the polyamide-imide has two steps: (i) the condensation of the diamine (6) with the acid anhydride chloride (7) to form a poly amic acid (8) and (ii) the thermally-induced imidisation from 8 to the full polymer 5.



Scheme 3.1: The two stage synthesis of a polyamide-imide: (i) the condensation of the diamine (6) with the acid anhydride chloride (7) to form a poly amic acid (8) and (ii) the thermally induced imidisation from the poly amic acid (8) to the polyamide-imide (5).

## 3.2 Solubility of Torlon LM in Various Solvents

The solvency of Torlon LM was addressed using the method in section 2.1. A good solvent is required as a medium for chemical modification and spin-coating of the polyamide-imide to make a thin film. Additionally, for interfacial studies, the polymer had to be insoluble in the base oil so that it will remain as a well defined surface. Table 3.1 shows the results of dissolution studies of the commercial polymer in various solvents. The table shows that the polymer is essentially insoluble in many solvents, but particularly soluble in DMF and DMSO. This is consistent with examples of Torlon and structurally similar polymers which have been found to be soluble in dimethylsulfoxide [74], dimethylformamide [71, 74, 75] and N-methyl-2-pyrrolidone [72, 73, 76]. The data in the table below also confirmed the insolubility of Torlon LM in dodecane. This will be the solvent used as a model base oil in our surface studies.

	Weight Percentage of Polyamide-imide					
Solvent	$0.1~{\rm wt}~\%$	0.2 wt %	0.5 wt %	$1~{\rm wt}~\%$	$2~{\rm wt}~\%$	
Acetone	Not	Not	Not	Not	Not	
	Soluble	Soluble	Soluble	Soluble	Soluble	
Chloroform	Not	Not	Not	Not	Not	
	Soluble	Soluble	Soluble	Soluble	Soluble	
DMF	Soluble	Soluble	Soluble	Soluble	Soluble	
DMSO	Soluble	Soluble	Soluble	Soluble	Soluble	
Dodecane	Not	Not	Not	Not	Not	
	Soluble	Soluble	Soluble	Soluble	Soluble	
Toluene	Not	Not	Not	Not	Not	
	Soluble	Soluble	Soluble	Soluble	Soluble	
Water	Not	Not	Not	Not	Not	
	Soluble	Soluble	Soluble	Soluble	Soluble	

Table 3.1: Table of Solubilities for Various Solvents

# 3.3 <sup>13</sup>C Solution NMR Spectroscopy of Torlon LM in d<sub>6</sub>-DMSO

The <sup>13</sup>C NMR spectrum was collected to confirm the inclusion of the viologencucurbit[8]uril binding sites on the polymer, indicated by the chemical shift and intensity of the peaks characteristic of the aromatic groups. The spectrum of the commercial Torlon LM in d<sub>6</sub>-DMSO is given in Figure 3.3.

The spectrum shows two regions that relate to the polymer chemical groups: (i) carbonyl carbons (from acids, amides and imides) at 180 ppm to 150 ppm and (ii) aromatic carbons at 150 ppm to 110 ppm. In addition, there is a low shift region that features resonances associated with residual N-methyl-2-pyrrolidone solvent, whose structure is shown in Fig-



Figure 3.2: The structure of N-methyl-2-pyrrolidone.

ure 3.2, from the synthesis of the polymer.



Figure 3.3: <sup>13</sup>C NMR spectrum of **5** in d<sub>6</sub>-DMSO. Peaks resulting from residual **9** are marked with a  $\diamond$ .



Figure 3.4: HSQC spectrum of the polyamide-imide with the corresponding <sup>1</sup>H (above) and <sup>13</sup>C (left) spectra. The peaks corresponding to the hydrogens of the methylene linker ( $\approx 4$  ppm) and residual DMSO ( $\approx 2.5$  ppm) in the <sup>1</sup>H spectrum are highlighted. These signals show a correlation with large peak in the <sup>13</sup>C spectrum at  $\approx 40$  ppm.

The peaks that correspond to the carbon of the methylene linker are not obviously present in the  ${}^{13}$ C spectrum, Figure 3.3. Heteronuclear Single Quantum Correlation Spectroscopy (HSQCS) is a convenient method that allows for cross-referencing proton NMR peaks with the carbon to which they are attached. The spectrum, given in Figure 3.4, shows that the carbon peaks for the methylene carbons are obscured by the larger resonance for the carbon environment in d<sub>6</sub>-DMSO (identifible as a septet at 39 ppm due to coupling to three deuteriums [77, 78]). Further analysis of the methylene region in the <sup>1</sup>H spectrum can be found in 3.4.

Similarly, the peak corresponding to the carbonyl carbon of **9** can be identified by Heteronuclear Multiple-Bond Correlation Spectroscopy (HMBCS). This NMR technique shows through bond correlations between protons and carbons which are further apart. The spectrum is shown in Figure 3.5. The protons associated with **9** (more detailed analysis shown in section 3.4.2) are seen to be correlated with a peak at 174 ppm. Hence this peak was assigned as the carbonyl carbon of **9** (marked in the figure with a line).



Figure 3.5: HMBC spectrum of the polyamide-imide with the corresponding  ${}^{1}\text{H}$  (above) and  ${}^{13}\text{C}$  (left) spectra. The peaks associated with hydrogens on NMP at 1.85, 2.17 and 3.27 ppm in the  ${}^{1}\text{H}$  NMR spectrum show a correlation with a peak in the  ${}^{13}\text{C}$  speatrum at 174 ppm. This allow for assignment of this as the signal corresponding to the carbonyl carbon of NMP.

## 3.4 <sup>1</sup>H Solution NMR Spectroscopy of Torlon LM in d<sub>6</sub>-DMSO

To confirm the reproduction of the polyamide-imide as well as the success of the modifications to include the viologen-cucurbit[8]uril binding site, the <sup>1</sup>H spectrum of the commercial material was collected. The proton spectrum of the commercial polymer can be considered as four broad sections: amide (10.68 to 10.18 ppm), aromatic (8.78 to 6.36 ppm), methylene (4.3 to 3.6 ppm) and solvent resonances (3.5 to 1.5 ppm). The aromatic region contains the resonances associated with the aromatic protons arising from the benzene rings present in the anhydride chloride and dianiline. The methylene region has resonances associated



Figure 3.6: <sup>1</sup>H NMR Spectrum of **5** in  $d_6$ -DMSO and its division into four regions as discussed in the text.

with the three possible methylene environments: Amide-Amide, Amide-Imide

and Imide-Imide [76] (whose structure is shown in Figure 3.8). Lastly, the low shift region contains peaks due to the presence of both N-methyl-2-pyrrolidone [79] (from the synthesis of the polymer) and undeuterated dimethylsulfoxide [77, 78].

We conclude that the features in the methylene region (4.3 to 3.5 ppm) can be used as convenient indicators of the polymer linkages and so quantify the extent of the imidisation reaction.

## 3.4.1 Determination of the Extent of Imidisation

The degree of conversion is the fraction of five-membered imides formed from the possible amide and carboxylic acid combination in **8**. This could be determined by two methods from the <sup>1</sup>H NMR spectrum.

## Comparison of Broad Polyamide-imide Regions in the <sup>1</sup> H NMR Spectrum

The amount of cyclo-imidisation can be calculated by comparing the peak areas of the amide, aromatic and methylene regions seen in the <sup>1</sup>H NMR spectrum. The proton labelling for uncyclised and cyclised repeat units can be seen in Figure 3.7.

If the imide ring is formed, then the ratio of the areas of the amide:aromatic:methylene regions should be 1:11:2 within a repeat unit; if the imide ring has not formed then the ratio should be 2:11:2. In the general case, if x is the fraction of rings formed then the ratio will be:

$$[x + 2(1 - x)] : [11x + 11(1 - x)] : [2x + 2(1 - x)]$$
(3.1)

Which simplifies to:

$$[2-x]:11:2 \tag{3.2}$$

Integrating over the regions of the data shown in Figure 3.6, the experimental ratio was determined to be 1.4:11:1.8; which gives x = 0.6. We can estimate the error in this value from the uncertainty in the methylene peak area. This peak should have a relative area of 2 (due to two protons in this environment in the repeat unit). However, the experimentally measured value was 1.8. This



Figure 3.7: Proton Labelling for amide (red), aromatic (blue) and methylene (purple) for an uncyclised (8) and cyclised (5) repeat unit of the polyamideimide

corresponds to a error of approximately 10%. We can use this value to estimate the error in the amide area (0.14). Therefore, the percentage of cyclised imides is determined to be  $60 \pm 14\%$  in the commercial polymer without thermal treatment.



Figure 3.8: The three basic types of linker and how they can be subdivided using amides and uncyclised imides.

### Analysis of the Methylene Region in the <sup>1</sup>H Spectrum

The analysis of ratio of the methylene linkers was done by taking the area under



(c) A Seven Lorentz Peak Model.

Figure 3.9: Three different methods to determine the area under the methylene peaks.

each of the peaks (divisions are shown in Figure 3.9a). It is clear that this approach does not capture the peak areas very well; particularly due to a spurious peak included in the amideamide area.

To improve upon this a four Lorentz peak model was used. A peak was taken for each of the obvious peaks in the methylene region. The fit is shown in Figure 3.9b. The fit was good ( $R^2 = 0.9766$ ); however, whilst the imide-imide peak was fitted nicely with a Lorentz line shape the other two showed deviations from this lineshape, most notably shouldering consistent with the presence of additional, overlapping peaks.

To avoid over-modelling the system, the number of peaks included was limited to that which was deemed structurally reasonable. This was done by breaking the amide into two forms: amides and uncyclised imides. This meant that the imide-amide peak was broken down into 2 peaks (imideamide and imide-uncyclised imide) and the amide-amide peak could be broken down into 3 peaks (amideamide, amide-uncyclised imide and uncyclised imide-uncyclised imide). These additional peaks improved the fit  $(R^2 = 0.9969)$  as well as providing a better visual fit to the data as shown in Figure 3.9c. The percentages of each linker are shown in Table 3.2.

Table 3.2: The percentages of each linker present calculated using three different methods.

Linkage	% NMR Integration	%4 Peak Model	%7 Peak Model
Imide-Imide	11.76~%	8.22~%	8.94~%
Imide-Amide	34.59~%	33.28~%	33.00~%
Amide-Amide	53.65~%	58.50~%	58.06~%

From these values the total percentage of imides  $(\%_{imides})$  can be calculated.

$$\%_{imide-imide} + \frac{1}{2}\%_{imide-amide} = \%_{imides}$$
(3.3)

At total cyclisation the total percentage of imides should be 50 %. Using x as the degree of cyclisation again, it is possible to work out an expression for x.

$$x = \frac{\%_{Imides}}{50} \tag{3.4}$$

Taking the values for the model with seven peaks, x = 0.51 or 51 %.

## 3.4.2 Weight Percentage of N-methyl-2-pyrrolidone (9)

The commercial polymer contains residual solvent, N-methyl-2-pyrrolidone, from

its synthesis. The amount of solvent can be determined from the proton spectrum. The Nmethyl-2-pyrrolidone peaks were assigned from the literature values [79]. The molecule is shown in Figure 3.10 and the relevant region of the spectrum is shown in Figure 3.11.



Figure 3.10: Structure and atom labeling for N-Methyl-2-pyrrolidone (9)

To calculate the number of NMP molecules per monomer unit, the areas of the NMP peaks were compared to those of the aromatic and the methylene linkages. The compared areas are shown in Table 3.3. The triplet corresponding to proton C was unusable due to an overlapping broad peak most likely corresponding to water [77, 78].



Figure 3.11: The NMP part of the Torlon Proton Spectrum

Analysis of the areas gives an average  $S = 0.199 \pm 0.004$ , which corresponds to approximately one solvent molecule for every 5 monomer units. This gives a weight percent of  $5.27 \pm 0.01\%$ . This is consident with the value given in the technical specifications of the polymer for 92 % solids [70].

NMP Proton	Area	Area w.r.t Methylene Protons Area w.r.t to Aromatic Region	S
А	$2 \ge S$	0.42	0.21
		0.39	0.195
D	2 x S	0.42	0.21
В		0.39	0.195
C	2 x S	N/A	N/A
0		N/A	N/A
D	$3 \ge S$	0.6	0.2
D		0.57	0.19

Table 3.3: Integration of the NMP peaks w.r.t either the Methylene or Aromatic Regions.

## 3.5 FT-IR Spectroscopy

The IR spectrum of the commercial polymer was collected using a diamond ATR top-plate. Assignment of the peaks in the IR spectrum was done via comparison with literature values for similar polymers ([71, 72, 80]) and model molecules. The model molecules can be seen in Figure 3.12, and were chosen as they represent a mixture of reacted and unreacted groups. Molecules containing the acid chloride or acid anhydride were excluded as they were considered unlikely to remain unhydrolysed. For example, the acid anhydride-amide combination can be found in the literature; however, it couldn't be isolated without hydrolysis of the anhydride [81]. A suitable example of a 1,2-diacid-amide combination could not be found in the literature.

Analysis of the proton NMR spectrum suggested only 50 % of the imides were formed. However, there was little sign of -OH stretching in the IR spectrum (Figure 3.13) as seen for **11** at 3700 - 2500 cm<sup>-1</sup>.

For the carbonyl region (1800 to 1600 cm<sup>-1</sup>), there were four peaks to assign; shown in the insert in Figure 3.13. A summary of the stretching frequencies for the carbonyls seen in the model molecules can be found in Table 3.4. Only one (11) of the imide-containing molecules had a reported value for the imide

carbonyl stretch, so the highest peak in the carbonyl regions  $(1774 \text{ cm}^{-1})$  was assigned to the imide stretching frequency. This is consistent with textbook values (1770 cm<sup>-1</sup>) [82]; however, the accompanying stretch at 1700 cm<sup>-1</sup> is obscured by other absorptions. An acid anhydride being responsible for this absorption was unlikely due to the high reactivity of the functional group and the lack of an accompanying higher frequency peak [82, 83].

The peak centered on 1715  $\text{cm}^{-1}$  was assigned to carboxylic carbonyls as it is consistent with the values seen for similar stretches in **11**, **12** and **13**.

The peaks seen at 1650 and 1599 cm<sup>-1</sup> were assigned to amides in two environments, *ortho*- (1650 cm<sup>-1</sup>) or *para*- (1599 cm<sup>-1</sup>) to a carboxylic acid. Both types are seen in **12** and two stretching frequencies reported (1655 and 1620 cm<sup>-1</sup>). Comparison with **13**, which only contains the *ortho*- version, allows for assignment of the higher frequency peak to the *ortho*- and so the low to *para*. This was then applied to the spectrum of **5**.



Figure 3.12: The structures of model molecules from the literature: N-phenyl-4-(carboxyanilino)phthalimide (10), 4-carboxy-N-phenylphthalimide (11), 2,4-bis(phenylcarbamoyl)benzoic acid (12) and 2-(phenylcarbamoyl)terephthalic acid (13).



Figure 3.13: FT-IR spectrum of 5. Insert shows a magnetification of the carbonyl region,  $1800 - 1500 \text{ cm}^{-1}$ , and labelling of the peaks within it.

Table 3.4: Summary of the carbonyl stretching frequencies for the model compounds **10**, **11**, **12** and **13**.

Model Molecule	$\begin{array}{c} \text{Amide} \\ \text{C=O } / \ \text{cm}^{-1} \end{array}$	Acid C=O / $cm^{-1}$	Imide C=O / $\rm cm^{-1}$	Reference
10	$\begin{array}{c} 1647 \\ 1625 \end{array}$	Not Seen	Not Reported	[84]
11	Not Seen	1680	1785	[85]
12	$1655 \\ 1620$	1723	Not Seen	[84]
		1704		
13	1648	1715	Not Seen	[84]
		1695		

## 3.6 Gel Permeation Chromatography

GPC allowed for the determination of the molecular weight and the polydispersity of the commercial polymer. Expulsion of the polymer was measured via UV-Vis spectroscopy; a plot of the UV-Vis spectra as a function of time can be seen in Figure 3.14. Above that plot is the UV-Vis spectrum of polymer in DMF. Matching the two spectra, it is possible to see that polymer appears at 17.5 minutes after the initial addition. With comparison to polystyrene of a known molecular weight, the molecular weight could be determined. However, this value is only an estimate as structurally the commercial polymer is less flexible than polystyrene and so its ability to fit in the pores of the stationary phase will be different. The molecular weight is 9881 g mol<sup>-1</sup>, which corresponds to  $\approx 27$  repeat units using an average value for the molecular weight of the repeat unit.



Figure 3.14: UV-Vis spectra during the GPC experiment. Above, a UV-Vis spectrum of the polyamide-imide in DMF.

## 3.7 BET Surface Area Analysis

The results of the BET surface area analysis are shown in Figure 3.15. Nitrogen gas was used as the adsorbate, giving a surface area of  $8.9536 \pm 0.0666 \text{ m}^2 \text{ g}^{-1}$ . This surface area should be sufficient to give high quality solution depletion isotherms



Figure 3.15: BET isotherm to determine the surface area of the polymer powder.

## 3.8 The Cycloimidisation Reaction

#### 3.8.1 Change in Mass With Heating

Analysing the change in mass is made difficult by the impurities in the Torlon LM powder. The supplied powder is only at most 95 % polymer, the rest is residual N-methylpyrrolidone (9) from the synthesis. The boiling point of NMP is 202 - 205 °C [86–88] which is in the middle of the temperature range for the cycloimidisation reaction [84]. However, it is possible to calculate an upper bound for the mass change during heating. There should be a decrease of at least 5.27 % due to the loss of the residual NMP. The average number of monomeric units had to be found in order that the mass of water loss could be calculated. This was done by calculating an average molecular weight.

$$M_w(Average) = xM_w(Cyclised) + (1-x)M_w(Uncyclised)$$
(3.5)

Thus the number of monomeric units in 1 g could be calculated.

Number of Monomeric Units 
$$= \frac{(1-S)}{M_w(Average)}$$
 (3.6)

The moles of water produced is simply this value multipled by the fraction of uncyclised imides present; the mass of water is then this multipled by the molecular weight of water (18.00 g mol<sup>-1</sup>). This gives 0.023 g of water produced. Coupled with the weight loss due to NMP, this gives an upper bound of  $7.58\pm0.03\%$ .

The results are shown in Figure 3.16. All of the result have a similar shape: a sharp increase over 90 mins then a plateau. At 50 °C the mass changes were very small, which fits with being far from the boiling point of NMP and the cycloimidisation temperature. There is an increase in mass change as the temperature moves closer to the boiling point of NMP, and further into the range for the cycloimidisation reaction. Both 200 and 250 °C plateau above the calculated maximum. This may be due to the evaporation of unreacted monomers in the polymer; most likely the trimellitic anhydride chloride <sup>1</sup> as the 4,4'-methylene dianiline has a rather high boiling point (398 - 399 °C [91]).

<sup>&</sup>lt;sup>1</sup>There are no examples of boiling points at atomspheric pressure. However, values for reduced pressure boiling points vary from 120 to 175  $^{\circ}$ C [89, 90]



Figure 3.16: Graph of mass change as a function of time for five different heating temperatures: 50 °C, 100 °C, 150 °C, 200 °C and 250 °C. The theoretical limit outlined in the text is given by the dashed line.

## 3.8.2 IR Spectroscopy

The extent of imidisation can be followed by comparing the intensity of peaks in the IR spectrum of the polyamide-imide. The ratio of the peak corresponding to the imide (1778 cm<sup>-1</sup>) to the other three carbonyl peaks in the spectrum over time can be found in Figure 3.17. Three regimes can be seen: (i) for 50 °C and 100°C the ratio appears to remain constant over the heating time, (ii) for 200 °C and 250 °C the ratio decreases and then plateaus indicating the proportion of imides has increased and (iii) for 150 °C the behaviour is the same as for (ii) but the plateau value lies half way between the ratios seen in (i) and (ii).

The timescale indicated by this analysis is consistent with the timescale suggested by the the mass change data above. The change in the ratio is finished by 90 mins, suggesting that equilibrium is reached. However, the IR analysis is complicated by the changing concentration of N-methyl-2-pyrrolidone, whose



Figure 3.17: The average of the ratio of the peak at 1778 cm<sup>-1</sup> to the peaks at 1715 cm<sup>-1</sup>, 1658 cm<sup>-1</sup> and 1599 cm<sup>-1</sup> over time whilst being heated at five different temperatures: 50 °C, 100 °C, 150 °C, 200 °C and 250 °C.

adsorption at 1684 cm<sup>-1</sup> [92], lies in the carbonyl region. For greater temporal resolution, the IR spectrum of the polymer was recorded during in-situ heating. Spectra were recorded every two minutes. As in Figure 3.18, the average of the ratio of the 1778 cm<sup>-1</sup> peak to the peaks at 1714 cm<sup>-1</sup>, 1658 cm<sup>-1</sup> and 1598 cm<sup>-1 2</sup> was taken. The smooth decrease in this ratio, and as it is proportional to  $\frac{[\text{Amide}]}{[\text{Imide}]}$ , means that the concentrations are changing: imide concentration increasing and amide concentration decreasing. This is what would be expected for the imidisation reaction. The ATR technique is only sensitive to functional groups on or close to the surface of the material, meaning that these measurements are only representative of the surface / near surface chemistry.

## 3.8.3 NMR Spectroscopy

Analysis using either the mass change or IR spectroscopy during heating cannot decouple the effect of the imidisation reaction and the loss of N-methyl-2-pyrrolidone via evaporation. It was shown in sections 3.4.1 and 3.4.2 that proton NMR can separate the two. ATR spectroscopy only gives information

<sup>&</sup>lt;sup>2</sup>Wavelength resolution is only  $2 \text{ cm}^{-1}$  for timed spectroscopy.



Figure 3.18: Average ratio of the peak corresponding to the Imide stretch to other stretches in the carbonyl region.

about the surface chemistry of the material. As NMR spectroscopy is a solution technique it will give information on the bulk composition of the polymer.

### Residual NMP

From comparison of the polymer and NMP proton resonances, it is possible to determine the wt% of residual NMP in the material. Figure 3.19 shows the wt% of NMP present as a function of time heated at 200 °C. Initially, there is a steep drop in the amount of NMP present, and then it reaches a plateau value at 0.5 to 1 wt%.

#### Percentage of the Imides Formed

In contrast to the weight percentage of NMP, the percentage of imides formed plateaus much faster. It reaches 75 to 85 % after thirty minutes as shown in Figure 3.20. There is a suggestion that the percentage is continuing to increase beyond 240 minutes perhaps indicating two distinct regimes: surface and bulk. Imidisation occurs quickly at the surface/near surface as the chains are more mobile and water loss is easier. The imidisation in the bulk is harder as the chains are more packed and water loss is harder as it must diffuse away through

the bulk.



Figure 3.19: Weight Percentage of NMP in the Polymer as a function of time heating at 200  $^\circ\mathrm{C}.$ 



Figure 3.20: The percentage of imides formed as a function of time heating at 200  $^{\circ}\mathrm{C}.$ 

## 3.9 Conclusions

In this chapter, the commercial polyamide-imide and its thermal behaviour were characterised. Bulk analysis of the polymer revealed that the imidisation reaction (Scheme 8.1) wasn't complete, with only 50 % of the imides being formed. The extent of the imidisation reaction can be controlled by thermal treatment of the polymer. For example heating at 200  $^{\circ}$ C for 30 minutes can increase this percentage to 80 %.

In addition, it is possible to measure the amount of residual NMP present in the polymer powder. Again, heating can be used to remove this solvent from the powder.

For the surface adsorption studies, a model of the surface as a distribution of functional groups (amides, imides and carboxylic acids) was adopted. The surface is covered with the polymer repeat units. The ratio of cyclised to uncyclised repeat units can be calculated from the proton NMR spectrum. For room temperature studies, the surface will be 50 % cyclised.

In order to determine the density of functional groups on the surface, the di-



Figure 3.21: A simplified model of the surface as a distribution of functional groups.

mensions of the simplified cyclised and uncyclised repeat unit were calculated from simple models of the molecules. The dimensions can be seen in Figure 3.22. The cyclised repeat unit is fairly linear and planar, whilst the uncyclised repeat unit is kinked. There are no x-ray crystal structures of these simplifications of the repeat units for comparison<sup>3</sup>. From these estimates, the density of imides  $(9.03 \times 10^{-7} \text{ moles m}^{-2})$ , amides  $(2.25 \times 10^{-6} \text{ moles m}^{-2})$  and carboxylic acids  $(6.76 \times 10^{-7} \text{ moles m}^{-2})$  can be calculated. These densities, and so the functionality of the surface, can then altered by the heating the polymer to cause amides and carboxylic acids to cyclise into imides.



(b) The dimensions of the uncyclised repeat unit.

Figure 3.22: Dimensions of the cyclised and uncyclised repeat units.

<sup>&</sup>lt;sup>3</sup>There several examples of solvent adducts for pyromellitic acid 1,4-dianilide, a structurally similar compound [93, 94]. Interestingly, the anilide groups are almost perpendicular to the central benzene ring.

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# Chapter 4

# Surface Studies of the Commercial Polyamide-imide

In this chapter, the surface behaviour of two classes of commercially interesting molecules, alkylphenols and water, adsorbed on the polyamide-imide surfaces were investigated. Initially, the adsorption was studied via solution depletion isotherms to determine if adsorption occurs, then the structure of the layers was determined by neutron reflection studies.

## 4.1 Alkylphenol Adsorption

Phenolates are an important class of engine oil additives tackling corrosion, lubrication and detergency [95]. A representative illustration of their structure is shown in Figure 4.1. The chemistry of these molecules is complex. They are considered to be oligometric molecules via sulfide or methylene bridges. Their alkyl chains are often branched and non-uniform, which is considered to assist with solubility in non-polar solvents, and they can feature a charged head group. However, the extent of charge separation in a low dielectric oil is somewhat unclear. For our initial investigations, we used phenol and *para* substituted straight chain alkyl phenols as our model molecules. This combination enabled us to focus on the effect of the functional group and the alkyl chain length in the adsorption behaviour.



Figure 4.1: Simplification of the general industrial additive for the surface studies.

## 4.1.1 Solution Depletion Isotherms of Alkylphenols in Dodecane

This experimental approach has been outlined in section 2.6 and determines the amount of a molecule adsorbed on the surface from the fall in concentration of the solution the powder is in. The key aspect of this technique rests on good analytical methods to determine the change in solution concentration on adsorption. These aspects are now discussed.

#### UV-Vis Spectroscopy of the Dodecane Background

Due to the lack of conjugation within alkanes, these molecules absorb in the far ultraviolet (FUV) with the absorption wavelength typically being below 200 nm. As discussed in the introduction, linear alkanes are a good choice for a model oil systems. This is partly due to their relation to real commercial systems, but also their relative simplicity, which helps in these fundamental studies. In this work, dodecane is used. Klevens reported the UV transmission limit for n-dodecane as 173 nm [96] so it should be a good background for a 200 - 900 nm spectrum.

The fifteen results, three different dodecane samples with five spectra taken of each, used for the average background can be seen overlaid in Figure 4.2. Turro *et al* reported a UV-Vis absorption in the 200 to 300 nm range due to the presence of oxygen-alkane charge transfer complexes [97], as going from air-saturation to argon-saturation reduced this absorption by 1.33 cm<sup>-1</sup> for nheptane. The formation of oxygen-alkane charge transfer complexes matches the increase in absorbance seen at wavelengths close to 200 nm in these dodecane spectra. The hump at  $\approx 280$  nm matches one seen by Willson *et al* prior to a sulfuric acid wash of n-hexane [98] suggesting this is due to residual manfacturing impurities. As the dodecane has an UV-Vis absorbance associated with it,



Figure 4.2: Comparison of the fifteen experimental spectra and the average background taken forward for dodecane.

any means of concentration determination depend on UV-Vis absorbance must correct for this. As the concentration of the alkylphenols used is low, the concentration of dodecane is effectively constant. As such the UV-Vis absorbance should remain constant and so can be simply subtracted from the observed spectrum, equation 4.1.

$$A_{Alkylphenol} = A_{Observed} - A_{Dodecane} \tag{4.1}$$

The error in the absorbance of the alkylphenol is given by propagating the error in the observed spectrum with that of the dodecane spectrum.

$$\Delta A_{Alkylphenol} = \sqrt{(\Delta A_{Observed})^2 + (\Delta A_{Dodecane})^2}$$
(4.2)

#### UV-Vis Spectroscopy of Polymer Tumbled Backgrounds

To check against significant contamination of the samples from the polyamideimide substrate itself, different masses of polymer were tumbled for 24 hours with dodecane. The spectra show a slight absorbance in the 200 - 300 nm region with its intensity increasing with the mass of polymer. This is due to impurities washed off from the powder itself or compounds remaining from the synthesis such as N-methylpyrrolidone whose absorption lies in the 200 - 240 nm region [99]. As with the absorbance of the dodecane background, this can be corrected for in the concentration analysis.

$$A_{Sample} = A_{Observed} - A_{Dodecane} - A_{Background} \tag{4.3}$$

With an error given by the following expression.

$$\Delta A_{Sample} = \sqrt{(\Delta A_{Observed})^2 + (\Delta A_{Dodecane})^2 + (\Delta A_{Background})^2} \qquad (4.4)$$

#### Determination of the Concentration of Alkylphenol

The concentration of alkylphenol present in the solution after mixing with the polyamide-imide powder was determined by UV-Vis spectroscopy. The UV-Vis spectra of phenol and its *para*-n-alkyl derivatives in dodecane had similiar features: two strongly absorbing bands, one at 200 to 250 nm and another at 250 to 300 nm [100]. At low to moderate concentrations the bands show a steady evolution as expected. At higher concentrations the bands distort, broadening with a shift to shorter wavelengths as the instrument's detector is saturated. These spectra can be seen in Figure 4.3. The onset of this behaviour appears to occur at 1 mM.

For the concentration determination, the peaks were chosen which give the best
sensitivity at low concentrations. These peak wavelengths are given in Table 4.1. These longer wavelength peaks were chosen because the shorter wavelength absorptions were prone to error due to absorptions from the alkane solvent. Several peaks were chosen to cross-check the concentration and ensure internal consistency. We require a robust quantitative relationship between the absorption and concentration. In Figure 4.3 this relationship is demonstrated for phenol and its *para*-n-alkyl derivatives at the particular wavelength. This figure confirms the pattern seen in the full spectra: a linear region of intensity with concentration followed by saturation. The parameters of the fits to the linear regions are shown in Table 4.1. In order to accurately determine the concentrated systems must be diluted. However, this introduces an additional dilution error and is undesirable.

Additive	Peak / nm	Slope	Error	Intercept	Error
	265	1248.708	0.739	0.004	0.001
Phenol	271	1867.654	1.452	-0.0003	0.0005
	278	1736.606	1.340	0.003	0.0004
	270	1313.053	6.782	-0.022	0.004
	273	1479.965	6.663	-0.017	0.004
4-Octylphenol	276	1682.805	6.501	-0.012	0.004
	279	1973.596	11.574	-0.001	0.007
	285	1739.915	11.404	0.002	0.007
	267	986.372	1.564	-0.018	0.001
	270	1313.610	1.540	-0.014	0.001
4 Norminhanal	273	1475.809	1.539	-0.008	0.001
4-monyipnenoi	276	1684.013	1.568	-0.005	0.001
	279	1998.726	2.189	-0.002	0.001
	285	1773.852	2.307	0.004	0.001

Table 4.1: Peak wavelengths and the fits for the linear regions of the alkylphenol UV-Vis spectra.



(c) 4-Nonylphenol.

Figure 4.3: UV-Vis spectra of different alkylphenols changing with concentration.



Figure 4.4: The correlation between concentration and the absorption at 273 nm for various alkylphenols.

#### Solution Depletion Isotherms at Room Temperature

The solution depletion isotherms for phenol, 4-octylphenol and 4-nonylphenol in dodecane can be seen in Figure 4.5 and Figure 4.6. All the molecules show adsorption to varying amounts. Phenol shows the largest amount of adsorption with no plateau in the number of moles on the surface. 4-octylphenol shows much lower adsorption (20 times lower than phenol) but, again, shows no immediate plateau in the number of surface moles. 4-Nonylphenol shows similar adsorption to the 4-octylphenol and has a clearer plateau at  $1.25 \times 10^{-6}$  mols m<sup>-2</sup> but increases again.



Figure 4.5: The solution depletion isotherms for phenol in dodecane.



(a) Solution depletion isotherm for 4-octylphenol in dodecane.



(b) Solution depletion isotherm for 4-nonylphenol in dodecane.



(c) Comparison of the solution depletion isotherms for 4-nonylphenol and 4-octylphenol.

Figure 4.6: Solution depletion isotherms for 4-octylphenol and 4-nonylphenol in dodecane.

This plateau area corresponds to an area per molecule of approximately 133 Å<sup>2</sup> suggesting the molecule is lying down. A comparison between the average solution depletion isotherms for 4-octylphenol and 4-nonylphenol can be seen in Figure 4.6c. Both molecules shown qualitatively similar behaviour, an increase at low equilibrium concentrations to a plateau at approximately  $1.25 \times 10^{-6}$  mols m<sup>-2</sup> before increasing with concentration. This may indicate a transition from lying down to standing up for the molecules. 4-nonylphenol increases slower than 4-octylphneol after the plateau region; this may be due to differences in solubility of the two molecules in dodecane.

#### Simple Molecular Models

The initial analysis of these isotherms was done by comparison with two sets of dimensions. The first is the model of the polymer surface as a distribution of functional groups as outlined in section 3.9. The second is by looking at the molecular dimensions and packing seen in crystal structures. However, the examples of *para*-substituted alkyl phenol crystal structures in the literature were limited. The longest alkyl chain seen was ethyl [101]; the molecules form a 3-fold helix via hydrogen bonding. This motif is common for phenol and its methyl substituted analogues [102–106] and has been shown by calculations as the most stable hydrogen bonding structure for pheno [107].

Both 4-octylphenol and 4-nonylphenol were re-crystallised from super-saturated solutions in dodecane formed by heating above the melting point of the alkylphenol then cooling slowly. Suitable crystals were analysed by single crystal x-ray diffraction. The crystallographic parameters can be found in appendix A1; only the structural features will be briefly discussed here. A total of three structures



(a) High pressure polymorph seen for phenol [107].



(b) High pressure polymorph seen for 2methylphenol [103].

Figure 4.7: Layer structures seen in the literature for phenol and alkylphenols.

were determined: 4-octylphenol and two structures of 4-nonylphenol. All of the structures consisted of hydrogen bonded columns assembled into layers as shown in Figure 4.8 and Figure 4.9. This contrasts with the helical structures seen for shorter *para*-substituted alkylphenols. However, it has been shown that phenol and 2-methylphenol both undergo pressure induced transformations into a similar flat, layer structure [103, 107]; these structures are reproduced in Figure 4.7.

In 4-octylphenol there are two unique hydrogen bonded chains with each layer having an alternate hydrogen bonding motif. The oxygen-oxygen distances between two hydrogen bonded molecules are similiar in the two columns: 2.861 Å and 2.871 Å . In both hydrogen bonding interactions the benzene rings of the phenols are rotated from the plane of the hydrogen bond by  $35.19^{\circ}$  and  $40.56^{\circ}$  respectively as shown in Figure 4.8a. The octyl chains are packed *cis*- with respect to the hydrogen bonding interactions. These columns are packed to layers with the hydrogen bonding directions anti-parallel to each other, however, the alkyl chains point in the same direction as shown in Figure 4.8b.



(a) The hydrogen bonding interaction viewed along the b axis showing the rotation of the benzene rings out of the place of the hydrogen bond.



(b) The stacking of hydrogen bonded columns into layers.

Figure 4.8: Details of the crystal structure of 4-octylphenol.

The two crystal structures of 4-nonylphenol are similiar in structure, both forming hydrogen bonded columns as shown in Figure 4.9. However, in the first structure (1) there are two alternating hydrogen bonding distances with  $O \cdots O$ distances of 2.922 Å and 2.811 Å whilst in the second the  $O \cdots O$  distances are the same, 2.859 Å. Unlike the structure determined for 4-octylphenol, there is no change between columns within a layer. In both structures, the benzene rings are rotated out of the plane of the hydrogen bonding interaction. In contrast to the structure of 4-octylphenol, the nonyl alkyl chains are arranged *trans* with respect to the hydrogen bonded column.



(a) Structure 1 recorded for 4-nonylphenol.



(b) Structure 2 recorded for 4-nonylphenol.

Figure 4.9: The two structures seen for 4-nonylphenol. The difference between the two is a change in the packing of the hydrogen bonded columns. Blue lines indicate short contacts between molecules.

Using these crystal structures, it is possible to calculate an area per molecule for the molecules lying down, parallel to the surface, in hydrogen bonded chains as well as standing perpendicular to the surface. In Figure 4.10, projections of the unit cell can be seen for phenol, 4-octylphenol and the two polytypes of 4-nonylphenol lying down. In Figure 4.11, projections of the unit cell can be seen for these molecules standing up. This can be used to calculate the area per molecule by taking the area of the projection and dividing it be the number of molecules in the unit cell projection. The results of these are shown in Table 4.2.

Table 4.2: Area per molecule derived from crystal structures for phenol, 4-octylphenol and 4-nonylphenol.

Moleculo	Unit Cell	Number of molecules	Area per
Molecule	Area (Å <sup>2</sup> )	per unit cell	Molecule (Å <sup>2</sup> )
Phenol	66.480	2	33.240
4-Octylphenol	303.569	4	75.892
4-Nonylphenol	167 797	0	00 000
Polytype 1	107.707	2	03.093
4-Nonylphenol	169 565	0	04 000
Polytype 2	108.000	2	84.282

Lying Down

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Moloculo	Unit Cell	Number of molecules	Area per
Molecule	Area Å^2	per unit cell	Molecule ${\rm \AA^2}$
Phenol	63.18	3	21.059
4-Octylphenol	42.91	2	21.455
4-Nonylphenol	19 69	9	91 91 /
Polytype 1	42.05	2	21.314
4-Nonylphenol	<b>49 69</b>	2	91 311
Polytype 2	42.02	2	21.011



Figure 4.10: Unit meshes for phenol, 4-octyphenol and 4-nonylphenol lying down so the area per molecule can be calculated.



Figure 4.11: Unit meshes for phenol, 4-octyphenol and 4-nonylphenol standing up so the area per molecule can be calculated.

The areas per molecule for phenol lying down and standing up are plotted as moles of molecules on the surface in 4.12a. It is clear the number of moles adsorbed exceeds the amount for either configuration. This suggests the formation of multilayers or, at least, a thick, unstructured layer. The value for the suggested plateau in the 4-octylphenol and 4-nonylphenol is also plotted on the phenol solution depletion isotherm. There doesn't appear to be any correlation with the behaviour seen for phenol.

This is repeated for 4-octylphenol and 4-nonylphenol in Figure 4.12. Both molecules appear to plateau below the value of monolayer of the alkylphenols lying down on the surface. However, both molecules increase above that value but still remain below the value for a close packed layer of molecules standing up on the surface. In conclusion, the molecules appear sparsely packed on the surface.

#### Correlation with the Surface Sites

In section 3.9, a simple model of the surface as a distribution of amides, imides and acids was outlined. A comparison can be made between the amount of alkylphenol adsorbed and this distribution of functional groups. The amount of phenol adsorbed quickly exceeds the number of imides  $(9.03 \times 10^{-7} \text{ moles m}^{-2})$ , amides  $(2.25 \times 10^{-6} \text{ moles m}^{-2})$  and carboxylic acids  $(6.76 \times 10^{-7} \text{ moles m}^{-2})$ as well as the sum of all of them  $(3.8 \times 10^{-6} \text{ moles m}^{-2})$ .

The adsorption behaviour of 4-octylphenol and 4-nonylphenol is different with an apparent plateau at approximately  $1.25 \times 10^{-6}$  moles m<sup>-2</sup>. This value is consistent with the density of imides  $(9.03 \times 10^{-7} \text{ moles m}^{-2})$  but isn't as high as the density of amides  $(2.25 \times 10^{-6} \text{ moles m}^{-2})$ .



(a) Phenol solution depletion isotherm with values for phenol standing up, lying down and the plateau region seen for the longer alkylphenols.



(b) The solution depletion isotherm for 4-octylphenol with the values for the molecular lying down and standing up.



(c) The solution depletion isotherm for 4-nonylphenol with the values for the molecular lying down and standing up.

Figure 4.12: Solution depletion isotherms for alkylphenols with values for the molecules standing up and lying down.

#### 4.1.2 Neutron Reflectivity Studies

Neutron reflectivity was used to characterise the adsorbed layers. Initially, the bare surface was characterised then adsorption at various concentrations of phenol and 4-octylphenol was studied.

#### Characterisation of the Bare Substrate for Phenol Adsorption

The bare surface was characterised in three different contrasts of dodecane:  $d_{26}$ -dodecane,  $h_{26}$ -dodecane and contrast-matched dodecane to the SLD of the polyamide-imide layer.

The reflectivity profile in deuterated dodecane has a critical Q value of 0.0144  $\mathring{A}^{-1}$  which gives a value for the difference in scattering length density of 4.13 × 10<sup>-6</sup>  $\mathring{A}^{-2}$  using equation 4.5. This compares well to the difference in scattering length densities between silicon (2.07 × 10<sup>-6</sup>  $\mathring{A}^{-2}$ ) and d<sub>26</sub>-dodecane (6.7 × 10<sup>-6</sup>  $\mathring{A}^{-2}$ ).

$$Q_c = 4\sqrt{\pi\Delta\rho} \tag{4.5}$$

Simple analysis of the fringes seen in the reflectivity profile gives a thickness for the polymer layer of 150 to 200 Å. This is calculated from the following equation, where  $Q_1$  is the position of the first fringe.

$$d = \frac{2\pi}{Q_1} \tag{4.6}$$

For h-dodecane contrast, no critical edge is seen over the range of Q measured. This is consistent with the calculated value. The first fringe position seen in the profile gives a similiar thickness to that seen in the d-dodecane profile, 150 to 200 Å.

The polyamide-imide contrast-matched dodecane profile showed fringes when there should not have been any. The intensity of the profile is down compared to that of the h-dodecane or d-dodecane contrasts which is consistent with a contrasted match solvent. The first fringe position seen in the profile is consistent with that of the other two profiles: 150 - 200 Å.



Figure 4.13: Initially, the 4 layer model was fitted to the h-dodecane and ddodecane contrasts only. The experimental (points) and modelled (lines) reflectivity profiles for the deuterated, protonated and contrast-matched contrasts (top). The SLD profiles used in the three models (bottom).

Material	SLD $(\mathring{A}^{-2})$	Thickness $(\mathring{A})$	Roughness $(\mathring{A})$
Silicon	$2.1{\times}10^{-6}$	Substrate	8.0
$SiO_2$	$4.2 \times 10^{-6}$	5.0	1.0
Torlon LM	$2.7{\times}10^{-6}$	146.9	7.5

Table 4.3: Parameters for the fits shown in Figure 4.13.

Initially a four layer model (Si-SiO<sub>2</sub>-Polyamide-Dodecane) was used for the system. Two contrasts, h-dodecane and d-dodecane, were fitted simultaneously. It provided a good fit to both the h-dodecane and d-dodecane contrasts but when this fitted model was applied to the contrast-matched contrast it didn't predict the fringes seen in the reflectivity profile as shown in Figure 4.13.



Figure 4.14: Results of the 4 layer model being fitted to the contrast matched experimental pattern. The experimental (points) and modelled (lines) reflectivity profiles for the deuterated, protonated and contrast-matched contrasts (top). The SLD profiles used in the three models (bottom).

Material	SLD $(\mathring{A}^{-2})$	Thickness $(\mathring{A})$	Roughness $(\mathring{A})$
Silicon	$2.1{\times}10^{-6}$	Substrate	5.0
$SiO_2$	$4.2{\times}10^{-6}$	4.2	0.06
Torlon LM	$2.0{\times}10^{-6}$	174.2	0.03

Table 4.4: Parameters for the fits shown in Figure 4.14.

It is possible to tailor the model's parameters to fit the reflectivity for the contrast matched system. It reveals a much thicker polymer layer with a lower scattering length density as shown in the bottom graph of Figure 4.14. However, when this model is used for the d- and h-dodecane systems then a large discrepancy is seen in peak position, as seen in the top graph of Figure 4.14. This fit was discarded. One possible reason for this discrepancy is a variation in the SLD within the polyamide-imide. This could be caused by the solvent used in the spin coating, dimethylformamide, remaining in the layer. A gaussian distribution was used for the volume fraction of DMF in the layer. This accounted for the increased reflectivity seen in the contrast matched profile. The DMF distribution, SLD model used and resulting fits to the experimental data can be seen in Figure 4.15.



Figure 4.15: Using a model that incorporates residual DMF at the silicon dioxide - polymer interface. The experimental (points) and modelled (lines) reflectivity profiles for the deuterated, protonated and contrast-matched contrasts (top). The SLD profiles used in the three models (bottom).

Table 4.5: Parameters for the fits shown in Figure 4.15.

Material	SLD $(\mathring{A}^{-2})$	Thickness $(\mathring{A})$	Roughness $(\mathring{A})$
Silicon	$2.1{\times}10^{-6}$	Substrate	5.7
$\mathrm{SiO}_2$	$4.2 \times 10^{-6}$	7.8	0.8
Torlon LM	$2.0{\times}10^{-6}$	143.0	5.6

#### 4.1. ALKYLPHENOL ADSORPTION

#### Neutron Reflectivity Profiles of Adsorbed Phenol Layers

The reflectivity profiles for the polamide-imide surface in conctact with solutions of  $d_6$ -phenol in dodecane at four different concentrations can be seen in Figure 4.16. Here the modelled reflectivity profile for the bare surface is plotted alongside each of the profiles at different concentrations. At the lowest concentration, the reflectivity profile is basically unchanged from the bare surface. It is clear that the profiles change as the concentration of phenol increases.



Figure 4.16: Experimental reflectivity profiles (dots) for the bare surface and varying concentrations of  $d_6$ -phenol in dodecane. A fit for the bare surface is shown for the experimental profile for the bare surface (solid) as well as each of the profiles for varying concentration (dashed).

In order to fit these profiles, the model shown in Figure 4.15 was taken and a layer corresponding to the phenol added on top. The SLD of this layer was taken as the SLD of bulk phenol. During the fitting process it could be varyed by changing the solvation of the layer. The properties of this layer (thickness, roughess, solvation) was then varyed to produce the best fit to the data. However, fitting these profiles proved difficult. The lowest concentration can be fitted with a thin, well solvated surface layer. However, the larger concentrations cannot be fitted by allowing for the removal of solvent from the layer or the layer becoming thicker. Instead, there appears to be a large jump in the behaviour with the formation of a relavitively thick layer,  $\approx$  the thickness of the polymer. These fits can be seen in Figure 4.17.

It is possible to match the fringe positions using a thicker layer but the fine structure in the fringes cannot be seen in the experimental data, making hard conclusions difficult.



Figure 4.17: Reflectivity profiles fitted using a model of a solvated phenol layer on top of the system given in Figure 4.15. Experimental (dots) and modelled (lines) reflectivity profiles for the bare surface and varying concentrations of  $d_6$ -phenol in dodecane.

d-Phenol	Thickness	Roughness	Solvation
Concentration (mM)	(Å)	(Å)	(%)
0.375	6.1	1	69.5
10	167.8	7.64	38.5
20	175.3	10	28.9
40	180.0	7.9	25.4

Table 4.6: Parameters for the fits shown in Figure 4.17.

# Neutron Reflectivity Profile of the Bare Polymer Surface for 4-Octylphenol Adsorption

As with the model of the bare polyamide-imide surface before phenol adsorption, a DMF-rich region at the silicon dioxide - polyamide-imide had to be included. The experimental and modelled reflectivity profiles along with the SLD profiles can be seen in Figure 4.18 with the parameters shown in Table 4.7.

Material	SLD $(\mathring{A}^{-2})$	Thickness $(\mathring{A})$	Roughness $(\mathring{A})$
Silicon	$2.1{\times}10^{-6}$	Substrate	4.0
$\mathrm{SiO}_2$	$4.2 \times 10^{-6}$	7.0	0.1
Torlon LM	$2.0 \times 10^{-6}$	140.1	8.8

Table 4.7: Parameters for the fits shown in Figure 4.18.

# Neutron Reflectivity Profiles for 4-Octylphenol Layers at the Dodecane-Polyamide-imide Interface

The neutron reflectivity profile was recorded for three concentrations (5 mM, 25 mM and 50 mM) so a comparison of the adsorbed amount could be made with the solution depletion isotherm. For this concentration dependence a single contrast,  $d_{17}$ -octylphenol in h-dodecane, was recorded to allow for a good exchange between samples. For the highest concentration, a second contrast, h-octylphenol in  $d_{26}$ -dodecane, was used so the structure could be confirmed. Due to the presence of DMF in the polymer layer, a custom layer was used in RASCAL. This prevented the fitting of the two contrasted simultaneously, so here they are presented as individual fits.

Table 4.8: Values of layer thickness, solvation and roughness.

Concentration	Layer	Layer	Layer
of 4-Octylphenol / mM	Thickness / Å	Solvation / $\%$	Roughness / Å
5	9.6	51.3	5.00
25	14.2	44.5	5.00
50	19.4	38.7	5.00



(a) The experimental (points) and modelled (lines) reflectivity profiles for the deuterated, protonated and contrast-matched contrasts.



(b) The SLD profiles for the deuterated, protonated and contrast-matched contrasts.

Figure 4.18: Fitting the reflectivity profiles for the polyamide-imide surface prior to adsorption of 4-octylphenol using a model of residual DMF at the silicon dioxide - polyamide-imide interface.

As with fitting the phenol layers, the model shown in Figure 4.18 was taken and a layer corresponding to the 4-octylphenol added on top. The experimental reflectivity profiles and fits to the data can be seen in Figure 4.19 with the values used for the layers shown in Table 4.8. As the concentration of 4-octylphenol increases, the thickness and number density of molecules in the layer increases. Initially, the reflectivity profile is very close to that of the bare surface. As the concentration increases, the peaks shift to higher Q.

The SLD profiles for each of the fits is shown in Figure 4.20. The growth of the 4-octylphenol monolayer can be seen in the SLD profiles as a rise in scattering length density at the polyamide-imide - dodecane interface.



Figure 4.19: Experimental (points) and fits (lines) neutron reflectivity profiles for bare polymer surface and increasing concentrations of  $d_{17}$ -octylphenol in h-dodecane. The dashed lines show the fit of the bare surface.

A second contrast was recorded for 50 mM 4-octylphenol in dodecane with protonated alkylphenol and deuterated dedecane. It was fitted using the layer parameters derived from the deuterated 4-octylphenol in protonated dodecane shown in Table 4.8. Those parameters gave a good fit to the experimental data suggesting that the fit derived was quite robust. The fit and a comparison to the bare surface is shown in Figure 4.21 with the fit for the bare surface showed as dashed black line.

An approximate length of 4-octyl phenol from the crystal structure in Figure 4.1.1 can be calculated. This, 14.4 Å , compares well with the 4-octyl phenol layer thickness seen at 25 mM (14.2 Å ) and 50 mM (19.6 Å ). The thinner layer at 5 mM, 9.6 Å , suggests that the molecule lies closer to the surface than at higher concentrations.



Figure 4.20: SLD profiles for the bare surface and in contact with varying concentrations of 4-octylphenol in dodecane.



Figure 4.21: Fit for the reflectivity profile of 50 mM concentration of 4octylphenol in  $d_{26}$ -dodecane using the parameters for 50 mM in Figure 4.21. Experimental (points) and fits (lines) neutron reflectivity profiles for bare polymer surface and a 50 mM concentration of 4-octylphenol in  $d_{26}$ -dodecane. The dashed lines show the fit of the bare surface.

### 4.1.3 Conclusions

The addition of a *para*-alkyl chain appears to radically change the adsorption behaviour of phenol. At low concentrations, phenol, 4-octylphenol and 4-nonylphenol appear to behave in a similiar fashion, forming a sparsely packed layer lying close to the surface of polymer.

As the concentration of adsorbate increases, the behaviour diverges. Phenol appears to shift to a much stronger adsorption with a larger amount of material on the surface. Neutron reflectivity measurements suggest that a thicker, solvated layer forms at the surface. For the alkylphenols, the initial layer appears to become more dense and alkyl chains fully extend into solvent but additional adsorption is limited.

## 4.2 Water Adsorption

Water, present as a by-product of the combustion process or entering the system via damage to the engine, is a common pollutant in engine oils. It can lead to a reduction in engine lubrication [108, 109] as well as damage to the engine parts [110, 111]. In this section, the adsorption of water is confirmed via solution depletion isotherms. The structure and behaviour of the adsorbed water was characterised by neutron reflectivity measurements.

#### 4.2.1 Solution Depletion Isotherms of Water in Dodecane

A series of solution depletion isotherms were carried out using different concentrations of water in dodecane. As the concentration of water present could vary due to the uptake of moisture from the atmosphere, the isotherms were conducted under nitrogen via the procedure described in Section 2.6.1.

In order to produce different concentrations of water in dodecane, water-saturated dodecane was mixed with dodecane dried over molecular sieves. The saturation concentration of water in dodecane was taken as  $2.69 \pm 0.01$  mM, an average of literature values [112, 113].

#### Determination of the Concentration of Water in Dodecane

The concentration of water present in the dodecane samples was determined by transmission IR spectroscopy. The IR spectra were taken against a dry dodecane background. Samples were made by mixing dry and water-saturated dodecane in different proportions. As the volume percentage of water-saturated dodecane increased, peaks appeared around  $3630 \text{ cm}^{-1}$  and  $3700 \text{ cm}^{-1}$ , consistent with other measurements of water in lubricants [114]. As expected, the intensities of both peaks were low. Via comparison with values and assignments seen in gas phase spectra [115], these two peaks were assigned as the symmetric and asymmetric stretches. The reduction in the frequency of these stretches can be explained on the basis of the Kirkwood-Bauer-Magat model, in which shifts in the vibrational freqency are due to the dielectric properties of the solvent [115].



Figure 4.22: IR spectra for dodecane solutions with varying quantities of water.

The size of this peak at known concentrations was used to calibrate the absorption so a known absorption could be used to calculate an unknown concentratiom. The resulting calibration graph can be seen in Figure 4.23. The data shows a reasonably linear relationship between peak height and concentration of water present.



Figure 4.23: The calibration graph for converting from an IR absorption to a water concentration.

#### Solution Depletion Isotherm of Water on Polyamide-imide

The adsorption of water can be seen in the solution depletion isotherm shown in Figure 4.24. From the maximum value on the isotherm it is possible to calculate an area per molecule of  $\approx 500 \text{ Å}^2$ . This is much larger than the molecular footprint of water, suggesting a complete monolayer doesn't form.



Figure 4.24: The solution depletion isotherm for the adsorption of water from dodecane onto the polyamide-imide powder.

# 4.2.2 Neutron Reflectivity Studies

In order to characterise the adsorption of water at the polyamide-imide surface, the neutron reflectivity profile was collected for a spin coated polyamide-imide film on a silicon wafer in contact with a water-saturated dodecane solution. The reversibility of the formation of any interation was tested by washing the polymer surface with dried dodecane.

#### 4.2. WATER ADSORPTION

#### Characterisation of the Bare Polyamide-imide

As outlined before, the bare polymer surface was best modelled using a polymer layer that contains residual DMF. This means that the layer has a lower SLD, caused by a higher concentration of DMF, close to the silicon dioxide polyamide-imide interface. The SLD then increases towards the outer surface of the polymer as the concentration of DMF decreases. This initial model was then fitted by varying the model parameters to get the best fit to the three solvent constrasts.

The reflectivity profiles for the bare polyamide-imide in contact with  $d_{26}$ -dodecane, h-dodecane and a mixture of  $d_{26}$ -dodecane and h-dodecane with a SLD is 2.65  $\times 10^{-6}$  Å<sup>-1</sup>. This was chosen as it is approximately the SLD of the polymer layer. The experimental profiles and fits can be seen in Figure 4.25 with the parameters used shown in Table 4.9. The experimental reflectivity profiles are shown by dots and the fits to these profiles generated by the models are shown by the solid line. The SLD profiles used by the model are shown below the reflectivity profiles.

Material	SLD $(\mathring{A}^{-2})$	Thickness $(\mathring{A})$	Roughness $(\mathring{A})$
Silicon	$2.1{\times}10^{-6}$	Substrate	4.0
$SiO_2$	$4.2{\times}10^{-6}$	6.1	2.9
Torlon LM	$2.65{ imes}10^{-6}$	148.9	9.9

Table 4.9: Parameters for the fits shown in Figure 4.25.



Figure 4.25: Fitting the neutron reflectivity profiles using a model that incorporates residual DMF at the silicon dioxide - polyamide-imide. Top: The experimental (dots) and modelled (solid) reflectivity profiles for the polyamideimide surface in contact with d-dodecane (blue), h-dodecane (red) and dodecane contrast matched to the polyamide-imide (green). Bottom: The SLD profiles used for the models showing the distribution of DMF close to the silicon dioxide - polymer interface.

# Neutron Reflectivity Profiles of the Polyamide-imide in Contact with Water Saturated Dodecane

The neutron reflectivity profile changed when the polymer film was brought into contact with water saturated dodecane indicating a change to the SLD profile of the system. The system could not be fitted with a simple, constant SLD block at the surface of the polyamide-imide. This is consistent with the area per molecule seen in the solution depletion isotherm, which was many times larger than the molecular area of water.

A model of water diffusion into the polymer film was used. As with the residual DMF in the film, a gaussian distribution, centered at the polymer-dodecane interface, was used for the volume fraction of water in the film. The calculated reflectivity profile for this model is shown in Figure 4.26 and fits the experimental data collected. As expected, the water volume fraction was highest close to the polymer-dodecane interface and dropped moving towards the silicon oxide-polymer interface. It appears that higher SLD of  $D_2O$  even starts to cancel out the lowering of the polymer film's SLD caused by the residual DMF close to the silicon oxide-polymer interface.



Figure 4.26: Reflectivity profiles fitted using a model of water diffusing into the polymer. Top: The experimental (dots) and modelled (solid / dashed) reflectivity profiles for the polyamide-imide surface in contact with  $D_2O$ -saturated h-dodecane (black) and h-dodecane (red). Bottom: The SLD profiles used for the models showing the distribution of DMF close to the silicon dioxide - polymer interface and  $D_2O$  at the polymer - dodecane interface.

# Neutron Reflection After the Polyamide-imde was Washed with Dry Dodecane

In an attempt to remove the water from the surface of the polymer it was washed with h-dodecane dried over molecular sieves. The reflectivity profile after this treatment can be seen in Figure 4.27.

It has changed again, moving back towards the profile seen for the bare surface; however, it doesn't entirely return to the bare surface profile. If it is modelled using the gaussian profile for the volume fraction of water used for the saturated case, it is possible to see a small amount of water left in polymer film.



Figure 4.27: Reflectivity profiles fitted using a model of water diffusing into the polymer. Top: The experimental (dots) and modelled (solid / dashed) reflectivity profiles for the polyamide-imide surface after washing with dried hdodecane (black) and h-dodecane (red) at the start. Bottom: The SLD profiles used for the models showing the distribution of DMF close to the silicon dioxide - polymer interface and  $D_2O$  at the polymer - dodecane interface.

## 4.2.3 Conclusions

Water is a common contaminate in engine oils and can lead to inefficiency and possible engine damage. In this section, the surface chemistry of water contaminated oil at a polymer coated bearing was investigated. The adsorption of water from dodecane onto the surface of a polyamide-imide was shown via solution depletion isotherms; however, the small amount adsorbed suggested no cohesive water layer was forming. Neutron reflection showed that the water appeared to diffuse into the polymer. In addition, the diffusion was shown to be reversible to a degree with the water being removed via washing with dry dodecane.

In the less controlled conditions of actual engines this investigation would suggest that the polymer contains water which will alter its physical, as well as surface, properties and so is an important consideration for the design process. 112

# Chapter 5

# Synthesis and Surface Studies of Cucurbit[8]uril Threaded Polyamide-imides

The incorporation of the viologen-cucurbit[8]uril binding unit into the commerical polymer will be done from the starting synthesis via a cucurbit[8]uril complexed or uncomplexed aryl viologen monomer. The scheme of work in this chapter is shown in Figure 5.1. Initially, the commercial polyamide-imide (Torlon LM) was re-created to shown the ability to, and act as a baseline for, further synthetic efforts. After that the diamine monomer, 4,4'-diaminodiphenylmethane, was entirely substituted for the aryl viologen monomer. To show the effect of the complexation by cucurbit[8]uril, two fully substituted polymers were synthesised; one complexed and one uncomplexed. The system could then be moved back towards the commerical polyamide-imide by removing the amount of the aryl viologen momomer incorporated.

Neutron reflection was used to study the adsorption of a second guest terminated polyethene glycol molecule as this technique requires little of the polymer but, due to the size of the adsorbing molecules, should be indicative of surface behaviour.

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Figure 5.1: The scheme of work for the synthesis of a polymer containing the viologen-cucurbit[8]uril binding site.
# 5.1 Reproducing the Commerical Polyamide-imide

Initially, the commercial polymer was recreated using the scheme shown in Scheme 8.1. This synthesis was done to provide a baseline for further synthetic efforts.



Scheme 5.1: The two stage synthesis of a polyamide-imide: (i) the condensation of the diamine (6) with the acid anhydride chloride (7) to form a poly amic acid (8) and (ii) the thermally induced imidisation from the poly amic acid (8) to the polyamide-imide (5).

# Synthesis of poly(trimellitic anhydride chloride-co-4 4-methylenedianiline)

4,4'-diaminodiphenylmethane, **6**, (3.9691 g, 20 mmoles) was added to an amber solution of trimellitic anhydride chloride, **7**, (4.21 g, 20 mmoles) in DMF (70 mL) and stirred at room temperature for 2.5 hours. The reaction mixture was then poured into water to precipitate the polyamide-imide as a light brown solid. The polymer was separated by filtration and then extracted with acetone. Filtered again, the resulting powder was dried under vacuum overnight.

# 5.1.1 ATR FT-IR Spectroscopy

A comparison of the synthesised polymer with the starting monomers can be seen in figure 5.2a.



(a) Comparison of the FT-IR spectra of the synthesised polymer (red) and starting monomers (blue and black).



(b) Comparison of the FT-IR spectra of the synthesised polymer (red) and Torlon LM (blue).

Figure 5.2: Solid IR spectra and comparison for the synthesised polymer with Torlon LM and ts starting monomers.

The disappearance of the peaks associated with the  $-NH_2$  stretch in the 4,4'methylenedianiline, as well as those for the carbonyl stretches of the acid anhydride and acid chloride in the trimellitic anhydride chloride in the spectrum of the synthesisd polymer, confirms the formation of the the amide linkages. When compared to the IR spectrum of Torlon LM, figure 5.2b, a high degree of similiarity can be seen. The major difference is increased absorption in the 3000-3500 cm<sup>-1</sup> region. This is assigned to carboxylic -OH stretches, indicating a lower amount of imidisation in the synthesised polymer compared to the commerical sample and so a higher amount of residue carboxylic acid. Alternatively, this could be due to residual water present.

## 5.1.2 Solution UV-Vis Spectroscopy

In order to properly characterise the UV-Vis spectrum of the synthesised polyamide-imides an appropriate solvent had to be chosen.

Two solvents were screened, DMSO and DMF. However, both have UV-Vis absorbances extending up to 268 nm that saturate the detector in places. The spectra are shown in Figure 5.3. DMF was chosen because it is the solvent for the spin coating experiments due to its lower boiling point [116, 117]



Figure 5.3: Comparison of the UV-Vis spectra of DMSO and DMF.

The UV-Vis spectra of solutions of

Torlon LM in DMSO at three different concentrations; 0.25, 0.5 and 1 mM, were collected. The raw spectra were corrected for the DMSO background. However, the wavelength region below 268 nm is still unusable as can be seen in Figure 5.4.



All three spectra contain a large absorption band that corresponds to the polyamide-imide. In all three samples the absorption is close to the limits of the device; this is more pronounced for the higher concentrations which show noisy, large absorptions at short wavelengths.

Figure 5.4: Comparison of the UV-Vis spectra of 0.25 (red), 0.5 (black) and 1 mM (blue) solutions of Torlon LM in DMSO.

The UV-Vis spectra of solutions of Torlon LM in DMF at two different concentrations, 0.1 and 1 mM, were

collected. As seen in the spectrum of DMF on its own, the region below 268 nm was unusable. Above, this a broad absorption is seen that extends to approxi-

mately 400 nm: this was assigned to the polyamide-imide. As the concentration is increased, the intensity of this absorption increases and the wavelength range extends to just above 400 nm as is seen in Figure 5.5. However, at higher concentrations the absorption saturates the detector causing a noisy line shape.



Figure 5.5: Comparison of the UV-Vis spectra of 0.1 (blue) and 1 mM (black) solutions of Torlon LM in DMF

The UV-Vis spectrum of a 0.1 mM solution of the synthesised polyamideimide was recorded. A comparison of this spectrum with that of the 0.1 mM solution of Torlon LM in DMF can be seen in Figure 5.6. The synthesised polyaimide-imide appears to absorb more strongly than the commerical polymer; however, in calculating the concentration it is assumed that each repeat unit is fully cyclised. The difference between the two spectra may be differences in the average molecular weight of the repeat unit

and so a difference in actual concentration.



Figure 5.6: Comparison of the UV-Vis Spectra of 0.1 mM solutions of Torlon LM (red) and the Synthesised Polyamide-imide (blue).

## 5.1.3 <sup>1</sup>H NMR Spectroscopy in d<sub>6</sub>-DMSO

The proton spectrum of 4,4'-methylenedianiline can be seen in Figure 5.8. The aromatic protons (6.811 ppm, 4H, dt, 9.7 and 2.4 Hz, -CHCHC(CH<sub>2</sub>)-; 6.462 ppm, 4H, dt, 9.7 and 2.4 Hz, -C(NH<sub>2</sub>)CHCH-) show the expected AA'BB' multiplity. Whilst the chemical shifts match those of the simulated spectrum, they vary from that reported by Banerjee *et al* (6.99 and 6.61 ppm) [118]. However, whilst the multiplicity reported is lower (a doublet), than observed here the coupling constants are approximately the same (8.2 Hz vs 9.7 Hz).

The four amine protons appear as a singlet at 4.802 ppm. This closely matches the simulated spectrum as well as the value reported by Gibson *et al* [119]. However, Banerjee *et al* do not observe a peak in this region and instead assign a peak at 3.54 ppm as that of the amine protons. In the spectrum recorded here, the singlet at that shift is more consistent with the methylene linkage between the two rings, having an area that corresponds to two protons. Additionally, this is the chemical shift that Gibson assigned for the methylene linkage.



(a) Proton numbering for 4,4'-methylenedianiline.

Proton	Observed $\delta$	Simulated $\delta$	$\delta$ (Gibson)	$\delta$ (Banerjee)
number	/  ppm	$/ \mathrm{ppm}$	$/ \mathrm{ppm}$	/ ppm
1	4.802	4.91	4.8	3.54
2	6.462	6.44	N/A	6.61
3	6.811	6.85	N/A	6.99
4	3.555	3.83	3.56	3.79

(b) Comparison of observed, simulated and literature  $^1{\rm H}$  assignments for 4,4'-methylenedianiline.

Figure 5.7: Proton numbering and literature values for 4,4'-methylenedianiline.



Figure 5.8: The <sup>1</sup>H NMR Spectrum for 4,4'-methylenedianiline; numbering shown in Figure 5.7a

The proton labelling for trimellitic anhydride chloride is shown in Figure 5.10a whilst the observed proton NMR spectrum is shown in Figure 5.9. The spectrum was assigned as follows: 8.206 ppm, 1 H d,  $J_{H-H}^4 = 1.5$  Hz,  $-C(CO_2)CHC$  (COCl)-; 8.114 ppm, 1 H, dd,  $J_{H-H}^4 = 1.5$  and  $J_{H-H}^3 = 8$  Hz, -CHCHC(COCl)-and 7.739 ppm, 1 H, d,  $J_{H-H}^3 = 8$  Hz,  $-C(CO_2)CHCH$ . The doublet, doublet of doublets, doublet pattern is consistent with that seen in the Sigma Aldrich sample <sup>1</sup>H NMR spectrum [120]; however, the chemical shifts are higher but the solvent used (CDCl<sub>3</sub>) is different to the solvent used for these measurements (d<sub>6</sub>-DMSO). The observed result differs from the simulated spectrum both in pattern and chemical shift (Table 5.1). A literature search yielded no examples of <sup>1</sup>H NMR spectrum of trimellitic anhydride chloride.

The spectrum has a low intensity, broad resonance between 10 and 12 ppm. This can be attributed to acidic protons due to hydrolysis of either the acid chloride or the anhydride. Hydrolysis of the acid chloride would yield 1,2,4-benzenetricarboxylic-1,2-anhydride (Figure 5.10b), a molecule extensively studied by Arjunan *et al.* They observed a peak at 13.58 ppm which they assigned as the carboxylic acid proton resonance [121]. The remaining aromatic proton positions fit with those observed here.

The proton NMR spectrum of the fully hydrolysed molecule, trimellitic acid (Figure 5.10c), was recorded by Biswas in  $d_6$ -DMSO [122] and Lammert in  $D_2O$ 

[123]. Both spectra are only shown in comparison; however, the pattern of peaks presented is consistent with what has been observed here. The chemical shifts roughly match for Biswas, though no values are given, whilst in the Lammert's spectrum they are all shifted up field. This could be due to the different solvent used. Bruck published the chemical shifts of the aromatic protons of trimellitic acid as well as other benzenepolycarboxylic acids [124]. The acidic proton peaks were too broad to be determined which is consistent with the observed spectrum in Figure 5.9. The chemical shifts presented by Bruck have the same pattern but all are shifted down field compared to those observed here. In addition, the proton spectrum matches the example spectrum provided by Sigma Aldrich both in pattern and chemical shift [125].



Figure 5.9: The <sup>1</sup>H NMR Spectrum for TMAC; numbering shown in figure 5.10a



Figure 5.10: Proton numbering for trimellitic anhydride chloride and its hydrolysed derivatives.

Table 5.1: Comparison of observed, simulated and literature  ${}^{1}$ H assignments for trimellitic anhydride chloride and its hydrolysed derivatives.

Ducton	Observed	TMAC TMAA			TMA		
Number	δ / nnm	Simulated	Simulated	Arjunan	Simulated	(Bruck)	
Number	o / ppm	$\delta$ / ppm	$\delta$ / ppm	/ ppm	$\delta$ / ppm	$\delta$ / ppm	
1	8.206	8.48	8.54	8.12	8.54	8.43	
2	8.114	8.66	8.43	8.42	8.43	8.32	
3	7.739	8.59	8.59	7.72	8.59	7.95	

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The <sup>1</sup>H NMR spectrum of the synthesised polymer is seen in Figure 5.11. It is similar to that of the commercial polyamide-imide, although it has a much greater resonance due to water, with the three main regions: amide, aromatic and methylene protons. However, there are some additional peaks present that may be due to incomplete polymerisation. The polymer spectrum shows the successfully synthesis of the polyamide-imide.



Figure 5.11: Comparison between the proton spectra of the synthesised (red) and commercial polyamide-imide (blue).

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## 5.1.4 Gel Permeation Chromatography

A comparison of the chromatographs for the commercial polymer and the reproduction synthesised here is shown in Figure 5.12. Both are shown as functions of the intensity recorded at 273 nm. The polyamide-imide synthesed appears shorter than the commercial polymer ( $M_w = 9881 \text{ g mol}^{-1} \text{ vs } 6603 \text{ g mol}^{-1}$ ).



Figure 5.12: A comparison of the chromatographs for the commercial polyamideimide (Black) and the reproduction synthesed here (Red).

# 5.2 Inclusion of the Viologen-Cucurbit[8]uril Binding Unit

Determining the inclusion of the viologen-cucurbit[8]uril unit is difficult as the aromatic region of the polyamide-imide proton NMR is complex and the resonances indicative of complexation would be weak. Therefore, initially, the 4,4'-methylenedianiline was entirely replaced with the viologen diamine.

## 5.2.1 100 % Viologen without Threaded Cucurbit[8]uril.

Synthesis of the Polyamide-imide



Scheme 5.2: Synthesis of the 100 % Aryl Viologen Monomer Polymer without threaded Cucurbit[8]uril.

The viologen monomer 14 (20 mg, 0.05 mmoles) was added to an amber solution of trimellitic anhydride chloride, 7, (10 mg, 0.05 mmoles) and triethylamine (10 eq) in DMF (5 mL) and stirred at room temperature for 2.5 hours. The reaction mixture was then poured into water to precipitate the polyamide-imide as a light brown solid. The polymer was separated by filtration and then extracted with

acetone. Filtered again, the resulting powder was dried under vacuum overnight.

#### NMR Spectroscopy of the Viologen Monomer

In order to determine the degree of incorporation of the viologen monomer, the proton NMR spectra of the starting material was recorded.

A literature review revealed no previous work on this exact molecule, Figure 5.13a, but a substructure search found a patent by Fujifilm for a similiar molecule for dye applications, Figure 5.13b. The proton NMR assignments are also shown in the figure. In place of the amine groups, the Fujifilm molecule has amides. The observed proton spectrum shares many similarities with this molecule: a broad absorption between 8.5 and 10 ppm is consistent with the position of the bipyridyl protons, while the broad absorption between 6.5 and 8 ppm corresponds to the benzyl protons. Porter's assignment of the proton spectrum of 1,1'-diphenyl-4,4'-bipyridinium dichloride supports this [126]; with the bipyridyl protons at 9.76 and 9.16 ppm and the benzyl protons at 8.01 -7.81 ppm. Assignment of the amine protons is harder. The peak at 3.5 ppm is an option but the integration is wrong; as it is twice the area of the entire aromatic proton region (6.5 to 10 ppm). That leaves the peak at 6.0 ppm: the integration ratio is 1:3 with the aromatic region. Considering the amine protons of the simpler molecule aniline have a chemical shift of 5.00 ppm [127], the addition of the electron-withdrawing viologen will shift the peak down field.



(b) Proton Assignments for the Fujifilm Dye Molecule.



(c) Proton Assignments for 1,1'-Diphenyl-4,4'-bipyridinium Dichloride.

Figure 5.13: Molecules of interest.



Figure 5.14: The Proton Spectrum of the viologen monomer in d<sub>6</sub>-DMSO

#### Proton NMR of the 100 % viologen Polyamide-imide

A comparison of the proton spectra of the viologen monomer, the trimellitic anhydride chloride, and the synthesed polyamide-imide between 5 and 11 ppm is shown in Figure 5.15. It shows that many of the resonances seen in the original monomers are preserved and several new ones seen, such as a peak between 10 and 11 ppm, possibly corresponding to the an amide proton indicating the formation of the amide linkers. Without the methylene linkage seen in the commercial polymer, the number and nature of linkers cannot be quantified. However, the increased complexity of the spectrum is consistent with that seen for the commercial polymer compared to the starting monomers.



Figure 5.15: Comparison of the proton spectra of the viologen monomer (black), the trimellitic anhydride chloride (red) and the synthesed polyamide-imide (blue) between 5 and 11 ppm.

## 5.2.2 100 % Viologen with Threaded Cucurbit[8]uril.

Synthesis of the Polyamide-imide



Scheme 5.3: Synthesis of the 100 % Aryl Viologen Monomer Polymer with threaded Cucurbit[8]uril.

The viologen monomer 14 (20 mg, 0.05 mmoles) and cucurbit[8]uril (66 mg, 0.05 mmoles) in DMF (5 mL) were stirred for 1 hour. To that was added an amber solution of trimellitic anhydride chloride, 7, (10 mg, 0.05 mmoles) and triethylamine (10 eq) in DMF (5 mL), and the resulting solution stirred at room temperature for 2.5 hours. The reaction mixture was then poured into water to precipitate the polyamide-imide as a light brown solid. The polymer was separated by filtration and then extracted with acetone. Filtered again, the resulting powder was dried under vacuum overnight.

#### Proton NMR Spectroscopy of the Polyamide-imide in d<sub>6</sub>-DMSO

The proton NMR spectra for the synthesised polyamide-imide, **15**, can be seen in Figure 5.16. The overall intensity is weak due to the low solubility of the polymer. When compared to the proton spectra of the uncomplexed and cucurbit[8]uril-complexed aryl viologen, similar peaks corresponding to both states can be seen as well as peaks corresponding to the cucurbit[8]uril. This suggests that the polymer is only partially threaded.



Figure 5.16: Comparison of the proton NMR spectra of the aryl viologen (black), the aryl viologen in the presence of cucurbit[8]uril (red) and the cucurbit[8]uril threaded polyamide-imide (blue).

# 5.3 Surface Studies of the Modified Polyamideimides

Neutron reflection was used to study the adsorption of an anthracene-terminated polyethylene glycol molecule. The molecule used was synthesised by Chi Hun and Professor Oren Scherman in the Department of Chemistry at the University of Cambridge, and can be seen in Figure 5.17. The experiment is outlined in Figure 5.17; for the commercial polyamide-imide and 100 % aryl viologen polymer without the cucurbit[8]uril there is not a directed binding interaction, and so a thinner layer is expected. With the complete viologen-cucurbit[8]uril binding unit present, the charge transfer interaction between the viologen and the anthracene creates a directed interaction leading to a thicker layer.



Figure 5.17: The anthracene terminated polyethylene glycol molecule and surface studies undertaken.

## 5.3.1 Neutron Reflectivity Studies

Due to technical difficulties at the ISIS facility, the characterisation of the interaction between the commercial and modified polyamide-imide surfaces and the polymer additive in solution was limited. Here the reflectivity profiles will be only qualitatively discussed.

For the commercial polyamide-imide, a large change can be seen when the surface is brought into contact with a solution containing the polygylcol additive. This change can be seen in Figure 5.18. For the modified polymers, both with and without threaded cucurbit[8]uril, there is little change in the reflectivity profile for the polymer additive in contrast-matched dodecane compared to the bare surface in contrast-matched dodecane. The reflectivity profiles are shown in Figure 5.18.



Figure 5.18: The reflectivity profiles for the commercial polymer, modified polymer with and without curcubit[8]uril in contact with contrast matched dodecane (black, blue and light blue) and a solution of polyglycol additive in contrast matched dodecane (red, green and purple). The reflectivity profiles have been offset for clarity.

# 5.4 Conclusions

In this chapter the successful reproduction of the commerical polyamide-imide Torlon LM was demonstrated. In addition, the incorporation of a viologen-based binding unit was shown. The production of a fully cucurbit[8]uril threaded version was unsuccessful, showing only limited threading.

A test of the surface properties of Torlon LM, the cucurbit[8]uril threaded and unthreaded polymers was undertaken using neutron reflection. The adsorbate was an anthracene-terminated polyethyleneglycol chain. On Torlon LM, a distinct change can be seen in the reflectivity profile for the polymer additive in polyamide-imide contrast-matched dodecane. For the two modified layers there was little change in the reflectivity profiles, suggesting little interaction between the surface and the additive, and certainly not the enhanced adsorption that had been hoped for.

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# Chapter 6

# Cucurbit[n]uril Interactions in Non-Polar Solvents

In the previous chapter, the behaviour of the cucurbit[8]uril threaded polymer was unexpected. In order to probe this as well as tailor the interactions between the additive in solution and the cucurbit[8]uril threaded polymer surface, the inclusion of a second guest in a cucurbit[8]uril in oil was studied. Cucurbit[8]uril is sparingly soluble in water and insoluble in non-polar solvents, making studies difficult. To overcome this limitation, the cucurbit[8]uril was incorporated into a rotaxane to prevent de-threading then precipitation of the cucurbituril. The rotaxane system is broken down into three components: the binding unit, the stoppers, and the counterions. An alkyl viologen was chosen as the binding unit so that the distance between the cucurbituril and the stoppers could be varied. A selection of stoppers were chosen from the literature [128, 129]. The counterion was chosen to maximise the solubility of the system.

# 6.1 Synthesis of an Oil-soluble Rotaxane

# 6.1.1 Changing the Viologen's counter-ion from $Br^-$ to $PF_6^-$

With the first guest being a dicationic viologen, the system will require some form of counterion. As the resulting rotaxane should be soluble in low polarity solvents, the counterion must interact weakly with the viologen. Hexafluorophosphate was chosen as the counterion as it has been shown to enhance the solubility of cucurbituril systems in organic solvents. Complexation of the host and guest takes place in water then the complex crashes out with the addition of ammonium hexaphosphate, with the ammonium chloride remaining in solution.

#### Experimental



Scheme 6.1: Complexation with cucurbit[8]uril and change of counterion from bromide to hexafluorophosphate.

A solution of cucurbit[8]uril (50.1 mg, 0.04 mmols) and alkyl viologen **18** (15.2 mg, 0.04 mmols) in water (10 mL) was stirred for a hour. To this, a saturated solution of ammonium hexafluorophosphate was added dropwise until no further precipitation occurred. The precipitate was separated by filtration and dried under vacuum. The product **19** was a white powder (60.0 mg, 0.03 mmols, 86 %).

#### Results

#### <sup>19</sup>F NMR Spectroscopy in DMSO

The appearance of a doublet  $(J_{P-F}^1 = 710 \text{ Hz})$  at -70.13 ppm in the <sup>19</sup>F spectrum of the product is consistent with literature values for the the PF<sub>6</sub> anion's chemical shift and coupling constant (See table Table 6.1). This, along with a observed higher DMSO solubility, suggests that the counter-ion exchange was successful.

Mologulo	§ / ppm	Solvent	Appeorance	$\mathbf{J}_{P-F}^1$	Ref	
Molecule	o / ppm	Solvent	Appearance	/ Hz		
Reaction Products	-76.9	$d_6$ -DMSO	Doublet	711	[130]	
$N(Bu)_4 PF_6$	-69.8	$d_3$ -MeCN	Doublet	707	[131]	
$\mathrm{LiPF}_{6}$	-69.8	$d_3$ -MeCN	Doublet	707	[131]	
$\mathrm{LiPF}_6$	-72.4	$d_3$ -MeCN	Doublet	708	[132]	
$PF_6^-$	-71	$d_6$ -Acetone	Doublet	708	[133]	

Table 6.1: Literature Values for the  $PF_6^-$  anion.

#### Mass Spectroscopy of the Host-Guest Complex

The mass spectrum of the product has peaks at m/z values of 786.7798 and 787.2810, which matches the simulated mass for the dicationic alkylviologencucurbit[8]uril complex. Additionally, the spectrum contained peaks associated with the parent ion and fragmentation products of the uncomplexed alkyl viologen. No 2:1 complex was seen in the Mass Spectrum.

#### NMR of the Starting Alkylviologen in DMSO

For the alkyl viologen only a few examples of this molecule were found in the literature. The proton shifts seen for these molecules are shown in Figure 6.1b and the <sup>13</sup>C shifts are shown in Figure 6.1c. The <sup>1</sup>H NMR spectrum of the starting alkylviologen is shown and assigned in figure Figure 6.2. The bipyridyl protons can be assigned as the two highest shifted peaks: the proton closest to the nitrogen was assigned to the doublet at 9.444 ppm  $(J_{H-H}^3 = 7 \text{ Hz})$  whilst the other was assigned to the doublet at 8.966 ppm  $(J_{H-H}^3 = 7 \text{ Hz})$ . Literature

values show a lot of variation possibly due to solvent choice. However, these values are close to the shifts seen for the hydrogen bromide salt in DMSO [134]. The singlet at 8.239 ppm was assigned to the amine's protons, and no coupling to the the adjacent CH<sub>2</sub> group could be seen. This shift is similiar to the literature value for the amine shift in DMSO. The triplet at 5.022 ppm ( $J_{H-H}^3 = 5.75$  Hz) was assigned to the CH<sub>2</sub> group closest to the pyridyl nitrogen, whilst the second CH<sub>2</sub> group was assigned to the singlet at 3.625 ppm. The coupling to the adjacent CH<sub>2</sub> group could not be resolved. However, the COSY spectrum revealed a correlation with the peak for the adjacent CH<sub>2</sub> group as well as a correlation with the corresponding to the amine's protons (Figure 6.3b). These shifts match the literature values seen for these protons (see Figure 6.1b).



(a) Proton and Carbon Labelling for 18.

	Counter	C 1 4		Proton Cl		DĆ		
Molecule	Ion	Solvent	1	2	3	4	5	Reference
HBr Salt	$\mathrm{Br}^-$	$d_6$ -DMSO	8.34 (d)	3.26 - 3.89 (m)	5.09 (m)	9.51 (d)	8.99 (d)	[134]
Neutral	$\mathrm{Br}^{-}$	$D_2O$	N / A	3.402 (m)	4.800 (m)	9.036 (d)	8.476 (d)	[135]
$ClO_4H$ Salt	$ClO_4^-$	$CD_3CN$ d <sub>6</sub> -DMSO	6.6	3.67 (t, $J_{H-H}^3$ = 6.4 Hz)	4.94 (t, J <sup>3</sup> <sub><i>H</i>-<i>H</i></sub> = 6.4 Hz)	8.99 (d, $J_{H-H}^{3}$ = 6.8 Hz)	8.53 (d, $J_{H-H}^3$ = 6.8 Hz)	[136]

(b)	Table of	$^{1}H$	chemical	shifts	seen	in	the	literature.	

Molecule	Counter	Solvent	Ca	Deference				
	Ion	Solvent	a	b	с	d	е	Reference
$ClO_4H$ Salt	$\text{ClO}_4^-$	$CD_3CN$ DMSO	38.9	58.1	146.8	126.4	148.8	[136]

(c) Table of  ${}^{13}C$  chemical shifts seen in the literature.

Figure 6.1: Literature summary of NMR Spectroscopy of the starting alkylviologen 18.

The  ${}^{13}$ C NMR spectrum can be seen in figure 6.3a. It could be assigned by comparision with an APT version of the carbon spectrum (figure 6.4b) and the HSQC spectrum (figure 6.4a). The carbons involved in the bipyridyl linkage (carbon e) were assigned to the peak at 148.728 ppm as it disappears in the APT spectrum due to having no attached protons. This is confirmed by the HSQC spectrum: this peak in the <sup>13</sup>C spectrum showed no correlation with any of the peaks in the proton spectrum. The two remaining carbons in the bipyridine rings were assigned by using the correlation between <sup>13</sup>C peaks and the proton peaks as shown in the HSQC spectrum (Figure 6.4a). The carbon nearest the nitrogen was assigned to the peak at 146.917 ppm; the other carbon was assigned to 126.591 ppm. For the alkyl carbons, the carbon-proton correlations allowed for the assignment of the peaks. The peak at 57.967 ppm was assigned to the carbon in the CH<sub>2</sub> closest to the pyridyl nitrogen. The other carbon was harder to assign as its peak couldn't be seen in the <sup>13</sup>C spectrum as it was obscured by the DMSO peak. It could be identified in the HSQC and APT spectra, and its chemical shift was given as 39.052 ppm. These carbon shifts compare favourably with the shifts reported by Gromov  $et \ al \ [136]$ .



Figure 6.2: <sup>1</sup>H NMR spectrum of alkyl viologen **18**.





Figure 6.3: The  ${}^{13}$ C NMR and COSY spectra of the starting alkyl viologen.







Figure 6.4: The HSQC and APT spectra of the starting alkyl viologen.

#### NMR Spectroscopy of the Host-Guest Complex 19

The <sup>1</sup>H NMR spectra of the alkylviologen and of the product are shown in figure 6.5c. The proton NMR spectrum was assigned by comparison to the literature as well as HSQC (figure 6.6c) and COSY spectra (figure 6.6b). The proton closest to the nitrogen of the pyridine ring was assigned to the peak at 8.843 ppm. It has experienced an upfield shift of 0.623 ppm and a loss of the doublet structure seen in the free viologen. The other proton on the pyridine ring was assigned to the peak at 7.494 ppm. It has experienced a larger upfield shift of 1.494 ppm and, again, the loss of the doublet structure seen in the free viologen. These assignments are confirmed by correlations between the protons seen in the COSY spectrum as well as carbon-proton correlations between these protons and carbon peaks in the 100 - 150 ppm range in the HSQC spectrum. The protons of the amine were assigned to the peak at 7.806 ppm; this assignment is confirmed by correlations with the alkyl protons seen in the COSY and NOESY spectra. Additionally, the peak shows no meaningful correlation with any peak in the carbon spectrum. These protons have experienced an upfield shift of 0.455 ppm relative to the free viologen. The protons of the CH<sub>2</sub> group closest to the nitrogen of the pyridine ring were assigned as the peak at 4.975 ppm. The chemical shift of these protons has not changed compared to the free viologen (they experienced an upfield shift of 0.069 ppm); however, they have lost their triplet structure. The protons of the CH<sub>2</sub> group adjacent to the amine were assigned to the peak at 3.637 ppm. Again, there is a small upfield shift of 0.01 ppm so their chemical shift can be considered unchanged. Like the uncomplexed viologen, the peak appears as a singlet. Assignment of these peaks was confirmed by proton correlations seen in the COSY spectrum. The peak at 3.637 ppm showed correlations with the  $CH_2$  peak at 4.975 ppm as well as the amine peak at 7.806 ppm whilst the alkyl protons only correlated with the protons on the adjacent  $CH_2$ .

The <sup>1</sup>H spectrum shows the appearance of peaks associated with the cucurbit[8]uril. The *endo*-proton of the methylene group is a doublet at 5.557 ppm  $(J_{H-H}^2 = 14.5 \text{ Hz})$ , whilst the *exo*-proton is a doublet at 4.201 ppm  $(J_{H-H}^2 = 15 \text{ Hz})$ . The proton on the bridging carbon is a singlet at 5.413 ppm. These shifts are consistent with those seen in the literature. The upfield shift of the bipyridyl and amine protons is consistent with shifts seen in the literature in complexed systems. No peaks could be seen for the uncomplexed viologen. A comparison of the areas of the host to guest protons reveals a 2:1 mixture of the viologen to the cucurbit[8]uril. This could be due to depletion because of the low solubility of cucurbit[8]uril in DMSO.





(a) Proton and carbon labelling for 18.

(b) Proton and carbon labelling for Cucurbit[8]uril.



(c) Comparison of the  $^1\mathrm{H}$  NMR spectrum of the  $\mathbf{18}$  before and after complexation.

Figure 6.5: The proton, carbon labelling and <sup>1</sup>H NMR spectrum for  $\mathbf{18}$ , cucurbit[8]uril and  $\mathbf{19}$ .



- cucurbit[8]uril mixture.

(c) HSQC spectrum of the alkyl viologen- cucurbit[8]uril mixture.

Figure 6.6:  $^{13}\mathrm{C},\,\mathrm{COSY}$  and HSQC spectra for alkyl viologen and cucurbit[8]uril mixture.



(d) NOESY spectrum of the alkyl viologen - cucurbit[8]uril mixture.



(e) Summary of NOE correlations between the the protons of the alkyl viologen and the 3 protons of the cucurbit[8]uril.



(f) Changes in the <sup>1</sup>H chemical shifts of the alkyl viologen protons.

## 6.1.2 Synthesis of The Rotaxanes

The first group chosen as a stopper was a triphenylmethyl group. It has previously been used successfully in the literature to secure a cucurbit[7]uril onto an axel [129].

#### Experimental



Scheme 6.2: Synthesis of 21.

Oxalyl chloride (18  $\mu$ L, 0.2 mmols, 3 equiv) was added dropwise to a mixture of triphenylacetic acid **20** (18 mg, 0.06 mmols) and 1 mol% dimethylformamide in dry dichloromethane (10 mL). The reaction was stirred for 18 hours at room temperature. The solvent and excess oxalyl chloride were removed under reduced pressure. The acid chloride was a crystalline white solid.

The acid chloride was re-dissolved in dry dimethylsulfoxide (0.5 mL) and a solution of **19** (52.3 mg, 0.03 mmols), triethylamine (8  $\mu$ L, 0.06 mmols, 2 equiv) and 5 mol% dimethylaminopyridine in dry dimethylsulfoxide (1 mL) added. The reaction was stirred for 72 hours at room temperature. Water (10 mL) was added to precipitate the product. The product was separated by filtration and dried under vacuum. The product **21** was a light pink solid (51.53 mg, 0.02 mmols, 76 %).


Scheme 6.3: Synthesis of 23.

Oxalyl chloride (18  $\mu$ L, 0.2 mmols, 3 equiv) was added dropwise to a mixture of 3,5-diethoxybenzoic acid **22** (18 mg, 0.06 mmols) and 1 mol% dimethylformamide in dry dichloromethane (10 mL). The reaction was stirred for 18 hours at room temperature. The solvent and excess oxalyl chloride were removed under reduced pressure. The acid chloride was a crystalline white solid.

The acid chloride (8 mg, 0.04 mmols) was re-dissolved in dry dimethylsulfoxide (0.5 mL) and a solution of **19** (30 mg, 0.01 mmols), triethylamine (8  $\mu$ L, 0.06 mmols, 2 equiv) and 5 mol% dimethylaminopyridine in dry dimethylsulfoxide (1 mL) added. The reaction was stirred for 72 hours at room temperature. Water (10 mL) was added to precipitate the product. The product was separated by filtration and dried under vacuum. The product **23** was a light yellow solid but its identify could not be confirmed.



Scheme 6.4: Synthesis of 25.

Oxalyl chloride (18  $\mu$ L, 0.2 mmols, 3 equiv) was added dropwise to a mixture of 3,5-di-tert-butyl-4-hydroxybenzoic acid **24** (29 mg, 0.1 mmols) and 1 mol% dimethylformamide in dry dichloromethane (10 mL). The reaction was stirred for 18 hours at room temperature. The solvent and excess oxalyl chloride were removed under reduced pressure. The acid chloride was a crystalline white solid.

The acid chloride (6 mg, 0.02 mmols) was re-dissolved in dry dimethylsulfoxide (0.5 mL) and a solution of **19** (30 mg, 0.01 mmols), triethylamine (8  $\mu$ L, 0.06 mmols, 6 equiv) and 5 mol% dimethylaminopyridine in dry dimethylsulfoxide (1 mL) added. The reaction was stirred for 72 hours at room temperature. Water (10 mL) was added to precipitate the product. The product was separated by filtration and dried under vacuum. The product **25** was a light yellow solid but its identify could not be confirmed.



Scheme 6.5: Synthesis of 26.

Oxalyl chloride (18  $\mu$ L, 0.2 mmols, 3 equiv) was added dropwise to a mixture of 3,5-di-tert-butyl-4-hydroxybenzoic acid **24** (29 mg, 0.1 mmols) and 1 mol% dimethylformamide in dry dichloromethane (10 mL). The reaction was stirred for 18 hours at room temperature. The solvent and excess oxalyl chloride were removed under reduced pressure. The acid chloride was a crystalline white solid.

The acid chloride (6 mg, 0.02 mmols) was re-dissolved in dry dimethylsulfoxide (0.5 mL) and a solution of **19** (30 mg, 0.01 mmols), triethylamine (8  $\mu$ L, 0.06 mmols, 6 equiv) and 5 mol% dimethylaminopyridine in dry dimethylsulfoxide (1 mL) added. The reaction was stirred for 72 hours at room temperature. A solution of potassium hydroxide in water (10 mL) was added to precipitate the product. The product was separated by filtration and dried under vacuum. The product **26** was a dark yellow solid but its identify could not be confirmed.

#### Results

All four of the rotaxanes showed limited solubility, with no solubility in alkanes as desired. Rotaxanes **23**, **25** and **26** proved insoluble in NMR solvents so their synthesis could not be confirmed.

The <sup>19</sup>F NMR spectrum of rotaxane **21** confirms the presence of the  $PF_6^-$  anion with a doublet at -70.125 ppm with  $J_{P-H}^1 = 710.64$  Hz. This agrees with literature values (Table 6.1) and the <sup>19</sup>F NMR spectrum of **19**. A comparison between the spectrum for the rotaxane and **19** are shown in Figure Figure 6.6.

The assigned proton NMR spectrum can be seen in Figure Figure 6.7. The protons of the cucurbit[8]uril were assigned by comparison to the values seen in the literature and the host-guest complex **19**. The hydrogens of the triphenyl stoppers were assigned by comparison with literature values for the triphenyl acetic acid and methyl triphenyl acetamide [137–139]. The hydrogens of the alkyl chains were assigned by comparison to the <sup>1</sup>H spectra of the free guest and the host-guest complex. These were used to assign the bipyridyl hydrogens as well. The hydrogen of the amide linker could not be properly assigned.

The bipyridyl hydrogens are shifted upfield, which is indicative of the complexation of the viologen by a cucurbit[8]uril. This suggests that the rotaxane has formed successfully.

#### 6.1.3 Conclusion

In order to study the interaction of the viologen-cucurbit[8]uril in organic solvents, particularly alkanes, rotaxanes were designed to allow the unit to be soluble in those solvents. Several rotaxane synthesises were attempted and only one proved successfully; the others formed insoluble solids so could not be characterised.



Figure 6.6:  $^{19}{\rm F}$  NMR spectroscopy of the starting alkylviologen (top) and rotaxane  ${\bf 21}$  (bottom).



Figure 6.7: <sup>1</sup>H NMR spectroscopy of the starting alkylviologen (top) and rotaxane **21** (bottom). Lines indicate the shift in the position of the viologen's aromatic hydrogens due to complexation by cucurbit[8]uril. Cucurbit[8]uril's hydrogens are indicated by  $\alpha$ ,  $\beta$  and  $\gamma$ .

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# Chapter 7

# Halogen Bonding in Cucurbit[n]urils

Studying halogen bonding interactions in cucurbit[n]urils presents a new way to bind guests into this synthetic host, particularly in non-polar solvents. In this chapter the halogen bonding interaction with species of increasing complexity will be built up, starting at simple ternary amides and ending with cucurbit[n]uril. Additionally, a set of solution studies will be presented showing these halogen bonding interactions in solution.

## 7.1 The Interaction of 2,5-Diiodo-1,3,4,6-tetrafluorobenzene (29) with Two Tertiary Amides

Two simple tertiary amides, N,N-dimethylformamide (28) and N-methylpyrrolidone (9), were chosen as they are similiar to the tertiary urea functionality seen in cucurbit[n]uril (highlighted in Figure 7.1), and as it is often demonstrated that the interplay between hydrogen and halogen bonding is complex, tertiary amides eliminate the possibility of strong hydrogen bonding. 2,5-Diiodo-1,3,4,6tetrafluorobenzene (29) is a common halogen bonding donor [32]; its fluorination enhances the  $\sigma$ -hole present on the iodine [140]. Additionally, there are currently no examples in the literature of co-crystal structures between 29 and tertiary amides. The structure of all three molecules is shown in Figure 7.1.



Figure 7.1: The structures of cucurbit[n]uril (2), N,N-dimethylformamide (28), N-methylpyriddone (9) and 2,5-diiodo-1,3,4,6-tetrafluorobenzene (29).

7.1.1 The Crystal Structure of a 1:2 Co-crystal of 2,5-Diiodo-1,3,4,6-tetrafluorobenzene (29) and N,N'-Dimethylformamide (28)



Figure 7.2: The halogen bonded three molecule unit in the 1:2 co-crystal of **29** and **28**. The short contacts of the halogen bonding interaction are marked as dashed lines; other short contacts are excluded.

The procedure for crystallisation and single crystal x-ray diffraction is shown in section 2.9. The x-ray crystal structure shows the formation of a 1:2 co-crystal. This section will focus on the intermolecular interactions present: further crystallographic information can be found in A.2. The central three molecule unit is shown in Figure 7.2.

Compared to the structure seen in the pure material, the molecular structure of 29 appears unchanged. All bond lengths have changes of less than 1 % of

the bond lengths in the pure material [141, 142]<sup>1</sup>. In the co-crystal structure, 2,5-diiodo-1,3,4,6-tetrafluorobenzene does not have the expected extension of the carbon-iodine bond seen for other halogen bonded materials [33].

There are several changes to the bond lengths of **28** compared to the pure material [144]. There is a shortening of the carbonyl's carbon-hydrogen bond (0.95 Å vs an average<sup>2</sup> of 0.975 Å - a decrease of 3 %), which coincides with a change in the intermolecular interactions involving that hydrogen. In the pure material, it has a short contact with the oxygen of a carbonyl in another molecule of **28** (2.418 Å or 88.9 % of the sum of the VdW radii of the two atoms), whilst in the co-crystal, it has a much longer contact with a fluorine of **29** (2.655 Å or 99.4 % of the sum of the VdW radii). Additionally, the amide's carbon-nitrogen bond length is shortened by 1 % and the average carbon-hydrogen bond length in the methyl groups is lengthened by 1 % compared to the bond lengths seen in the crystal structure of the pure material.

The iodine - oxygen distance in the co-crystal is 2.832 Å or 80.9 % of the sum of the VdW radii of the two atoms. The interaction is almost linear with the bond angle  $\angle$  CIO being 179.39 °. The oxygen-iodine interaction is at 23.99 ° to the plane of the amide. The short interaction distance and linear nature of the interaction indicate a halogen bond between **29** and **28** [33]. There is an additional contact with the carbon of the amide: 3.57 Å or 97.0 % of the sum of the VdW radii. The plane of **29**'s ring is rotated out of the plane of the halogen bonding interaction by 71.12 °; however, computational studies for a pyridine-iodopentafluorobenzene system suggest the halogen bonding interaction has little dependence on the ring orientation [145].

<sup>&</sup>lt;sup>1</sup>There is a third polymorph reported in the literature [143] but the atomic coordinates are unavailable in the Cambridge Crystallographic Database.

 $<sup>^{2}</sup>$ The structure contains two unique molecules of **28** so an average of the bond lengths is taken.

In Figure 7.3, the contact can be seen between the oxygen of the carbonyl of **28** and a hydrogen of a methyl group on another **28**. The oxygen-hydrogen distance is 2.56 Å or 94.12 % of the sum of the VdW radii of the two atoms and the  $\angle$  CHO is 151.64 °. Both of these measurements suggest a weak hydrogen bond [31]. The interaction is close to the plane of the amide, being elevated by 11.13 ° only. These weak hydrogen bonds assemble the three molecule units into a layer consisting of stacked, zig-zag chains (Figure 7.4).



There are two short contact distances between these layers of chains. The shorter of the two is a fluorine-fluorine contact between two molecules of **29** in adjacent layers, shown in Figure 7.5a. The fluorine-fluorine distance is 2.882 Å which corresponds 98 %

Figure 7.3: Oxygen-Hydrogen interaction between adjacent molecules of **28**.

of the sum of the VdW radii of the two atoms. Halogen-Halogen interactions are broken down into two types: type I ( $\angle$  CXX  $\approx \angle$  XXC), and type II ( $\angle$  CXX  $\approx 180^{\circ}$  and  $\angle$  XXC  $\approx 90^{\circ}$ ) [146]. The  $\angle$  CFF and  $\angle$  FFC are 134.37 ° and 162.66 ° respectively. By considering the measured angles it can be concluded



Figure 7.4: Stacking of zig-zag chains of the three molecule unit via the oxygenhydrogen contacts. Black lines indicate halogen bond short contacts whilst blue lines indicate hydrogen bond short contacts.

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that this fluorine-fluorine interaction is most likely type I, and arises from the crystallographic symmetry of the system as the fluorines lie either side of a centre of inversion. The other interlayer short contact is between a fluorine on **29** and the hydrogen of the amide; the interaction is shown in Figure 7.5b. The fluorine-hydrogen distance is 2.655 Å or 99.5 % of the sum of the VdW radii. This can be assigned to a very weak hydrogen bond [31].



Figure 7.5: Illustrations of the short contacts between layers.

## 7.1.2 The Crystal Structure of a 1:1 Co-crystal of 2,5-Diiodo-1,3,4,6-tetrafluorobenzene (29) and N-Methylpyrroliddone (9)

Single crystal x-ray diffraction suggests the formation of a 1:1 co-crystal. Whilst the postion of **29** could be determined, the N-methylpyrroliddone is disordered over a 2-fold axis (Figure 7.6). Further crystallographic details can be found in A.2.

The structure of **29** found in the co-crystal is, again, very similar to that seen in the pure material [141, 142], with no changes in the bond lengths of greater than 1 %. Like the co-crystal with **28** there is no significant extension of the carbon-iodine bond, which is seen as a characteristic of a halogen bond [33]. For **9**, the bond lengths are similar to that seen in the pure material [147]. There are two reductions in bond lengths. (i) the carbonyl is shortened by 1.3 % compared to that seen in the pure material. In the pure material, the carbonyl makes several



Figure 7.6: Illustration of the disordered NMP molecules in the co-crystal

weak hydrogen bonds to the protons of the ring and the N-methyl group; in the co-crystal it makes a weak hydrogen bond with a hydrogen of the NMP ring and a much stronger interaction with the iodine of **29**. Also, (ii) the carbon-hydrogen bonds of the methyl group are shortened: the contacts have changed from the carbonyl in the pure material (2.65 Å and 2.572 Å) to the iodine and fluorine of **29** in the co-crystal (3.157 Å and 2.500 Å respectively) suggesting a reduction in intermolecular interactions involving this methyl group.

There are two different interactions between the iodine of **29** and the amide group in **9**. These are shown in Figure 7.7. In the first, there is just a short contact between the oxygen of the amide and the iodine of **29**. This is marked in black in Figure 7.7. This contact distance is 2.873 Å or 82.09 % of the sum of the VdW radii of the two atoms; longer than the contact distance in the previous co-crystal. The interaction is, again, linear ( $\angle$  CIO = 175.57°) and the angle with the carbonyl is 139.91°. The contact lies close to the plane of the amide at 36.41°. The second iodine-oxygen contact has the same iodine-oxygen distance but has a short contact with the carbon of the amide (3.625 Å or 98.5 % of the VdW radii). The  $\angle$  CIO is the same but now the  $\angle$  IOC is smaller at 119.53°; consistent with the short contact with the carbon of the amide. The short contact distances and linear nature of these interactions leads to conclusion they are halogen bonds [33]. The two interactions occur either side of the plane of the amide, as shown in Figure 7.8.



Figure 7.7: The halogen bonding interactions featuring a bifurcated oxygen acceptor. Two different halogen bonding interactions are identified: one with the oxygen and carbon of the amide (yellow) and one with just the oxygen (black).



Figure 7.8: The halogen bonding interactions take place either side of the plane of the amide.



(a) Layer formation from halogen bonded chains.



(b) Short contacts between a ring hydrogen and two carbons of **29**.

Figure 7.9: Illustrations of the layer structure and inter-chain short contact.



Figure 7.10: The short contact between a fluorine on **29** and a methyl hydrogen.

These halogen bonding interactions lead to the formation of zig-zag chains of molecules. These chains are then stack into layers as shown in Fig-There is a short conure 7.9a. tact between a hydrogen on the ring with the carbons of 29 that can be seen in Figure 7.9b. The contact distances are 2.738 Å and 2.61 Å , or 94.4 % and 90.0% of the VdW radii of the two atoms. The  $\angle$  CHC of 161.43  $^{\circ}$  and 144.82  $^{\circ}$  suggest a reasonably linear interaction. The hvdrogen is also perpendicular to the plane of the ring  $(86.79^{\circ})$  suggesting an interaction with the  $\pi$  system.

Between these layers is a set of weak interactions. There is a short contact between the fluorine of **29** and a methyl hydrogen on **9**. The contact distance is 2.500 Å or 93.63 % of the VdW radii of the atoms. This contact is shown in Figure 7.10. With  $\angle$  CHF = 129.56 ° and  $\angle$  HFC = 169.58 °, this weak hydrogen bond is the shortest contact between molecules in adjacent layers. As well as the



(a) Short contact between a iodine on **29** and a methyl hydrogen.

(b) Short contact between the oxygen of the amide and a ring hydrogen.

Figure 7.11: Illustrations of the interlayer short contacts.

fluorine, the iodines on **29** make a short contact with a methyl hydrogen. The iodine-hydrogen length is 3.157 Å. The  $\angle$  HIC is 116.21° and by considering an electrostatic potential map of **29** (Figure 7.12) [148], it is possible to conclude that this is an interaction of the hydrogen with the electron-rich region of the iodine perpendicular to the carbon-iodine bond. Lastly, the oxygen of the amide makes a short contact with a ring hydrogen. The hydrogen-oxygen distance is 2.71 Å or 99.6 % of the VdW radii. This weak hydrogen bond occurs almost perpendicular (74.60 °) to the dominate halogen bonding interaction.



Figure 7.12: Electrostatic potential energy map of 2,5-diiodo-1,3,4,6-tetrafluorobenzene. Taken from [148].

#### 7.1.3 Comparison with Structures seen in the Literature

A survey of the literature provides limited examples of halogen bonds between amides and **29**; the interaction parameters are summarised in Table 7.1. Firstly, none of the amides are tertiary making the structures presented here the first co-crystals of this kind for **29**.

The structures show two types of halogen bond: through the oxygen alone or through the oxygen and the carbon of the amide. Both these coordination types are seen in the co-crystal of **29** and **9**. The oxygen - iodine distances range

Amide	$\begin{array}{l} \mathrm{I} \cdots \mathrm{O} \setminus \mathrm{\mathring{A}} \\ (\% \ \mathrm{VdW}) \end{array}$	$\begin{array}{l} \mathrm{I}  \cdots  \mathrm{C}  \setminus  \mathring{\mathrm{A}} \\ (\%   \mathrm{VdW}) \end{array}$	$\angle \operatorname{CIO} \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	Torsional $\angle \setminus^{\circ}$	Ref.
Acetamide	2.973 (84.9)	3.614 (98.2)	176.5	116.93	[149]
N-methyl benzenamide	2.884 (82.4)	3.645 (99.0)	169.54	93.81	[1 10]
N-methyl acetamide	3.004 (85.8)	$3.515 \\ (95.5)$	173.39	81.81	[150]
${ m N,N'-bis}$ (Pyrid-3-ylmethyl) oxamide <sup>a</sup>	2.893 (82.7)	No Contact	176.23	24.45	[151]
N-(pyridin-2-yl) acetamide	2.876 (82.2)	No Contact	175.90	168.86	
N-(3-pyridyl) acetamide All halogen bond via the N-((4-pyridyl)methyl) acetamide molecular hydrogen bonds				[152]	
Isonicotinamide					[153]

Table 7.1: Summary of the interaction parameters for **29** and amide compounds seen in the literature.

 $^a$  Appears as a tertiary co-crystal with  ${\bf 29}$  and pyridine-3,5-dicarboxylic acid.

from 2.876 Å to 3.004 Å , making the two distances seen in these co-crystals (2.832 Å and 2.873 Å) the shortest contact distances seen.

Previously, amides have been used as a model compound to study the interplay between halogen and hydrogen bonding with many reported structures showing both. Hydrogen and halogen bonding interactions with amides are usually characterised using latitudinal (a) and longitudinal (b) angles of the oxygen surface. A visual description of these angles and a demonstration of them with respect to the co-crystal of 2,5-diiodotetrafluorobenzene and DMF can be seen in Figure 7.13.



(c) The latitudinal angle for the co-crystal of 29 and 28. The plane containing the amide is given in red.

(d) The longitudinal angle for the cocrystal of **29** and **28**.

Figure 7.13: Description and examples of the latitudinal and longitudinal angles.

Latitudinal and longitudinal angles for all the iodine-oxygen interactions for amides with **29** are graphed in Figure 7.14a, with the points' color corresponding to the percentage of the sum of the VdW radii for the interaction distance. Whilst the range of angles is large, the range of interaction distances is small indicating little variation with position. The shape of the point corresponds to the type of hydrogen bonding the oxygen is involved in: strong (diamonds), weak (squares) or none (circles).



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(a) Halogen bonds for amides with strong (diamonds), weak (squares) or no (circles) additional hydrogen bonding interaction.



(b) Halogen bonds for amides with strong hydrogen bonding and the corresponding N-H hydrogen bond (stars).



(c) Halogen bond for amides with weak hydrogen bonding and the corresponding C - H hydrogen bonds (stars).



Figure 7.14: Halogen and hydrogen bonding interactions for amides with **29**. Colour corresponds to the interaction distance expressed as a percentage of the sum of the VdW radii of the two atoms.

This idea is further explored in 7.14b where the angles of the halogen and its corresponding hydrogen bond are plotted. In this case, all the hydrogen bonding interactions are with the N-H bond of another amide molecule. It can be seen that the hydrogen bond lengths are short whilst the halogen bond lengths are, on the whole, longer. The hydrogen bond tends to sit closer to the plane of the amide whilst the halogen bonds are clustered perpendicular to it. This is consistent with observations of orthogonality with biological halogen and hydrogen bonding interactions as well as synthetic systems [154].

Previously, there were no examples of other interactions with the amide's oxygen except for with N-H bonds. However, the two structures presented here both contain weak hydrogen bonding interactions between the oxygen and a C-H bond. The latitudinal and longitudinal angles for these hydrogen and their corresponding halogen bonding interactions are shown in 7.14c. In a reversal of that seen for hydrogen bonding to N-H bonds, the halogen bonds are shorter and the hydrogen bonds are longer. Additionally, the halogen bonds tend to be closer to the plane of the amide and the hydrogen bonds perpendicular to it.

Taking these two observations into account, it can be seen that those halogen bonding interactions without additional hydrogen bonding present (circles in 7.14a) are generally shorter and closer to the plane of the amide, like the co-crystals presented here, whose amide oxygen is involved in weak hydrogen bonding.

#### Halogen Bonding involving N,N-dimethylformamide

There are several examples of halogen bonds between carbon - iodine and N,Ndimethylformamide in the literature [155–164]. The halogen bond we have reported for the co-crystal of **29** with **28** is the shortest reported C - I...O distance (2.832 Å) for **28**; however, the halogen bonding interaction between **28** and diiodoacetylene is very close (2.834 Å) [156].

As seen for **29** there is a wide range of different interactions involving the amide's oxygen. They can be broken down in three groups depending on the nature of additional hydrogen bonding taking place. Whilst the **28** has no hydrogen

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bond donor sites, several of the structures exhibit hydrogen bonding to water molecules [155, 158, 161], often bound to metals [155, 161]; these are assigned as strong hydrogen bonds. Unlike amides interacting with **29**, weak hydrogen bonding interactions with either alkyl C-H bonds [134, 159, 162, 164] (such as the methyl groups of **28**) or aromatic C-H bonds [155, 158, 163] are present. These are grouped as weak hydrogen bonding interactions. Lastly, there is a group of structures with no additional interactions [156–158, 164]. Within this group are examples of the amide's carbonyl acting as a bifurcated acceptor [156, 157]; these will be discussed later in regard to the co-crystal of **29** and **9**.

As before the interactions will be discussed in terms of their latitudinal and longitudinal angles to see whether the patterns seen for the **29** and amide acceptors remain, and how this new co-crystal of **29** and **28** fits in the literature. All the C - I···O interactions are summarised in Figure 7.15a. The general appearance of these plots appears similar to halogen bonds to **29** in Figure 7.14a with two areas: clustered around the poles or the equator. In contrast to the interactions of **9** the variation in interaction distance is larger; this is due, in part, to the variation of donor molecules used as electron density on the donor plays an important part in determining the strength of interaction.

For the halogen bonding interactions where the oxygen is also engaged in strong hydrogen bonding, the general trend is the same as for **29**, with the halogen bonding interactions tending to be longer and more perpendicular to the plane of the amide and the hydrogen bonding interactions shorter and closer to the plane of the amide. Several structures contain mixes of strong and weak hydrogen bonding (triangles); their behaviour is consistent with just having the strong hydrogen bonding interaction.

The orientation for halogen bonding and weak hydrogen bonding interactions (Figure 7.15c) is less clear. Whilst the halogen bonding interactions tend to be shorter and the hydrogen bonding interactions longer, there appears a wider range of orientations. Those systems that contain both types of hydrogen bonding appear perpendicular to the plane of the amide (consistent with the strong hydrogen bonds lying close to the plane). For halogen bonding interactions with only additional weak hydrogen interactions the trend is weaker, and the halogen interactions generally lie closer to the plane of the amide than the hydrogen

interactions.



(a) Halogen Bonds for **28** with strong (diamond), weak (square), both (triangle) or no (circle) additional hydrogen bonding interaction.



(b) Halogen Bonds for **28** with just strong hydrogen bonding (diamond), both strong and weak hydrogen bonding (triangle) and the corresponding strong hydrogen bond (stars).



(c) Halogen Bonds for **28** with weak hydrogen bonding (square), both strong and weak hydrogen bonding (triangle) and the corresponding alkyl (circle) or aromatic (star) C-H hydrogen bonds.



Figure 7.15: Halogen and Hydrogen bonding interactions for **28** with C - I donors. Colour corresponds to the interaction distance expressed as a percentage of the sum of the VdW radii of the two atoms.

#### Halogen Bonding Interactions Involving N-methyl-2-pyrrolidone

Whilst **29** is a very common halogen bond donor and **28** appears to be a common acceptor, there is only one example of **9** acting as an acceptor for a C - I bond [165]. If the search is widened to C - X bonds then there is a second example featuring a C - Cl bond [166]. For the C - I  $\cdots$  O contact, **9** is interacting with 3,4-diiodofuran (**30**); both the structure of **30** and the short contacts in the crystal structure involving the amide's carbonyl are shown in Figure 7.16.

Unlike the co-crystal with **29**, the amide is only involved with a single iodine. However, the structure shows two distinct halogen bonds: one with the oxygen alone, and one with the oxygen and the carbon of the carbonyl. These two motifs are present on a single amide in the co-crystal with **29**.



(a) Molecular Structure(b) Crystal Structure showing short contacts (dashed) involving of 3,4-Diiodofuran (**30** the amide of **9**.

Figure 7.16: Structure of 3,4-diiodofuran (**30**) and the Crystal Structure of the 1:2 co-crystal of **9** and **30**.

The interatomic distances and angles for the halogen bonding interactions are summarised in Table 7.2. The C - I  $\cdots$  O distance in **29** ·**9** (2.873 Å) is shorter than either of the distances seen in this structure (2.888 Å or 2.901 Å). However, the halogen bonds present in the literature structure are more linear and lie closer to the plane of the amide.

In both structures, the amide is engaged in additional hydrogen bonding; a

summary of the interaction distances and angles is given in Table 7.3. In the co-crystal with **29** shown here, the hydrogen bonding is weak with a longer  $H \cdots O$  distance and, like seen earlier, lies close to perpendicular to the amide plane. In the structure with **30**, the hydrogen bonding is stronger with a much shorter  $H \cdots O$  distances and, in terms of a percentage of the sum of VdW radii, it is close in length to the halogen bonding interaction. As was seen for **29** interacting with amides and **28** interacting with halogen bond donors earlier, this strong hydrogen bonding interaction occurs closer to the plane of the amide.

Table 7.2: Summary of the Halogen Bonding interactions present in the two co-crystals involving **9** 

Co-Crystal	$\mathrm{I} \cdots \mathrm{O} \setminus \mathrm{\AA}$ (% VdW)	$\mathrm{I} \cdots \mathrm{C} \setminus \mathrm{\mathring{A}}$ (% VdW)	$\angle CIO$ \°	$\begin{array}{c} \text{Torsional} \\ \angle \backslash^{\circ} \end{array}$	Ref.
29.9	2.873(82.09)	3.625 (98.51)	175.57	155.8	
	$2.873 \ (82.09)$	None	175.57	-36.41	
$30.9_2$	2.888 (82.51)	$3.655\ (99.32)$	177.99	175.95	[16]
	$2.901 \ (82.89)$	None	176.88	176.19	[105]

Table 7.3: Summary of the additional Hydrogen Bonding interactions present in the two co-crystals involving **9** 

Co-Crystal	$egin{array}{lll} \mathrm{H} \cdots \mathrm{O} \setminus \mathrm{\AA} \ (\% \ \mathrm{VdW}) \end{array}$	∠ CHO \°	$\begin{array}{c} {\rm Torsional} \\ {\scriptstyle \angle \setminus ^{\circ}} \end{array}$	Ref.
29.9	2.71 (99.63) 2.71 (00.62)	162.91	58.54	
80.0	2.211 (99.03) $2.299 (84.22)$	162.91 152.77	-127.18 23.94	[105]
<b>30</b> ·9 <sub>2</sub>	$2.252 \ (82.79)$	157.27	9.76	[105]

In the co-crystal of **29** and **9** the oxygen of the amide acts as a bifurcated acceptor allowing for the formation of chains. There are several examples of amides acting as bifurcated acceptors for C-I bonds in the literature [156, 157, 167–171], and they can be broken down by the number of contacts made with the oxygen.

Those that only make short contacts with the two iodines [156, 168, 169, 171]

and sets that make an additional one [157, 170] and two contacts [167]. It is to latter class that the co-crystal presented here belongs.

Previously a hierarchy of interactions (Strong Hydrogen Bonds > Halogen Bonds > Weak Hydrogen Bonds) and positions (In the same plane as the amide > perpendicular to the amide)was established. This continues when dealing with bifurcated acceptors. In the structure published by Waldmann as well as two short contacts with iodines (3.025 Å and 3.042 Å), the oxygen of the amide makes two short contacts with hydrogens (2.176 Å and 2.436 Å) in N - H bonds [167]. Those hydrogen bonding interactions lie close to the plane of the amide, whilst the halogen bonding interactions occur perpendicular to the plane as shown in Figure 7.17. In the cocrystal of **29** and **9** the oxygen makes two additional contacts with hydrogens in C-H bonds. These are weaker



Figure 7.17: Longitudinal and Latitudinal angles for halogen bonds and hydrogen bonds in cocrystal **29**.**9** (circle / square) and the structure reported by Waldmann (diamond / triangle). The color of the marker indicates the interaction distance as a percentage of the sum of the VdW radii of the atoms involved.

than the corresponding hydrogen bonding in previous structure ( $H \cdots O = 2.71$  Å for both). Correspondingly, the halogen bonding interactions now lie closer to the plane of the amide and the hydrogen bonding interactions away from it. This can be seen in Figure 7.17.

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## 7.2 Halogen Bonding in Cucurbit[n]urils

## 7.2.1 Suitable Solvent System for Halogen Bond Donors and Cucurbit[n]uril

The halogen bond donors 2,5-diiodo-1,3,4,6-tetrafluorobenzene (29) and 2,4,6-triiodo-1,3,5-trifluorobenzene (31) are not soluble in water, so a suitable solvent system had to be found. The results of solubility trials are shown in Table 7.4. Formic acid is a common solvent for cucurbit[n]uril so was used as basis for these tests. The formic acid - pyridine and the formic acid - heptane mixtures were taken forward for crystallisation studies, and only the miscible mixture formic acid-pyridine for solution studies.

Table 7.4: $\$$	Solubility of cucurbit[n]	uril and	2,5-diiodo-1	1,3,4,6-tetrafl	uorobenzene
( <b>29</b> ) in 1:1	two solvent systems.				

		Solubility of		
Solvent 1	Solvent 2	C1:+[]:1	2,5-diiodo-1,3,4,6-	
		Cucurbit[ii]ufii	tetra fluor ob enzene	
Formic Acid		Soluble	Not Soluble	
Formic Acid	Water	Soluble	Not Soluble	
Formic Acid	Ethanol	Not soluble	Soluble	
Formic Acid $^{a}$	Heptane	Soluble	Soluble	
Formic Acid	Pyridine	Soluble	Soluble	
Formic Acid	Tris-(2-ethyl	Not Soluble	Soluble	
	hexyl)amine	Not Soluble		
Formic Acid	Triethylamine	Not Soluble	Soluble	

 $^{a}$ Immiscible Mixture

## 7.2.2 The Interaction of Halogen Bond Donors with Pyridine

The halogen bond donors used in this study show two different types of connectivity: bifunctional (2.5-diiodo-1,3,4,6-tetrafluorobenzene **29**), and trifunctional (2,4,6-triiodo-1,3,5-trifluorobenzene **31**). The structure of **29** can be seen in Figure 7.1 and the two new structures can be seen in Figure 7.18. In formic acid / pyridine mixtures, there was the possibility of precipitating the pyridine co-crystal.



Figure 7.18: The structures of 2,4,6-triiodo-1,3,5-trifluorobenzene **31** and pyridine **32**.

#### Crystal structure of a 1:2 co-crystal of 2,5-diiodo-1,3,4,6-tetrafluorobenzene (29) and pyridine (32)

To investigate the possible interaction between 2,5-diiodo-1,3,4,6-tetrafluorobenzene (29) and pyridine (32), a co-crystal was precipitated from a pyridine solution of 29 via the diffusion of water. A stoichiometry of 1:2 was shown via x-ray diffraction.

Comparing the structure of the 2,5-diiodo-1,3,4,6-tetrafluorobenzene seen in the crystal structure of the co-crystal with that of the pure material structures seen in the literature [141, 142], there is little change in the average carbon-fluorine bond lengths (1.348 Å vs 1.351 Å or 1.346 Å) or average carbon-carbon bond lengths (1.380 Å vs 1.372 Å or 1.382 Å). There is a lengthening of the carbon-iodine bonds (2.108 Å vs 2.079 Å or 2.075 Å). This is consistent with increasing contact. In the structure described by Pawley, the iodine has no short intermolecular contacts and the carbon-iodine bond length is 2.075 Å. In the structure observed by Friščić, the iodine has two iodine-iodine intermolecular short contacts (3.956 Å, 99.9 %) and a longer carbon-iodine bond at 2.079 Å. In this co-crystal, the iodine has short intermolecular contacts with the nitrogen (2.835 Å, 80.3 %) and *ortho*-carbon (3.533 Å, 96 %) of the pyridine as well as two carbons in an adjacent 2,5-diiodo-1,3,4,6-tetrafluorobenzene (3.636 Å and 3.631 Å, 98.8 % and 98.7 %). Coincidentally there is a lengthening of the carbon-iodine bond to 2.108 Å. Lengthening of the carbon-iodine bond is considered an

indicator of halogen bond formation [33].

The structure of the pyrdine in the co-crystal is similar to that seen in the crystal structure of the pure material [172]. There is a slight shortening of the carbon-nitrogen bond (1.317 Å vs an average of 1.336 Å) of the carbon involved in the short intermolecular contact with the iodine of 2,5-diiodo-1,3,4,6-tetrafluorobenzene, as well as a general decrease in the length of the carbon-hydrogen bonds (averages of 0.950 Å vs 0.964 Å). However, this is distorted by an interaction in the pure material between the *ortho*-hydrogen on one ring with the nitrogen of another.

The symmetric halogen-bonded three molecular unit is shown in Figure 7.19. The iodine-nitrogen contact distance is 2.835 Å or 80.3 % of the Van de Waals radii of the two atoms. The bond angle  $\angle$  CIN is 173.53 °, and so close to the expected 180° predicted from  $\sigma$ -hole theory [34] and collaborated by calculations [140]. The pyridine is rotated to make a further short contact between the *ortho*-carbon of the pyridine and the iodine. This results in two different values for  $\angle$  INC. One side is turned towards the iodine (111.27 °), and the other away (131.24 °). Additionally, the plane containing the pyridine is rotated by 20.15 ° with respect to the plane of the ring in **29**, although calculations show little dependence of the halogen bonding interaction on the relative orientation of the rings [145].

2,5-Diiodo-1,3,4,6-tetrafluorobenzene completes both of its available halogen bonding opportunities. The pyridines rotate in the same direction to make the short contact between an *ortho*-carbon and the iodine.



Figure 7.19: The halogen bonded three molecule system. Dotted lines indicate short contacts.



(a) Stacking of the three molecule unit via iodine-carbon contacts.



Figure 7.20: Illustration of the inter-unit structure of the co-crystal.

The packing of these three-molecular units can be seen in Figure 7.20a. They appear to be linked via iodine-carbon contacts of length 3.636 Å and 3.631 Å corresponding to 98.8 % and 98.7 % of the Van der Waals radii of the two atoms. Consulting the electrostatic potential surface of 2,5-diiodo-1,3,4,6-tetrafluorobenzene [148], it is possible to understand this interaction as one between the electron-rich region on the iodine perpendicular to the carbon-iodine bond with the electron-poor carbons of the ring. The angle between these carbons and the carbon-iodine bond ( $\angle$  CIC = 77.6 ° and 99.55 °) is consistent with an interaction with this perpendicular electron rich region; in fact, if the midpoint of the carbon-carbon bond is taken, the angle is 88.63 °. This motif can be seen in two further structures in the literature: a co-crystal with 1,1'-bis(pyridin-4-ylmethyl)-1H,1'H-2,2'-biimidazole [173], and one

with bis(N-((4-pyridyl)methyl)acetamide) [152]. These stacks are then arranged into herringbone layers (Figure 7.20b), and these layers are stacked against each other (Figure 7.20c).

### The Crystal Structure of a 2:3 Co-crystal of 2,4,6-Triiodo-1,3,5-Trifluorobenzene (31) and Pyridine (32)

To investigate any potential interactions with pyridine a crystal was precipitated from a pyridine solution of **31** via the diffusion of water. The crystal was determined to a 2:3 co-crystal of 2,4,6-triiodo-1,3,5-trifluorobenzene-pyridine via x-ray diffraction. The co-crystal's crystal structure is shown in Figure 7.21. As



Figure 7.21: Halogen bonding interaction seen in the 2,4,6-triiodo-1,3,5-trifluorobenzene-pyridine co-crystal. Short contacts are denoted by dashed lines.

expected, it shows only two nitrogen-iodine interactions per molecule of **31**. One of the pyridines bridges between two molecules of **31** with symmetric nitrogen-iodine interactions.

In comparison with the crystal structure of **31** [174], there is a slight expansion of the ring with the average carbon-carbon bond length increasing from 1.378 to 1.385 Å, consistent with the donation of electron density into the system. There is a lengthening of the carbon-fluorine bonds (the average bond length increases from 1.329 to 1.344 Å), but there is little correlation with fluorine short contacts. For example, one of the fluorines has short contacts to a carbon and a hydrogen in the pyridine and a bond length of 1.343 Å, whilst another fluorine that has no intermolecular short contacts has a carbon-fluorine

bond length of 1.344 Å. The carbon-iodine bonds show lengthening with the average bond length increasing from 2.073 to 2.092 Å; however, this lengthening correlates strongly with the iodine's environment. The iodine with the longest carbon-iodine bond (2.112 Å) has three short contacts with carbon (3.636 Å, 98.8 % of the sum of the VdW radii), nitrogen (2.835 Å, 80.3 %) and iodine (3.955 Å, 99.9 %). The next longest (2.085 Å) only has a short contact with nitrogen (3.051 Å, 86.3 %), whilst the shortest (2.079 Å) has a short contact with iodine (3.955 Å, 99.9 %) and fluorine (3.416 Å, 99.0 %).

The pyridine that is halogen bonded to a single molecule of **31** has a structure very similar to that seen in the crystal structure of pure pyridine with all its bond lengths lying within observed error. The other pyridine is different: whilst its carbon-hydrogen bond lengths appear the same, the carbon-carbon bond lengths are shorter (1.364 and 1.359 Å) than the average lengths seen in the other pyridine of the structure (1.377 and 1.373 Å) and the solid pyridine structure (1.381 and 1.373 Å).

The structure shows two distinct halogen bonding interactions. The first, between a pyridyl nitrogen and a single iodine of **31**, has a nitrogen-iodine distance of 2.835 Å or 80.3 % of the VdW radii. The  $\angle$  CIN is 176.04 °, which is close to the expected 180 °. The angle between the plane containing the ring of the pyridine and the iodine is 168.36 °. The pyridine which is interacting with two iodines has a nitrogen-iodine length of 3.051 Å or 86.3 % of the VdW radii. The  $\angle$  CIN is 165.65 °, which is close to the expected 180 °. The angle between the plane containing the ring of the pyridine and the iodine is 133.46°. The DFT simulations presented by Van der Boom predicted a nitrogen-iodine distance of 2.822 Å or 79.9 % of the VdW radii for a two pyridine system. Whilst is unfair to compare this to the halogen bonding interaction of the bridging pyridine, the singly bonded pyridine has a nitrogen-iodine length comparable to this: 2.835 Å.

#### Discussion

Halogen bonding interactions involving **29** and pyridyl donors are common in the literature, with 79 out of  $208^3$  crystal structures that feature **29** in the CCDC

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 $<sup>^{3}</sup>$ CSD Version 5.37

having pyridyl donors. As with the amides, this interaction can be interpreted in terms of latitudinal (a) and longitudinal (b) angles with respect to the nitrogen of the pyridine. The longitudinal angle is chosen as the smaller of the two  $\angle$  INCs. These two angles are illustrated in Figure 7.22



Figure 7.22: Illustrations of the latitudinal (a) and longitudinal (b) angles for pyridyl donors.

These longitudinal and latitudinal angles are shown in Figure 7.23a. A general trend can be seen. The closer to the plane of the pyridine and the closer the  $\angle$  INC is to 120 °, the shorter the interaction distance between the nitrogen and the iodine. Within the range of -30 ° to 30 ° for latitudinal and 0 ° to 30 ° for longitudinal angles, there appears to be little sensitivity, with most interaction distances lying between 80 and 90 % of the sum of the VdW radii. However, outside of this region there are few interactions, suggesting a narrow band where interactions are possible, but little variation within that band beyond the general trend described above. The interaction in the structure presented here is highlighted by a black outline on the diagram. It sits comfortably in the trends seen for other pyridyl donors.

The same analysis can be applied to structures of **31** with pyridyl donors seen in the literature. This can be seen in Figure 7.23b. The results follow the trend seen for **29**, with a tight grouping of results between latitudinal angles of 30 ° and -30 ° and longitudinal angles up to 30 °. Again, the interaction distances are pretty contstant in this region, with a slight trend of shortening with lower angles. In contrast to the plot for **29**, there are a few examples of interactions at steeper angles. As expected these interaction distances are noticably longer than those at lower angles. The interaction distance for the single interaction pyridine is highlighted with a black border and follows the trends seen in the literature.



Figure 7.23: Latitudinal and longitudinal angles for interaction between **29**, **31** and pyridyl acceptors. The point corresponding to the structure presented here has a black border. Colour corresponds to the interaction distance expressed as a percentage of the sum of the VdW radii of the two atoms.



Figure 7.24: Latitudinal and longitudinal angles for interaction between pyridine and iodine donors. The point corresponding to the structure presented here has a black border. Colour corresponds to the interaction distance expressed as a percentage of the sum of the VdW radii of the two atoms.

There are few examples of crystal structures containing halogen bonding interactions involving a pyridine and an iodine acceptor in the literature. The longitudinal and latitudinal angles for these interactions are shown in Figure 7.24. The general trend seen for 29 and **31** continues here: inthe teraction distances are shorter for lower angles. Noticeably the interaction distance rises more quickly as the longitudinal angle increases thanwhen the latitudinal angle does. The structures presented in this section are highlighted with Both fit with the black outlines. general trend seen in the literature.

The three plots above can be elabo-

rated upon by comparison with a electrostatic potential map of pyridine. The maps shown in Figure 7.25 were calculated using MOPAC. As expected, the nitrogen has increased electron density and there is a reduction of electron density on the hydrogens. It can be seen that the electron-rich region extends latitudinally more than longitudinally. This explains the different rates of interaction distance lengthening with angle increase.

In the co-crystal of **31** and pyridine there are two distinct halogen bonding interactions. One pyridine interacts with a single iodine whilst the other acts as a bifurcated acceptor bridging between two molecules of **31**. Pyridines acting as a bifurcated acceptor for carbon-iodine bonds are a rare motif. Jones *et al* showed the existence of two types of interaction. In Type I interactions, the two halogen bonds are approximately symmetrically distributed above and below the plane of the pyridine's ring. In Type II interactions, one halogen bond lies in the plane of the pyridine's ring and the other perpendicular to it.



Figure 7.25: Electrostatic potential map of pyridine from the side (left) and the top (right).

The interaction parameters for the structures found in the literature are shown in Figure 7.26. The two types of interaction can be clearly seen. For Type I, both interactions have similar lengths and are distributed either side of the plane of the pyridine ring. For Type II, there are a cluster of points corresponding to short interaction distances that appear at small longitudinal and latitudinal angles, whilst a second group with long interaction distances appear closer to the poles. The interaction in the co-crystal presented here is highlighted by a black border. It sits well with the Type I interactions. It is the third symmetric Type I interaction seen and the second involving **31**; however, the iodine-nitrogen distances seen here are shorter (3.051 Å compared to 3.224 Å).

## 7.2.3 Crystallisation of the Halogen bond Donors with Cucurbit[n]uril

A solution of the halogen bond donor layered on top of a solution of cucurbituril in formic acid was used in attempts to crystallise a halogen-bonded inclusion complex. Whilst crystals could be obtained, a good quality diffraction pattern could not.



Figure 7.26: The latitudinal and longitudinal angles for Type I (circle) and Type I (diamond) bifurcated pyridyl halogen bond acceptors.

# 7.3 Solution NMR Studies of Halogen Bonding in Cucurbit[n]urils

This section describes NMR experiments to determine if halogen bond donors are complexed by cucurbit[n]urils in solution. Three systems were chosen showing a range of molecular architectures and solvents.

### Iodomethane (33) and Cucurbit[6]uril (34) in Water and Formic Acid-Water mixtures

The structures of these two molecules are shown in Figure 7.27. Most cucurbituril studies are conducted in water where the molecule is most soluble; however, typical halogen bond donors such as **29** or **31** are not water soluble. Iodomethane is a simple iodoalkane that is water soluble, and so is a good starting point.

#### 4,4'-diiodooctafluoroazobenzene (35) and Cucurbit[8]uril (36)

Synthesised by Dr Tomislav Friščić and Alex Bushuyev (Department of Chemistry, McGill University, Canada), 4,4'-diiodooctafluoroazobenzene has shown potential as a photo-responsive material, as well as a useful halogen bond donor [175]. Azobenzenes are a common molecular motif for guests for cucurbit[8]uril to create photoresponsive systems [176–186].



Figure 7.27: The structures of some of the molecules used in solution studies. The structure of **29** was shown in Figure 7.1.
## 7.3.1 Complexation of Iodomethane by Cucurbit[6]uril in Water and a Formic Acid-Water Mixture

### NMR Spectroscopy of Iodomethane in Water

The <sup>1</sup>H spectrum of iodomethane can be seen in Figure 7.28. As expected, it is a single peak at 2.09 ppm. This is consistent with values seen in the literature [187–189].

## NMR Spectroscopy of a 1:1 mixture of Iodomethane and Cucurbit[6]uril in Water

The <sup>1</sup>H NMR spectrum of a 1:1 mixture of **33** and **34** can be seen in Figure 7.28. The resonance for the methyl iodide is shifted by 0.83 ppm to 1.26 ppm with the addition of **34**. Integration confirms a 1:1 mixture present.



Figure 7.28: <sup>1</sup>H NMR spectra of methyliodide (lower) and a mixture of methyliodide and cucurbit[6]uril (upper) in water. Cucurbit[6]uril peaks are marked with diamonds.

#### NMR Spectroscopy of Iodomethane in Formic Acid - Water

The <sup>1</sup>H spectrum of iodomethane can be seen in Figure 7.29. The peak corresponding to the methyl group has been shifted to a lower value of 0.6432 ppm.

## NMR Spectroscopy of Cucurbit[6]uril in a Formic Acid - Water Mixture

The <sup>1</sup>H NMR spectrum of cucurbit[6]uril has the characteristic doublet-singletdoublet structure seen for these homologues. However, all peaks have an upfield shift. The coupling constant for the geminal coupling between the protons of the methylene group is 15.5 Hz.

## NMR Spectroscopy of a 1:1 mixture of Iodomethane and Cucurbit[6]uril in a Formic Acid - Water Mixtures

The proton NMR spectrum for the mixture of iodomethane and cucurbit[6]uril appears to show two resonances for the protons of the iodomethane. This suggests that the exchange between the complexed and uncomplexed states for the iodomethane is slow compared to the NMR time scale. The presence of these two peaks allows for the calculation of the equilibrium constant for the complexation of iodomethane; k = 120.49.

#### Discussion

The upfield shift of a guest's protons was quickly adopted as a sign of encapsulation by a cucurbit[6]uril. This shielding effect arises from the low polarisability of the molecule's interior. From the shift seen on the additional of **34** to a solution of methyl iodide in water, it can be concluded that **33** is complexed. For the formic acid - water mixture, an upfield shifted peak is seen in addition to the original peak. Variation in the chemical shifts for the formic acid - water mixtures may be due to variation in the solvent due to evaporation of the formic acid.

The encapsulation of methane was shown in solution [190] and gas sorption isotherms [191]. In water (pH 3) the binding constant was  $< 2 \times 10^3$  M<sup>-1</sup>,



Figure 7.29: <sup>1</sup>H NMR spectra of methyliodide (lower), cucurbit[6]uril (middle) and a mixture of methyliodide and cucurbit[6]uril (upper) in a formic acid - water mixture.

whilst in a sodium acetate solution (pH 5.5) it was  $< 0.05 \times 10^3 \text{ M}^{-1}$ . Complexation was confirmed via <sup>1</sup>H NMR spectroscopy with short hydrocarbons used showing an upfield shift of 0.71 - 0.92 ppm: this is consistent with the shift of 0.83 ppm seen here. However, for these alkanes exchange appeared slow on the NMR timescale: with resonances present for both complexed and uncomplexed material. This contrasts with the results for **33** where only a single peak is seen, with no evidence of a peak corresponding to the uncomplex molecule at 2.09 ppm. However, it chimes with that seen for the formic aicd - water mixtures, which suggests a possible capping of the cucurbituril.

Whilst these results suggest differing complexation behaviour a solution NMR titration experiment with increasing concentrations of methyliodide would allow for more conclusive probing of these systems.

## 7.3.2 Complexation of 4,4'-Diiodooctafluoroazobenzene (35) by Cucurbit[8]uril (36) in DMSO

# $^{19}{\rm F}$ NMR spectroscopy of 4,4'-diiodooctafluoro-trans-azobenzene (35) in DMSO

The <sup>19</sup>F NMR spectrum of **35** in DMSO is shown in figure 7.31b. The two peaks seen are consistent with the symmetry of the molecule and the number of environments present, as shown in figure 7.31a.



(a) Structures and fluorine labelling for 2,5-diiodo-1,3,4,6-tetrafluorobenzene (**29**), 4-iodo-2,3,5,6-tetrafluoroaniline (**37**) and a 4-iodo-2,3,5,6-tetrafluoroazobenzene derivative (**38**).

Molecule	Solvent	$\frac{\delta \text{ (Fluorine a)}}{ \text{ ppm}}$	$\delta \text{ (Fluorine b)} \\ \setminus \text{ ppm}$	Reference
29	d <sub>3</sub> -MeCN	-11	19.6	[192]
29	$\mathrm{CDCl}_3$	-11	8.55	[193, 194]
29	$d_{12}$ -Pentane	-11	9.44	[195,  196]
<b>37</b>	$CDCl_3$	-124.41	-159.9	[107]
38	$CDCl_3$	-122.48	-151.12	[197]

(b) Summary of the <sup>19</sup>F NMR spectra.

Figure 7.30:  $^{19}\mathrm{F}$  chemical shifts and structures for similiar molecules seen in the literature.

The assignment of these peaks was done by comparison with similar molecules seen in the literature; these molecules and their chemical shifts are summarised in Figure 7.30.



(a) The structure and fluorine assignments.



(b) The <sup>19</sup>F NMR spectrum.

Figure 7.31: The <sup>19</sup>F NMR and assignments for 4,4'-diiodo-2,3,5,6,2',3',5',6'- octafluoro-*trans*-azobenzene (**35**).

The fluorines adjacent to the iodine in 1,4-diiodo-2,3,5,6-tetrafluorobenzene **29** have shifts of -118 to -119 ppm [192–196] depending on solvent choice. The

nitrogen substituted molecules **37** and **38** have two resonances each; one at -122 to -124 ppm, and another at -151 to -159 ppm [197]. Through comparison with **29**, the less negative chemical shift is assigned to the fluorine adjacent to the iodine, whilst the more negative chemical shift is assigned to the fluorine adjacent to the nitrogen substituent. The same logic leads to the assignment seen in Figure 7.31 for molecule **35**.

### <sup>19</sup>F NMR Spectroscopy of Cucurbit[8]uril (36)

The <sup>19</sup>F spectrum of the Cucurbit[8]uril has a pair of resonances at -68.737 and -70.627 ppm, shown in figure Figure 7.32. These were assigned to a doublet ( $\delta = -69.682 \text{ ppm}, \text{J}_{F-P}^1 = 710 \text{ Hz}$ ) due to the presence of PF<sub>6</sub><sup>-</sup>. This was assigned by comparison with shifts and coupling constants seen in the literature (shown in figure Table 7.5).



Figure 7.32: <sup>19</sup>F NMR spectrum of cucurbit[8]uril.

Molecule	Solvent	$\delta \; \backslash \; \mathrm{ppm}$	$\mathbf{J}_{F-P}^1 \setminus \mathbf{Hz}$	Reference
$\mathrm{PF}_6^-$	$d_6$ -DMSO	-76.9	711	[130]
$NBu_4PF_6$	$d_3$ -MeCN	-69.8	707	[101]
$\mathrm{LiPF}_{6}$	$d_3$ -MeCN	-69.8	707	[131]
$\mathrm{LiPF}_{6}$	$\mathrm{d}_6\text{-}\mathrm{PC} \setminus \mathrm{d}_6\text{-}\mathrm{DMC}$	-72.4	708	[132]

Table 7.5: Summary of the  $^{19}\mathrm{F}$  NMR spectra for  $\mathrm{PF}_6^-$  seen in the literature.

### <sup>19</sup>F NMR Spectroscopy of a Mixture of 35 and 36

The NMR spectrum of the 1:1 mixture showed the two signals associated with the free **35** as well as the doublet due to the  $PF_6^-$  impurity present in the **36** ( $\delta = -69.715$ ,  $J_{F-P}^1 = 710.64$  Hz). Additionally, there were two new peaks, each shifted downfield relative to free **35** as shown in Figure 7.33.



Figure 7.33: Additional peaks (marked with a +) which appear in the <sup>19</sup>F NMR spectrum of a mixture of trans-azobenzene (**35**) and cucurbit[8]uril.

#### Discussion

Nau *et al* showed that the inclusion of hexafluorobenzene as well as other perfluorinated molecules in cucurbit<sup>[7]</sup>uril resulted in a downfield shift in the fluorine NMR [198]. They reported that none of the guest molecules showed complexation with 36. This, coupled with their resemblance to the free 35 peaks, meant that these peaks were assigned as complexed **35**.

Azobenzyl derivatives have been shown to bind to cucurbit[8]uril and cucurbit[7]uril in the cis-isomer [199, 200]. This conformation change upon binding has been confirmed in solid state structures [201, 202]. The binding constants were small:  $< 10^3$  M<sup>-1</sup> (cucurbit[8]uril) and  $1.03 \pm 0.02 \times 10^3$  M<sup>-1</sup> (cucurbit[7]uril). This weak binding means that it is often excluded in favour of other binders such as cyclohexylamine [200] or viologens [199, 202, 203]. However, the trans isomer is an effective second guest for the formation of ternary complexes in cucurbit[8]uril. The inclusion of azo groups allows for photocontrol of the release of molecules [176], the formation of polymers [177] and the assembly of hybrid raspberry-like particles [178, 179], polymer microcapsules [180], supramolecular nano-particles [181, 182] and particles [183–185] and bacteria [186] at functionalised surfaces.



Figure 7.34: The structures of the (a) trans and (b) cis isomers of 35. Structures redrawn from crystal structures presented in [175].

Based on the evidence in the literature, it can be assumed that the azobenzene molecule switches to the *cis* isomer to maximise space filling within the cavity. However, this isomerisation can be prevented if interactions with the carbonyl portals (e.g. ammonium ions) are sufficiently strong.

#### 7.4. CONCLUSIONS

The crystal structures, Figure 7.34, of both trans- and cis-4,4'-diiodoocta-

fluoroazobenzene have been recorded and so allow comparison of their shape with the cavity in cucur-The distance between a bit[8]uril. oxygen in the upper portal of cucurbit[8]uril with its counterpart in the lower portal is 6.165 Å. The iodineiodine distance in the *trans* isomer is 13.207 Å , whilst in the cis isomer it is 9.747 Å. The VdW radii of oxygen and iodine are, respectively, 1.52 and 1.98 Å. Defining an interaction as having an interatomic distance shorter than the sum of the VdW radii of the two atoms, it is possible to show that even if the upper oxygen and iodine are at the minimum interaction distance, the distance between



Figure 7.35: Comparison of the interoxygen distance in cucurbit[8]uril with the inter-iodine distances in the *trans* and *cis* isomers of **35**.

the lower oxygen and iodine is greater than the sum of the VdW radii, which suggests that only one iodine can interact with the cucurbituril's carbonyls. For the *cis* isomer it is possible for both iodines to interact with carbonyls. This is summarised in Figure 7.35.

## 7.4 Conclusions

In this chapter, the crystal structures of 2,5-diiodo-1,3,4,6-tetrafluorobenzene with two tertiary amides (dimethylformamide and N-methylpyrrolidone) were presented. These structures each exhibited halogen bonding interactions and had the shortest iodine-oxygen distances for amide interactions with **29** and halogen bonding interactions for either tertiary amide. Both systems followed the general structural trends seen in the literature, with these shorter interactions lying closer to the plane of the amide. The co-crystal with N-methylpyrrolidone features the amide acting as a bifurcated acceptor for both halogen and hydrogen bonding interactions. In contrast to another example in the literature,

the weaker hydrogen bonding interactions here meant that the halogen bonding interactions occured closer to the plane of the amide rather than perpendicular to it as in [167].

The challenge of studying halogen bonding interactions in cucurbiturils is solutising both the host and the chosen halogen bond donor. A range of formic acid mixtures were tested as solvent systems. A 1:1 mixture of formic acid and pyridine was shown to dissolve both cucurbit[n]uril and the common halogen bond donor **29**.

Pyridyl halogen bond acceptors are very common so the effect of this solvent choice needed to be determined. From pyridine solutions, co-crystals of donors 2,5-diiodo-1,3,4,6-tetrafluorobenzene and 2,4,6-triiodo-1,3,5-trifluorobenzene with this acceptor could be isolated. For **29**, the expected 1:2 co-crystal formed, and the structure and interactions of this three molecule unit was very similiar to that seen for more complicated pyridyl acceptors such as 4,4-bipyridine and dipyridyl ethylene. In the literature, it is more common to observe **31** forming only two of the possible three halogen bonding interactions. The co-crystal presented here had a unexpected 2:3 schiometery and featured a pyridine bridging between two molecules of **31**, as well as a single pyridine-iodine interaction. This single interaction was consistent with interactions seen in the literature for both pyridine and **31**. The bifurcated system was a Type II interaction with two identical halogen bonds and has the shortest iodine-nitrogen interaction distance for Type II interactions.

For solution studies, the low solubility of the cucurbituril family meant that two of the studies were done in cucurbituril-saturated systems. For iodomethane, a single upfield shifted peak was seen corresponding to fast exchanging inclusion complex. Interestingly, *trans*-4,4'-diiodooctafluoroazobenzene in a cucurbit[8]uril - saturated DMSO solution showed a slow exchange, with resonances present for both the complexed and uncomplexed molecules. The equilibrium constant for the iodomethane-cucurbit[6]uril complex in a formic acid - water mixture was determined as the resonances for the complexed and uncomplexed iodomethane could be seen. It is comparable to the equilibrium constants seen for methyl and ethyl ammonium ions.

## Chapter 8

# Conclusions and Further Work

## 8.1 Conclusions

In bearings, boundary lubrication is important in high load situations. This lubrication is often dependent on the formation of organic layers at the surface of the bearings; in turn, these layers are controlled by their interactions with the surface. This project set out to investigate and then control the interaction of molecules at the surface of a polyamide-imide in non-polar solvents.

The logic of the project is set out in Figure 8.1. Initially, the commercial polyamide-imide was characterised and a simple model of the surface outlined. The adsorption of a common type of friction modifier, *para*-alkylphenol, and an engine oil contaminant, water, was investigated to understand the sort of non-covalent interactions present. To alter these non-covalent interactions, a polymer was designed containing viologen-cucurbit[8]uril binding units, and the behaviour of a second guest with a polymer tail was investigated by neutron reflectometry. To investigate the effectiveness of the binding in the viologen-cucurbit[8]uril unit in alkane solutions, a series of rotaxanes were synthesised. Halogen bonding was then investigated as a possible alternative binding interaction for guests in cucurbit[n]uril.



Figure 8.1: The approaches taken within this project.

#### 8.1.1 Characterisation of the Commercial Polyamide-imide

The polymer was characterised by various techniques to understand the functional groups present in the system.

The key conclusion of these investigations was that the second step of the polymer's synthesis (Scheme 8.1) was incomplete, leading to a mixture of imides, carboxylic acids and amides. This distribution could be determined by <sup>1</sup>H NMR spectroscopy. The degree of imidisation could be controlled by heat treatment. Heating at 150 °C-200 °C achieving the formation of 75 % of the imides present.

	Density / Moles $m^{-2}$		
	A . 1	After 2 hrs	
	As received	at 200 $^{\circ}\mathrm{C}$	
Amides	$2.25 \ge 10^{-6}$	$2.05 \ge 10^{-6}$	
Carboxylic Acids	$6.76 \ge 10^{-7}$	$1.86 \ge 10^{-7}$	
Imides	$9.03 \ge 10^{-6}$	$1.68 \ge 10^{-6}$	

Figure 8.2: Distribution of functional groups before and after heating.



Scheme 8.1: The two stage synthesis of a polyamide-imide: (i) the condensation of the diamine (6) with the acid anhydride chloride (7) to form a poly amic acid (8) and (ii) the thermally induced imidisation from the poly amic acid (8) to the polyamide-imide (5).

A simple model of the polymer's surface as a distribution of functional groups was developed. An example of the density of functional groups is shown in Figure 8.2. The thermal treatment varied these densities. The functional groups could then be divided by their hydrogen bonding capability: amides (acceptor/donor), carboxylic acids (acceptor/donor), and imides (donor). This meant that the surface could be simplified further into hydrogen acceptors and donors. The heat treatment affected this distribution and so the hydrogen bonding behaviour of the surface would change with heating.

## 8.1.2 The Adsorption of Alkylphenols and Water at the Surface of the Polyamide-imide from Dodecane

Alkylphenolates are a class of friction modifiers with complex structures. Based around phenol, they are oligometric with great variation in the composition of their alkyl tails. For these studies, straight chain *para*-alkylphenols were used as model compounds. Solution depletion isotherms and neutron reflection studies showed that phenol adsorbed as a thick, multi-layered structure. These techniques showed that the addition of an alkyl tail results in a reduction of the adsorbed amount. The alkylphenols appear to adsorb as a sparsely packed layer with the molecules increasingly stood up as the adsorbed amount increases. It is assumed that the hydroxyl groups are interacting with the polymer surface. Solution depletion isotherms under an inert atmosphere allowed for the measurement of the adsorption of the water on the polymer's surface. This, coupled with neutron reflection, revealed the diffusion of water into the surface. Most of the water can be removed by washing with dry dodecane.

## 8.1.3 The Inclusion of Viologen - Cucurbit[8]uril Binding Sites in a Polyamide-imide

The commercial polymer, Torlon LM, was successfully reproduced and this provided a baseline for further synthetic efforts. The complexity of the polyamideimide's <sup>1</sup>H NMR spectrum meant that proving complexation of the viologen units by cucurbit[8]uril was difficult. Initially, a polymer containing only the binding site was developed. By comparing the proton NMR of un-complexed and cucurbit[8]uril-complexed viologen polymers, it was possible to prove complexation by shifts in the proton peaks of the viologen.

A polyethylene glycol functionalised naphthalene was synthesised by our collaborators, Professor Oren Scherman and Chi Hu. The adsorption of this polymer on Torlon LM and the un-complexed and cucurbit[8]uril-complexed viologen polymers was studied by neutron reflection. On Torlon LM, a large change in the neutron reflectivity profile was seen, whilst for the synthetic polymers no change was seen suggesting that viologen-cucurbit[8]uril binding unit was not working as expected.

## 8.1.4 Studies of the Viologen - Cucurbit[8]uril Binding Unit in Alkanes

This unexpected adsorption behaviour prompted the investigation of second guest binding in alkanes. Rotaxanes incorporating the viologen-cucurbit[8]uril binding unit were designed to maximise their possible alkane solubility by having stoppers featuring benzene rings and tertiary butyl groups. These rotaxanes were synthesised, but low solubility prevented further characterisation.

#### 8.1.5 Halogen Bonding in Cucurbit[n]urils

As well as investigating the binding of second guests via viologen-cucurbit[8]uril bearing rotaxanes, the possibility of using halogen bonding as a guest binding interaction was explored due to the generally higher solubility of halogen bonding donors in non-polar solvents compared to typical cucurbituril guests.

Whilst the crystallisation of a halogen-bonded cucurbituril inclusion complex was unsuccessful, the structures of several novel halogen bonded co-crystals were determined. This included the first tertiary amide co-crystals for 1,4diiodotetrafluorobenzene using dimethylformamide and N-methylpyrrolidone, as well as the shortest nitrogen-iodine distances to a bifurcated pyridine acceptor in the co-crystal of 1,3,5-triiodo-2,4,6-trfluorobenzene and pyridine.

Solution studies showed the inclusion of halogen bonded donors into cucurbit[n]urils. <sup>1</sup>H NMR studies of methyl iodide and cucurbit[6]uril in water confirmed inclusion by a upfield shift of the methyl iodides protons. Exchange between the complexed and free molecules was fast as a single resonance was seen. However, if the solvent was 50:50 formic acid/water, exchange became slow allowing free and complexed peaks to be seen. A possible mechanism for this could be the capping of the cucurbituril with a hydronium ion that prevents easy exchange of the methyl iodide. <sup>19</sup>F NMR showed the inclusion of *trans*diiodooctrafluoroazobenzene in cucurbit[8]uril as the peaks associated with the guest undergo a downfield shift.

## 8.2 Further Work

### 8.2.1 Characterisation of the Polyamide-imide

The characterisation of the commerical polymer revealed that a mixture of functionalities are present in the bulk. The effect of this inhomogeneality was only considered from the point of view of providing a known substrate. These polymers are spray coated onto steel or aluminium. The presence of these substrates or any filler material may alter the distribution of these functional groups via, for example, the segregation of acid groups to metal surfaces. Studying the adsorption of the polymer onto metal surfaces would help to clarify this. Initially, the adsorption of small molecule analogues of the polymer would be considered. For example, amine or carboxylic acid end groups would be modelled using aniline or benzoic acid. The repeat unit would be broken down into three key functionalities: carboxylic acids, amides, and imides, and each represented by a small molecule analogue as shown in Figure 8.3.



Figure 8.3: Division of the polymer into small molecule analogues.

This small molecule adsorption will be studied in a similiar way to the adsorption of molecules onto the surface of the polymer was done here. However, it will require different solvent systems to mimic the coating application conditions such as *N*-methylpyrrolidone and dimethylformamide.

### 8.2.2 Polyamide-imide Surface Interactions

The adsorption of both alkylphenols and water was investigated. Whilst the structure of the adsorbed layers could be determined with isotherms and neutron reflectometry, the exact nature of the binding present could only be theorised. The presence and influence of hydrogen bonding could be investigated by replacing the hydrogen bond acceptor/donor alkyl phenols with alkyl methoxybenzenes (a hydrogen bonding acceptor only) or phenyl alkanes and looking at the change in adsorption behaviour, as shown in Figure 8.4



Figure 8.4: Modifications to the starting alkylphenols to probe the mechanism of adsorption.

The work done in this project was only at room temperature, but the operating conditions of engines offer a wide range of both pressures and temperatures. Studying the adsorption of alkylphenols and other additives over a temperature range (particularly above the melting point of the adsorbate) would allow a better understanding of the system in realistic conditions.

The use of small molecule analogues of the surface would allow for the study of interaction in alkane solutions. Similar to the work done on halogen bonding in cucurbit[n]urils, it would be possible to use solution NMR techniques as well as isothermal calorimetry and infrared spectroscopy to rank interactions of additives with these small molecule analogues, and so predict which parts of the polymer are playing the largest role in binding molecules to the surface. This would allow for optimisation of both the polymer surface as well as the adsorbate.

The functionalities present on the surface allow for the possibility of chemical reactions to chemadsorb molecules as shown in Figure 8.5. The imide group appears to be the most useful handle, with room temperature ring opening reaction appearing in the literature [204]. The possibility of reactions at the surface allows for on the fly modification of the molecules in the system. The side product of the binding reaction may itself be a useful component, e.g. an anticorrosive surface molecule whose binding releases a molecule that helps remove corrosion products into the system.



Figure 8.5: Nucleophilic ring opening of an imide in the polymer.

## 8.2.3 The Incorporation of Surface Viologen-Cucurbit[8]uril binding sites in a Polyamide-imide

Whilst the synthesis of a polyamide-imide incorporating the viologen-cucurbit[8]uril binding site was successful, investigations into the binding of a second guest containing polymer produced an unexpected results. These measurements were done with a 100 % substituted system with and without the threaded cucurbit[8]uril, due to both the ease of determining if the threading was successful, and to maximise the effect seen. It would be interesting to repeat the exper-

#### 8.2. FURTHER WORK

iment with the lower substitution level and see if the second guest polymer's behavour moves towards that of the unsubstituted polyamide-imide.

Expanding on the idea of chemabsorption outlined in section 8.2.2, it could be possible to incorporate the binding sites in situ as shown in Figure 8.6. This would also allow for replenishment of the binding sites during use.



Figure 8.6: Using nucleophilic ring opening to attach the viologen binding unit to the surface. Cucurbit[8]uril is represented by a rectangle.

## 8.2.4 Understanding Cucurbit[n]uril Host-Guest Interactions in Non-Polar Solvents

Whilst the synthesis of the rotaxanes was successful they could not be fully characterised due to low solubility. This work can be extending by further development of the stoppers to encourage solubility. For example, the 2-ethyl hexyl group is a good solubilizing group for non-polar solvents and could be incorporated either directly on the benzene ring (**39**) or via ether linkages (**40**), both are shown in Figure 8.7.



Figure 8.7: Examples of potential stoppers incorporating (2-ethyl)hexyl chains either directly on the benzene ring (**39**) or via ether linkages (**40**).

In addition to rotaxanes for measuring second guest binding, it would be interesting to extend this work to cucurbit[n]uril host-guest chemistry more widely. However, the low solubility of these molecules limits the number of systems to which they are applicable. The use of substituted cucurbit[n]urils (**41** and **42**) is one way around this problem, with the literature showing substitution enhancing their solubility in both water and organic solvents [205–208].



Figure 8.8: Commonly used dimethyl substituted glycolurils (**41** and **42**) and Possible Cucurbituril Alternatives: Hemicucurbit[n]uril (**43**) and macrocycles starting with propyldiureas (**44**).

An alternative would be to move towards other cucurbituril-like molecules such

as hemicucurbiturils (43) [209] (shown in Figure 8.8) and pressocucurbiturils [210–212] (which uses propyldiureas (44) as a monomer). These have improved solubility but differing binding characteristics.

### 8.2.5 Halogen Bonding in Cucurbit[n]uril

This project provided limited evidence of halogen bonding as a viable guest binding method for this class of macrocycles. The biggest factor that limited these investigations was the lack of a suitable co-solvent for halogen bond donors and the cucurbit[n]uril. This can be overcome by changing the macrocycle as was outlined in 8.2.4.

In these studies, the halogen bond donors were not based upon common cucurbit[n]uril guest motifs, but, well-studied donors from the literature [32]. It would be interesting to take host-guest motifs and convert them into halogen bond donor versions. For example, a halogen bond donor version of the methylviologen guest would be 4,4-diiodoperfluorobiphenyl as shown in Figure 8.9. This would also open up the opportunity to vary the substitution pattern on the two rings. Alkyl diamines are often used as guests, and the halogen bond donor equivalent would be the perfluorinated diiodo alkanes as shown for hexyl diamine in Figure 8.9.



Figure 8.9: The halogen bond donor analogues for two common cucurbit[n]uril guests; methylviologen to 4,4-diiodoperfluorobiphenyl (top) and hexyl diamine to diiodo perfluorohexane (bottom).

# Appendices

## Appendix A

# **Crystallographic Data**

## A.1 The Crystal Structures of 4-Octylphenol and Two Polytypes of 4-Nonylphenol.

		4-octylphenol	4-nonylphenol 1A	4-nonylphenol 2A
Formula		$C_{14}H_{22}O$	$\mathrm{C_{15}H_{24}O}$	$\mathrm{C_{15}H_{24}O}$
Space Group		C2	P-1	P-1
	a	57.456(3)	5.2667(13)	5.2665(3)
Cell Lengths / $\mathring{A}$	b	5.2835(2)	8.094(2)	8.0937(5)
	с	8.1216(4)	31.858(7)	32.007(2)
	$\alpha$	90	88.978(15)	96.501(5)
Cell Angles	$\beta$	94.452(3)	87.608(13)	92.371(5)
	$\gamma$	90	90.291(14)	90.308(4)
Cell Volume / $\mathring{A}^3$		2458.03	1356.64	1354.31
Ζ		8	4	4
$\mathbf{Z}^{\prime}$		0	0	0
R-Factor / $\%$		7.41	20.17	9.07

90

99.922(2)

90

1417.43

4

0

3.24

		$29.28_{2}$	29.9
Formula		$C_6F_4I_2{\cdot}2(C_3H_7NO)$	$C_6F_4I_2 \cdot C_5H_9NO$
Space Group		$P2_1/n$	C 2/c
	$\mathbf{a}$	5.8997(2)	8.8778(4)
ell Lengths / $\mathring{A}$	b	24.2464(8)	8.8930(4)
	c	6.0031(2)	18.2260(7)

90

101.328(2)90

841.993

2

0

3.35

 $\alpha$ 

 $\beta$ 

 $\gamma$ 

Cell Angles

Cell Volume /  $\mathring{A}^3$ 

Ζ

 $\mathbf{Z}^{\prime}$ 

R-Factor / %

## A.2 Co-crystals of 2,5-Diiodo-1,3,4,6-tetrafluorobenzene and Tertiary Amides.

		$29{\cdot}32_2$	$31_2{\cdot}32_3$
Formula		$C_6F_4I_2{\cdot}2(C_5H_5N)$	$2(C_6F_3I_3)\cdot 3(C_5H_5N)$
Space Group		$P2_1/n$	Рbсn
	a	9.0145(4)	5.22110(10)
Cell Lengths / $\mathring{A}$	b	5.1877(2)	17.3518(3)
	$\mathbf{c}$	18.6266(11)	36.7826(5)
	$\alpha$	90	90
Cell Angles	$\beta$	92.000(2)	90
	$\gamma$	90	90
Cell Volume / $\mathring{A}^3$		870.533	3332.34
Z		2	4
$\mathbf{Z}^{\prime}$		0	0
R-Factor / $\%$		2.91	3.22

## A.3 Co-crystals with Pyridine

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