Inclusion behaviour of related organic host compounds

by

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Publication and conference

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The inclusion behaviour of the two host compounds, 9-(4-methoxyphenyl)-9H-xanthen-9-ol (A1) and 9-(4-methylphenyl)-9H-xanthen-9-ol (A10) were investigated. These host compounds are large, bulky, rigid and they contain functionalities that allow them to selectively interact with other molecules, such as the guests in this work. The host molecules form inclusion complexes with small organic guest molecules. The host-guest interactions are the interesting focus of this study.

The host A1 included the guests: cyclohexane, 1,4-dioxane and N,N-dimethylformamide. Kinetics of desolvation were studied for the 1,4-dioxane and N,N-dimethylformamide compounds. Guest-exchange reactions were performed. The host A1 was also used in the separation of 1, 4-dioxane and benzene.

The host A10 included the guests; benzene, 1,4-dioxane, cyclohexane, cyclohexanone, N,N-dimethylacetamide and N,N-dimethylformamide. Kinetics of desolvation were studied for the benzene and cyclohexane compounds. The host A10 was used in the separation of the following pairs of guests: benzene and 1,4-dioxane; N,N-dimethylformamide and N,N-dimethylacetamide.

The structures of the compounds were elucidated using single crystal X-ray diffraction. Thermal analysis was performed in order to determine the thermal
stabilities of the complexes, including techniques such as thermogravimetry, differential scanning calorimetry and melting point measurement. The reactions in the guest exchange experiments were monitored using differential scanning calorimetry.

Competition experiments were performed to determine the selectivity of a host for a series of related guests. These experiments were conducted between pairs of guests.
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<td>Crystal structure solution</td>
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</table>
Supramolecular chemistry and inclusion compounds

This type of chemistry is involved in diverse disciplines and fields, having complete control over supramolecules, molecular assemblies and materials.

Supramolecular Chemistry is the chemistry of multicomponent molecular assemblies. The component structural units are held together by a variety of weaker (non-covalent) interactions.

It is highly interdisciplinary in nature and has applications in related fields of physics and biology where it has been used in a considerable number of systems binding organic components into larger assemblies. This has resulted in a change in focus from single molecules, which are constructed step by step through the formation of direct covalent linkages, towards molecular assemblies, with their usual non-covalent weak intermolecular contacts.

Much of the work has focused on molecular design for achieving complementarity between single molecule hosts and guests.
Inclusion Compounds

Inclusion compounds have been known since the beginning of the second last century. In 1811 Sir Humphrey Davy discovered the chlorine hydrate (Cl\textsubscript{2}•6H\textsubscript{2}O) of an inclusion compound and was studied by Michael Faraday in 1823. E. Mittscherlich recognized the idea of a polymorphic compound. In 1828 F. Wöhler first synthesized the compound urea.

Coordination chemistry was firstly introduced in 1893 by Alfred Werner, implying that the two compounds could bind to one another if there was some kind of interaction. Emil Fischer expanded the process and in 1894 introduced the ‘lock and key’ concept giving a more visual understanding of molecular recognition. It was in 1912 that Max von Laue first discovered X-ray diffraction and in 1913 the structure of sodium chloride was determined by Bragg. The term ‘hydrogen bond’ was first used by L. Pauling in 1935, followed by the first mention of the weak hydrogen bond in 1936 by O. R. Wulf. In 1948 H. Powell proposed structures for the ß–quinol inclusion compounds and introduced the term ‘clathrate’ to describe the total encapsulation of a guest within a host framework cavity.

In 1952 F. Cramer referred to molecules able to enclose other molecules in their structure without covalent bonding as inclusion compounds and recognized that no functional groups and no chemical reaction was needed.
Inclusion compounds can be classified into two categories. A schematic diagram is shown in Figure 1.1.

(a) Molecular inclusion: is the formation of a molecular complex, where a convex guest fits into the cavity of one host molecule.

(b) Lattice inclusion: is the inclusion of guest molecules into the cavities between different host molecules in the crystal lattice (clathrate formation).

Figure 1.1 Schematic drawing illustrating the two basic types of inclusion.
A clathrate is formed when the guest is entirely enclosed by the host framework and is not limited to cage inclusion compounds but can incorporate other shapes as well \(^\text{16}\). Figure 1.2 shows types of voids that are created by the host framework in solid state host-guest compounds \(^\text{17}\).

![Diagram of lattice clathrates](image)

**Figure 1.2** Examples of topologies of lattice clathrates; (a) cages or pocket (b) interconnected cages, (c) channels, (d) intersecting channels (e) layers
**Intermolecular Interactions**

The central focus of the field of supramolecular chemistry is the variety of non-covalent interactions such as hydrogen bonding, C–H⋯π, π–π stacking, dipole-dipole and van der Waals interactions and hydrophobic binding which are considered to stabilize the various components of a particular complex.\(^\text{18}\)

**Hydrogen Bonding**

The hydrogen bond can be described as D–H⋯A, where D is a donor atom, H is a hydrogen and A is an acceptor atom.\(^\text{21-22}\) The hydrogen bond plays a major role in the formation of supramolecular systems. Hydrogen bonding occurs most commonly between donor groups (D) such as: C–H, N–H, O–H, F–H, P–H, S–H, Cl–H, Br–H and I–H and acceptor (A) groups such as N, O, P, S, Cl, Br, I, alkenes, alkynes, aromatic π-systems and transition metals.\(^\text{18-20}\) Hydrogen bonds are classified as very strong, strong, and weak based on their ability to determine and control supramolecular structure.\(^\text{22}\) The hydrogen bond is usually bent, rather than linear as shown in the description above and hydrogen bond parameters are given in Table 1.

**Table 1. Typical Parameters of Hydrogen bonds**\(^\text{23}\).

<table>
<thead>
<tr>
<th>Hydrogen bond type</th>
<th>Very strong</th>
<th>Strong</th>
<th>Weak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length H⋯A(Å)</td>
<td>1.2 – 1.5</td>
<td>1.5 – 2.2</td>
<td>2.2 – 3.2</td>
</tr>
<tr>
<td>&lt;D–H⋯A(°)</td>
<td>175 – 180</td>
<td>130 – 180</td>
<td>90 – 150</td>
</tr>
</tbody>
</table>
C–H⋯π Interactions

Edge-to-face interactions of aromatic rings fall into this category. In 1998 studies done by Braga on organometallic crystals found average distances from the centroid of the aromatic ring to the oxygen or carbon atom in (C)O–H⋯π to be 3.41(3) and 3.69(2) Å respectively. It is understood that this intermolecular interaction stabilizes the crystal structure.

π–π Stacking

This represents the interaction of π clouds of two aromatic rings. This is a directional force as it stabilizes the helical structure of DNA, and the packing of the host and guest compounds in crystals. There are two general types of π–π stacking: face- to- face and edge- to- face. In the case of face- to- face interactions the two aromatic rings may not be directly above each other as this is repulsive.

This interaction is attributed to weak electrostatic forces as well as dispersive forces which might be of greater importance. The strength of this interaction varies from 0-50 kJ mol⁻¹.

Van der Waals Interactions

Van der Waals interactions are described as repulsive and dispersive intermolecular forces. The repulsive forces balance the dispersion forces and define molecular shape and conformation. Dispersive forces are attractive in nature and result from the interactions of fluctuating multipoles in adjacent molecules. These forces are non-directional, are less than 5 kJ mol⁻¹ in strength and are most important in compounds where small organic guests are included in crystal lattices or molecular cavities.
Host Design

A good host is defined as having the following qualities.  

- Molecular bulkiness, for a low density packing with the possibility of cavities.
- Rigidity, to maintain and sustain cavities
- Functional groups, to provide suitable host-guest interactions.

Many organic host compounds have been synthesised based on these principles including those containing hydroxyl functional groups for hydrogen bonding.

Host molecules can be classified according to their shape and functionality. A few host compounds and their characteristics are given below:

- **Scissor Type Hosts**: These are characterised by the shape of the molecule given in Figure 2. The classic examples of these hosts are:

![Scissors type hosts](image)

**Figure 2.** Scissors type hosts, **A**: 2,2-dihydroxy-1,1-binaphthyl and **B**: 1,1-binaphthyl-2,2-dicarboxylic acid.

These hosts have been extensively studied, and have been shown to form inclusion compounds with a variety of guests with differing host:guest ratios. Compound **A** enclathrates alcohols, amines, oxides, amides and ketones. Compound **B** successfully includes aliphatic alcohols, carboxylic acids and amides.
Scissor type host compounds are still extensively studied and a recent paper published by Muraoka et al. have described, “reversible operation of chiral molecular scissors by redox and UV light” 40.

- The **Hexa Type Host** 41 is the common feature in the clathrates formed by hydroquinone, phenol and Dianin's compound where the linking of the OH groups of the host molecules forms a hydrogen bonded network such that the oxygen atoms form a hexagonal arrangement. This is illustrated in Figure 3 (a) and compared to (b) hexasubstituted benzene. The hydroxyl group plays a major role in maintaining the 'open' clathrate structure.

![Figure 3. (a) Hexagonal arrangement, (b) hexa substituted benzene](image)

The classic example of the hexa substituted benzene host is hexakis(phenylthio)benzene. This example is shown in Figure 4 and has been found to include a variety of guests with differing host:guest ratios 42. It has successfully enclathrated carbon tetrachlorides (CCl₄), methyltrichlorides (CHCl₃) and bromotrichlorides (CCl₃Br) 43. Saha et al. have discussed an organic hexahost of this type in a paper entitled “Helical water chains in aquapores of organic hexahost: remarkable halogen-substitution effect on the handedness of water helix” 44.

![Figure 4. The Hexa Host Type structure, hexakis (phenylthio) benzene.](image)
• A Cavitand Host is a single host molecule which possesses an intramolecular cavity and the guest molecule resides completely within the host cavity. An example of a cavitand host is illustrated in Figure 5.

![β-cyclodextrin](image)

Figure 5. A typical host for cavitand inclusion formation.

Other well studied host molecules of this type include Pederson's crown ethers, cyclophanes and calix[n]arenes. Recent work has involved the study of water-soluble cavitands which are desirable because most biological processes occur in water.
Physical Methods of Characterization

Thermal Analysis

Thermal analysis is a very useful tool for the study of inclusion compounds. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are the most common techniques used. A typical TGA experiment measures weight loss as a function of temperature. Each specific weight loss is expressed as a percentage and this allows the calculation of the host to guest ratio. The reproducibility of the weight loss is generally of the order of ± 1%. The onset temperature cannot be determined by TGA because the commencement of weight loss is dependent on particle size and heating rate. TGA is also used extensively in the study of kinetics of desolvation of host-guest compounds. Both isothermal and non-isothermal methods have been employed in this study and are described in Chapter 2.

DSC measures the enthalpy changes of a solid that occur during heating. These enthalpy changes are usually due to guest loss or a phase change. The area under the DSC peak is dependent on the particle size, heating rate, flow rate of the purging gas and the geometry of the calorimeter. The onset temperatures \((T_{on})\) for a given inclusion compound are dependent on the host-guest interactions and on the inherent physical properties of the guest included.

X-ray diffraction

X-ray diffraction is an essential tool as it allows for the accurate assignment of the positions of the atoms in a crystal structure as well as details about the molecular packing. This technique gives us information about the intermolecular interactions taking place, as an indication of how the structure is stabilized.
Guest Exchange Reactions

There are two possible mechanisms for any guest exchange reaction:

(a) \( \text{H} \cdot n\text{G}_1(\text{s, } \beta) + m\text{G}_2(\text{liquid or vapour}) \rightarrow \text{H} \cdot m\text{G}_2(\text{s, } \beta) + n\text{G}_1(\text{liquid or vapour}) \)

In (a) the host-guest compound retains its structure throughout the exchange reaction. This mechanism is uncommon for organic hosts and the classic example is the host gossypol, which forms a clathrate with dichloromethane as guest, retains its structure on desorption, and absorbs other volatile guests.

(b) \( \text{H} \cdot n\text{G}_1(\text{s, } \beta) \rightarrow \text{H}_1(\text{s, } \alpha) + n\text{G}_1(\text{liquid or vapour}) \)
\( \text{H}_1(\text{s, } \alpha) + m\text{G}_2 \rightarrow \text{H} \cdot m\text{G}_2(\text{s, } \beta) \)

In (b) the host-guest system desorbs the original guest \( \text{G}_1 \) to yield the apohost in its \( \alpha \), nonporous phase, which in turn forms a new inclusion compound with the incoming guest \( \text{G}_2 \). The exchange of \( p \)-xylene with benzene in the clathrates formed with 9-(3-chlorophenyl)-9H-xanthen-9-ol is an example of this.
Applications of Host-Guest Chemistry

The applications of host-guest chemistry have grown tremendously and have been reported in a set of 10 volumes of 'Comprehensive Supramolecular Chemistry' \(^{60}\). Amongst the topics covered are:

- Catalysis, pollution control and storage of reagents.
- Alteration of physical and chemical properties of pharmaceutical drugs by inclusion in cyclodextrins.
- Separation of isomers, chiral resolution, polymerisation and liquid crystals.

Inclusion compounds have found various practical applications \(^{15}\):

- In the separation of racemates with the help of urea.
- In pharmacology, for the protection of drugs from oxidation, forms of decomposition and also to effect rapid absorption by the body.
- The fixation of volatile fragrances and drugs.

There is hope that inclusion compounds of pesticides will be safer and easier to handle.
Aspects of this Study

The host 9-(4-methoxyphenyl)-9H-xanthen-9-ol (A1) and 9-(4-methylphenyl)-9H-xanthen-9-ol (A10), possess similar geometries and a different functionality of methoxy (A1) and methyl group (A10) in the para-position.

One of the aims of this study was to determine the effect of this on the type of interactions that occur between the host and guest molecules as well as packing arrangements of the crystal structures.

Therefore a wide variety of guests were included according to their size, geometry or acceptor/donor capabilities. These included aromatic guests like benzene, various six membered aliphatic rings e.g. cyclohexane, cyclohexanol and amides e.g. N,N-dimethylformamide and N,N-dimethylacetamide. The physical properties of the guests used in this study are listed in Table 2. They are all liquids at room temperature. Separation of certain guests was attempted using the above mentioned hosts in competition experiments between, for example, benzene and 1,4-dioxane.

The thermal stability of the resultant inclusion compounds was investigated and where possible gas chromatography (GC) was used to determine the selectivity of each host for a series of guests. Guest exchange experiments were performed between A1 inclusion compounds and selected guests.
Physical Properties of Guests Included

The melting points, boiling points and vapour pressures of the guests are given below. The data were obtained from Aldrich Advancing Science 61.

Table 2. Physical Properties of Guests Studied

<table>
<thead>
<tr>
<th>Guest</th>
<th>Molecular formula</th>
<th>m.p.(°C)</th>
<th>b.p.(°C)</th>
<th>V.p.(mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>5.5</td>
<td>80</td>
<td>74.6 / 20</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>C₄H₈O₂</td>
<td>10-12</td>
<td>100-102</td>
<td>27 / 20</td>
</tr>
<tr>
<td>N,N-dimethylacetamide</td>
<td>CH₂CON(CH₃)₂</td>
<td>-20</td>
<td>165-166</td>
<td>2 / 25</td>
</tr>
<tr>
<td>N,N-dimethylformamide</td>
<td>CHON(CH₃)₂</td>
<td>-61</td>
<td>153</td>
<td>2.7 / 20</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>C₆H₁₂</td>
<td>4-7</td>
<td>80.7</td>
<td>77 / 20</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>C₆H₁₁OH</td>
<td>22</td>
<td>160-161</td>
<td>1 / 20</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>C₆H₁₀(=O)</td>
<td>-47</td>
<td>155</td>
<td>3.4 / 20</td>
</tr>
</tbody>
</table>
References:


2. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vögtle
   *Comprehensive Supramolecular Chemistry*, Vol. 1-10, eds.,


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CHAPTER 2 EXPERIMENTAL

Host Compounds

The two host compounds, 9-(4-methoxyphenyl)-9H-xanthen-9-ol, A1, and 9-(4-methyl-phenyl)-9H-xanthen-9-ol, A10, were synthesised by Jana Taljaard of the Nelson Mandela Metropolitan University.

![Image of A1](image1)

Figure 2.1 Schematic representation of A1.

![Image of A10](image2)

Figure 2.2 Schematic representation of A10.

Guest Compounds

Benzene was supplied by BDH Chemicals Ltd England; cyclohexane, cyclohexanone, 1,4-dioxane, N,N-dimethyl acetamide and N,N-dimethyl formamide were supplied by Merck & Co. All solvents were dried using molecular sieves. Benzene and 1,4-dioxane were distilled for the competition experiments.
Crystal Growth

The host compounds were dissolved and heated in the liquid guests to give dilute solutions at 333 K. Both A1 and A10 had low solubility in cyclohexane and a small amount of ethanol was added as a co-solvent. The solutions were left to cool to room temperature resulting in the formation of crystals and after cooling were sealed with parafilm.

Thermal Analysis

Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed on a Perkin-Elmer Pyris 6 system. Samples of the crystals taken from the mother liquor were blotted dry with filter paper and crushed before analysis. TGA measures weight loss of the inclusion compounds as a function of time or temperature under controlled conditions. It was also used to study the kinetics of desolvation using both isothermal and non-isothermal methods. DSC measures thermal decomposition, the onset temperatures of the inclusion compounds and the melting point of the host.

The DSC instrument was calibrated using indium (onset temperature, $T_{on} = 156.6^\circ C$). TG and DSC experiments were performed at temperatures of 303-573 K at a heating rate of 10 K min$^{-1}$ under flowing dry nitrogen at 20 ml min$^{-1}$. Sample sizes of 3-5 mg were placed in 50 µl pierced aluminium pans and nitrogen gas was used as the inert atmosphere. The sample size, flow rate and heating rate of the purge gas influence the TGA and DSC results.

Kinetics

Isothermal and non-isothermal methods were utilized for determining the kinetics of decomposition of the host-guest compounds studied. These two methods are recognized and have been used comprehensively. The outlines of both methods are given below. For the kinetic studies crystals and powders were used. The powders were formed from stirred solutions of host in the liquid guest and crystals were crushed to limit the outcome of particle size on the results. It is preferred to grow powdered samples since this limits the effect of particle size on the activation energy and results in a more consistent particle
size distribution. From the literature, it can be seen that sample size affects the onset temperature of guest release which would change the kinetics of desolvation. If it is not possible to grow powders then crystals are crushed for analysis.

**Isothermal Kinetics**

Sequences of TG runs were carried out at selected temperatures. The resultant TG runs were converted into $\alpha$ vs time curves, and fitted to different kinetic models. The $\alpha$ vs time curves can be acceleratory, sigmoidal or deceleratory and can be explained by definite rate expressions.

Table 2.1 lists the kinetic models that have been obtained from Brown. The Arrhenius equation was used to determine the activation energy for the reactions.

Arrhenius equation: $\ln k = -\frac{E_a}{RT} + \ln A$

where $k =$ rate constant,

$E_a =$ activation energy,

$A =$ pre-exponential factor

and $T =$ absolute temperature

**Non Isothermal Kinetics**

Sequences of ramped TG runs were performed over selected temperature ranges and at different heating rates. Flynn and Wall developed this method for the analysis of the thermogravimetric rate, which is the rate of weight loss against temperature. The thermogravimetric rate is explained by the equation:

$$\frac{dC}{dT} = \frac{A}{\beta} f(C) e^{\frac{E}{RT}},$$

where $C =$ degree of mass loss and $\beta =$ heating rate.

Then reduced to: $\frac{d \log \beta}{d 1/T} \equiv (0.457 / R) E$. An activation energy range can be obtained from plots of $(-\log \beta)$ vs $1/T$. 

Table 2.1 Significant rate equations for solid state reactions.

<table>
<thead>
<tr>
<th>Category</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Acceleratory</strong></td>
<td></td>
</tr>
<tr>
<td>P1 power law</td>
<td>$\alpha^{1/n}$</td>
</tr>
<tr>
<td>E1 exponential law</td>
<td>$\ln \alpha$</td>
</tr>
<tr>
<td><strong>2. Sigmoidal</strong></td>
<td></td>
</tr>
<tr>
<td>A2 Avrami-Erofeev</td>
<td>$[-\ln(1-\alpha)]^{1/2}$</td>
</tr>
<tr>
<td>A3 Avrami-Erofeev</td>
<td>$[ \ln (1-\alpha)]^{1/3}$</td>
</tr>
<tr>
<td>A4 Avrami- Erofeev</td>
<td>$[-\ln (1-\alpha)]^{1/4}$</td>
</tr>
<tr>
<td>B1 Prout Tompkins</td>
<td>$\ln[ \alpha / (1-\alpha)]$</td>
</tr>
<tr>
<td><strong>3. Deceleratory Geometric Models</strong></td>
<td></td>
</tr>
<tr>
<td>R2 contracting area</td>
<td>$1-(1-\alpha)^{1/2}$</td>
</tr>
<tr>
<td>R3 contracting sphere</td>
<td>$1-(1-\alpha)^{1/3}$</td>
</tr>
<tr>
<td><strong>Diffusion Models</strong></td>
<td></td>
</tr>
<tr>
<td>D1 one-dimensional</td>
<td>$\alpha^2$</td>
</tr>
<tr>
<td>D2 two-dimensional</td>
<td>$(1-\alpha) \ln(1-\alpha) + \alpha$</td>
</tr>
<tr>
<td>D3 three-dimensional</td>
<td>$[1-(1-\alpha)^{1/3}]^2$</td>
</tr>
<tr>
<td>D4 Ginstling-Brounshtein</td>
<td>$(1-2\alpha/3) - (1-\alpha)^{2/3}$</td>
</tr>
<tr>
<td><strong>Order of reaction models</strong></td>
<td></td>
</tr>
<tr>
<td>F1 first order</td>
<td>$-\ln (1-\alpha)$</td>
</tr>
<tr>
<td>F2 second order</td>
<td>$1/(1-\alpha)$</td>
</tr>
<tr>
<td>F3 third order</td>
<td>$[1/(1-\alpha)]^2$</td>
</tr>
</tbody>
</table>

$\alpha =$ fraction decomposed

$\alpha = \left( \frac{m_i - m}{m_i - m_f} \right)$ and $m_i =$ initial mass

$m_f =$ final mass
Characterisation

Fisher-John Apparatus

Crystals were placed on a Marienfeld 22x22 cm cover glass and covered with a drop of silicone oil. Upon heating, crystals were monitored to determine decomposition temperatures and observe the changes that occur in the crystal. If, during heating, bubbles were observed this signified that an inclusion compound had been formed.

Competition Experiments

Two component competition experiments classified as competition between two guests were carried out on selected host-guest systems. In the two component competition, a series of 11 vials were set up containing mixtures of two guests such that the mole fraction of one guest was increased in the range from 0 to 1. The host compound was added and dissolved by heating. The total guest:host ratio was kept at least at 10:1 such that the guest was always in excess. The solutions were allowed to cool to room temperature then closed and sealed with parafilm over a period of a few days. The resultant crystals were dried on filter paper, dissolved in chloroform and placed in vials. The dissolved crystal was absorbed using a 10 μl syringe and 1 μl of the concentration was injected and analysed by gas chromatography. The original mother liquors were also analysed by gas chromatography. Calibration curves were drawn and area concentrations were plotted against mol fraction of 0.1 to 1.
Guest Exchange

Initial compounds H·G1(s) were exposed to vapours of another guest G2 (solvent) in a tight sealed container as shown in the diagram below. DSC was used to monitor the reaction over a time period which varied from a few hours to a few days. All experiments were carried out at room temperature.

![Diagram](image)

Gas Chromatography

Gas chromatography (GC) was performed on an Agilent 6890N gas chromatograph. Analyses were performed on a polar Carbowax capillary column (30m x 320μm x 0.25μm). The computer package ChemStation was used to monitor and analyse the results. The vials containing mixtures of guests and those containing the original mother liquors were analysed. The gas chromatograph was calibrated using mixtures of known concentrations.

X-ray Powder Diffraction (PXRD)

Powder samples were placed on X-ray insensitive Mylar film. Samples were then mounted on a Huber D-83253 Imaging plate appliance fitted with a Guinier Camera 670, a Huber MC 9300 power supply unit and a Phillips X-ray generator. The generator settings were kept constant at 20 mA and 40 kV while the sample was bombarded with CuKα radiation (λ = 1.54059Å).

We were experiencing technical problems with the PXRD instrument which resulted in a large noise:signal ratio and gave results which looked amorphous. See Figure 3.6 and Figure 3.11.

However the TG trace of the powder matched that of the crystal.
Crystal Structure Analysis

The crystal unit cell parameters and crystal system were determined on a Nonius Kappa CCD diffractometer using 1.2 kW monochromated MoKα radiation (λ = 0.7107 Å) generated by a NONIUS FR590 generator operated at 53 kV and 23 mA. Data collections were done at room temperature, typically at 293-295 K, or at low temperature (113 K).

The space groups were determined by using the collected intensities and pre-determined cell parameters as inputs to the XPREP program. The graphical user interface X-Seed v1.5 was used to run SHELXS-97 to solve the crystal structures: Structural models were refined in SHELXL-97 and were achieved using full matrix least-squares minimization of the function:

$$\sum W(F_0^2 - kF_C^2)^2$$

( the weighted sum of the squares of the differences between the observed and the calculated intensities).

The agreement between the observed (F₀) and the calculated (F_C) structure factors were monitored by assessing the residual index R, defined by R₁ or wR₂.

$$R_1 = \frac{\sum |F_0| - |F_C|}{\sum |F_0|}$$

To give a satisfactory model, both the R₁ and the wR₂ indices should be low when the calculated intensities of the refinement express the agreement against the observed intensities and the measured structure factors are weighted according to their reliability.

$$wR_2 = \left[ \frac{\sum w(F_0^2 - F_C^2)^2}{\sum w(F_0^2)^2} \right]^{1/2}$$

The weighting scheme w was used to yield a constant distribution in terms of a and b, and further refined in the final cycles of structure refinement.

$$w = \frac{1}{\sigma^2(F_0^2) + (aP)^2 + bP}$$
and
\[ P = \frac{\max(0, F_o^2) + 2F_c^2}{3} \]

SHELXL-97 refines against \( F^2 \), which leads to greater deviations of the Goodness of Fit, \( S \), from unity than the refinement against \( F \).

The Goodness of Fit is expressed as follows:

\[ S = \left[ \frac{\sum w \left( |F_o|^2 - |F_c|^2 \right)^2}{(N-n_p)} \right]^{1/2} \]

where \( N \) is the number of reflections and \( n_p \) is the total number of parameters refined.

**Computational**

X-ray powder patterns were calculated using LAZY PULVERIX\(^9\) and compared to experimental powder patterns for characterization. All the crystal packing diagrams were generated with POV-Ray\(^{10}\). The program LAYER\(^{11}\) was utilized to test out systematic absence and space group symmetry. For verification of types of voids occupied by guest molecules, the program SECTION\(^{12}\) was used to slice through cross sections of the unit cell. In a typical example the host molecules were represented in van der Waals radii with the guest molecules excluded. X-SEED\(^{13}\) was used as a graphical interface for the programs SHELXS-97, SHELXL-97, LAZY PULVERIX, Pov-Ray, LAYER and SECTION. The Cambridge Structural Database\(^{14}\) (CSD) was used to search and analyse published crystal structures.
Table 2.2 Host-guest compounds studied in this thesis.

For Host A1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Guest</th>
<th>H:G ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1·CHEX</td>
<td>cyclohexane</td>
<td>1:½</td>
</tr>
<tr>
<td>A1·DIOX</td>
<td>1,4-dioxane</td>
<td>1:½</td>
</tr>
<tr>
<td>n·DMF</td>
<td>N,N-dimethylformamide</td>
<td>1:1</td>
</tr>
</tbody>
</table>

For Host A10

<table>
<thead>
<tr>
<th>Compound</th>
<th>Guest</th>
<th>H:G RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>A10·BENZ</td>
<td>benzene</td>
<td>1:½</td>
</tr>
<tr>
<td>A10·CHEX</td>
<td>cyclohexane</td>
<td>1:½</td>
</tr>
<tr>
<td>A10·CHEXONE</td>
<td>cyclohexanone</td>
<td>1:1</td>
</tr>
<tr>
<td>A10·DIOX</td>
<td>1,4-dioxane</td>
<td>1:½</td>
</tr>
<tr>
<td>A10·DMA</td>
<td>N,N-dimethylacetamide</td>
<td>1:1</td>
</tr>
<tr>
<td>A10·DMF</td>
<td>N,N-dimethylformamide</td>
<td>1:1</td>
</tr>
</tbody>
</table>

References


The inclusion compounds formed between the host, A1, and the guests cyclohexane (CHEX), 1,4-dioxane (DIOX) and N,N-dimethylformamide (DMF) will be discussed.

The crystal structures, thermal stabilities and kinetics of desolvation were studied.

Labelling of the host, A1, is given below with the guests included.

![Chemical structures](image)

1, 4-dioxane

cyclohexane

9-(4-methoxyphenyl)-9H-xanthen-9-ol (A1)

N, N-dimethylformamide

Figure 3.1 A schematic diagram of the host, A1, and guests.
The host, A1, was dissolved in the liquid guests to give dilute solutions. A1 is only slightly soluble in cyclohexane and a co-solvent, ethanol, which does not form an inclusion compound with the host, was added until a clear solution was obtained. The solutions were left to evaporate slowly at room temperature until suitable crystals were formed.

Table 3.1 Crystal Data, experimental and refinement parameters.

<table>
<thead>
<tr>
<th></th>
<th>A1•CHEX</th>
<th>A1•DIOX</th>
<th>A1•DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guest</td>
<td>Cyclohexane</td>
<td>dioxane</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>Host:guest ratio</td>
<td>1:½</td>
<td>1:½</td>
<td>1:1</td>
</tr>
<tr>
<td>Mg mol⁻¹</td>
<td>346.41</td>
<td>348.38</td>
<td>377.42</td>
</tr>
<tr>
<td>Crystal symmetry</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>aÅ</td>
<td>8.4834(17)</td>
<td>8.4075(17)</td>
<td>9.0685(18)</td>
</tr>
<tr>
<td>bÅ</td>
<td>9.1242(18)</td>
<td>9.0908(18)</td>
<td>9.6815(19)</td>
</tr>
<tr>
<td>cÅ</td>
<td>12.712(3)</td>
<td>12.442(3)</td>
<td>12.311(3)</td>
</tr>
<tr>
<td>α°</td>
<td>96.10(3)</td>
<td>97.04(3)</td>
<td>72.36(3)</td>
</tr>
<tr>
<td>β°</td>
<td>104.73(3)</td>
<td>101.33(3)</td>
<td>73.95(3)</td>
</tr>
<tr>
<td>γ°</td>
<td>110.41(3)</td>
<td>111.15(3)</td>
<td>78.05(3)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>VÅ³</td>
<td>871.0(4)</td>
<td>849.9(4)</td>
<td>980.9(4)</td>
</tr>
<tr>
<td>μ(Mo-Kα)mm⁻¹</td>
<td>0.086</td>
<td>0.093</td>
<td>0.087</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>113(2)</td>
<td>113(2)</td>
<td>113(2)</td>
</tr>
<tr>
<td>Range scanned,</td>
<td>2.44-25.64</td>
<td>2.68 - 26.37</td>
<td>3.02 - 25.69</td>
</tr>
<tr>
<td>Index range</td>
<td>h:-10,9; k:-10,11; l:±15</td>
<td>h:±10; k: ±11; l:±15</td>
<td>h:0,11; k:±11; l:-13,15</td>
</tr>
<tr>
<td>No. reflections</td>
<td>5676</td>
<td>6199</td>
<td>3695</td>
</tr>
<tr>
<td>collected reflections</td>
<td>3263</td>
<td>3422</td>
<td>3695</td>
</tr>
<tr>
<td>No. reflections with</td>
<td>2572</td>
<td>2419</td>
<td>2813</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3263 / 2 / 240</td>
<td>3422 / 2 / 240</td>
<td>3695/ 2/ 260</td>
</tr>
<tr>
<td>Goodness of fit, S</td>
<td>1.044</td>
<td>1.030</td>
<td>1.033</td>
</tr>
<tr>
<td>Final R indices</td>
<td>R₁ = 0.0383</td>
<td>R₁ = 0.0396</td>
<td>R₁ = 0.0416</td>
</tr>
<tr>
<td>(l&gt;2σ(l))</td>
<td>wR₂=0.0955</td>
<td>wR₂=0.0854</td>
<td>wR₂=0.1010</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0523,</td>
<td>R₁ = 0.0682,</td>
<td>R₁ = 0.0607,</td>
</tr>
<tr>
<td>Largest diff peak and hole (eÅ⁻³)</td>
<td>0.165 and -0.235</td>
<td>0.223 and 0.220</td>
<td>0.177 and 0.247</td>
</tr>
</tbody>
</table>
A1·CHEX

C$_{20}$H$_{16}$O$_3$·$\frac{1}{2}$C$_6$H$_{12}$

Guest: cyclohexane

Space Group: P -1

\[ \begin{align*}
\text{a} &= 8.483(17) \text{ Å} & \alpha &= 96.10(3) ^\circ \\
\text{b} &= 9.124(18) \text{ Å} & \beta &= 104.73(3) ^\circ \\
\text{c} &= 12.71(3) \text{ Å} & \gamma &= 110.41(3) ^\circ \\
\text{Volume} &= 871.0(4) \text{ Å}^3 \\
Z &= 2
\end{align*} \]

Crystal Structure and Refinement

The crystal unit cell parameters of A1·CHEX were obtained from a Nonius Kappa CCD diffractometer. The crystal structure showed that it belongs to a triclinic system with space group P -1. The TG curve confirmed that the inclusion compound has a $1: \frac{1}{2}$ host guest ratio.

The crystal structure was solved by direct methods. The non-hydrogen atoms were found in the difference map. All non-hydrogen atoms of the host and guest were refined anisotropically.

The unit cell contains of two host molecules and one guest molecule (Z=2). The host atoms were found in general positions and the guest was found on a centre of inversion. All hydrogen atoms were found in the electron density maps including the hydroxyl hydrogen of the host. Aromatic hydrogens were fixed at distances of C–H= 0.95 Å. The guest CH$_2$— hydrogens were fixed with C–H distances of 0.99 Å. The hydroxyl hydrogens were refined isotropically and were placed in calculated positions using the correlation between O–H distances and O–O distances$^1$. The bond angles and bond lengths are all in accepted ranges$^2$. 
Table 3.2 Hydrogen bonding details of A1-CHEX.

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>D***A/Å</th>
<th>D-H/Å</th>
<th>H***A/Å</th>
<th>D-H***A/</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>O1\textsuperscript{a}</td>
<td>2.865(2)</td>
<td>0.961(1)</td>
<td>1.904(1)</td>
<td>178(2)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: -x,-y+1,-z+2

Crystal Packing

The host molecules form dimers of the form (Host)-OH···O-(Host). Thus, hydrogen bonding was observed between the hydroxyl oxygen of one host and the ether oxygen of a neighbouring host. These host dimers are located in columns along the [011] direction. The guest molecules lie in constricted channels formed by the packing of the p-methoxy phenyl moieties of the host which are effectively cavities. The cavities were mapped using the program SECTION\textsuperscript{3} and the dimensions of each cavity were approximately 5.09 Å x 6.76 Å x 6.36 Å.

The cyclohexane molecule lies on a centre of symmetry at Wyckoff position \( \alpha \) and exhibits the expected chair conformation. No significant contacts between guest and host molecules were detected, thus this is a true clathrate structure. The closest C-H···π contact between the host and the guest is 3.689 Å. This is the distance from C1G to the centroid of one of the aromatic rings of the host molecule defined by (C7, C8, C9, C10, C11, and C12). The angle C1G-H1G···centroid is 138.21°. This compares favourably with the average value of 3.69(2) Å given by Braga\textsuperscript{4} for a C–H···π distance with the average angle given as 142(2)°.
Figure 3.2  Packing diagram of A1·CHEX down [100].

Thermal Analysis

The DSC curve gave two endotherms of which the first (T_on=380.2K) corresponds to the loss of guest and the second (T_on=390.4K) is due to the host melt.

The TG curve showed two steps which individually do not correspond to a stoichiometric loss of guest. The first step is consistent with the loss of 0.35 of the total guest and the second step corresponds to the loss of 0.64 of the total guest. The total experimental guest loss was 13.7% (calculated guest loss= 12.1%).
Figure 3.3 TG and DSC curves for Al-CHEX.
A1•DIOX

C_{20}H_{16}O_3•\frac{1}{2}C_4H_6O_2

Guest: 1, 4-dioxane

Space Group: P -1

a=8.4075(17)Å  \hspace{1cm} \alpha= 97.04(3) °

b=9.0908(18) Å  \hspace{1cm} \beta= 101.33(3) °

c=12.442(3) Å  \hspace{1cm} \gamma=111.15(3) °

Volume= 849.9(4) Å³

Z=2

Crystal Structure and Refinement

The TG analysis verified a host:guest ratio of 1:½. The reflection conditions were the same as those found for A1•CHEX. The space group P -1 was assigned.

Again the non-hydrogen atoms of the host and the guest were found in the electron density maps with the host atoms situated in general positions and the guests on centres of inversion. All the hydrogens were treated in exactly the same way as was observed for the A1•CHEX structure.

Table 3.3 Hydrogen bonding details of A1•DIOX.

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>D···A/Å</th>
<th>D-H/Å</th>
<th>H···A/Å</th>
<th>D-H···A°</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>O1\textsuperscript{b}</td>
<td>2.868(2)</td>
<td>0.970(1)</td>
<td>1.900(1)</td>
<td>176(2)</td>
</tr>
</tbody>
</table>

\textsuperscript{b}.-x, -y+1, -z+1
A1-CHEX and A1-DIOX are isostructural with respect to the host. Again the host molecules form hydrogen bonded dimers with the guest molecules situated in constricted channels. The size of the vacancy occupied by the dioxane guests was determined as 5.25 Å x 6.73 Å x 6.38 Å which compares favourably with the size of the cavities in the cyclohexane compound.

The shortest C–H···π contacts between the host and the guest are:

- 3.779 Å for the distance between C1G and the centroid of one of the aromatic rings of the host molecule defined by (C1, C2, C3, C4, C5, C6), the corresponding angle C1G–H1G–centroid is 154.34°.
- 3.792 Å for the distance between C2G and the centroid of the aromatic ring defined by (C14, C15, C16, C17, C18, C19), the angle C2G–H2G–centroid is 152.88°.

Figure 3.4 Packing diagram of A1-DIOX down [100].
Thermal Analysis

A single mass loss step was observed in the TG experiment (Figure 3.5). There is a good correlation between the experimental mass loss which is 12.1% and the calculated mass loss which is 12.6%.

A single endotherm was observed in the DSC due to the host dissolution in the 1,4-dioxane.

Figure 3.5 TG and DSC curve for A1•DIOX.

Kinetics of decomposition

Non-isothermal methods were used to determine the kinetics of desolvation.

Non-isothermal Kinetics

A powder form of A1•DIOX was grown at 298 K and the structure was verified using powder x-ray diffraction. There was generally good agreement between the experimentally obtained powder pattern and the calculated one generated from the program LAZY PULVERIX. These are shown in Figure 3.6. TG experiments were performed over a temperature range of 303-473 K at heating rates 1, 2, 5 and 10 K min⁻¹. The TG curves were analysed at percentage mass losses of 2 % to 10 % using the Flynn and Wall method and converted into plots of -log β vs 1/T. The activation energy was calculated in the range 133-162 kJmol⁻¹.
The host decomposes soon after the guest is released and this results in the decomposition curves of **A1•DIOX** giving inconsistent mass loss values at different temperatures. Thus isothermal kinetics could not be performed.

![Experimental and calculated powder patterns of A1•DIOX.](image)

**Figure 3.6** Experimental and calculated powder patterns of **A1•DIOX**.

The experimental pattern was obtained at room temperature and calculated one was derived from a structure at low temperatures.

![Plot of -log β vs. 1/T for A1•DIOX.](image)

**Figure 3.7** Plot of $-\log \beta$ vs. $1/T$ for **A1•DIOX**.
A1-DMF

C<sub>20</sub>H<sub>16</sub>O<sub>3</sub> • C<sub>3</sub>H<sub>7</sub>NO
Guest: N,N -dimethylformamide
Space Group: P -1

a=9.069(17) Å  α= 72.36(3)°
b=9.682(19) Å  β= 73.95(3)°
c=12.31(25) Å  γ=78.05(3)°
Volume= 980.9(4) Å<sup>3</sup>
Z=2

Crystal Structure and Refinement

TG analysis demonstrated a host:guest ratio of 1:1. The structure was successfully solved in the space group P -1.

All the non-hydrogen atoms of the host and guest were found and refined by direct methods. Both the host and guest molecules were found in general positions. The non-hydrogen atoms of the host were refined anisotropically. The asymmetric unit consists of one host and one guest molecule. The hydroxyl hydrogens were fixed in calculated positions based on the relationship between O···O distances<sup>1</sup> and O–H distances.

Table 3.4 Hydrogen bonding details of A1-DMF.

<table>
<thead>
<tr>
<th>Donor (D)</th>
<th>Acceptor (A)</th>
<th>D···A/Å</th>
<th>D-H/Å</th>
<th>H···A/Å</th>
<th>D-H···A&lt;sup&gt;o&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>O1G&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.763(2)</td>
<td>0.960(1)</td>
<td>1.820(1)</td>
<td>167(1)</td>
</tr>
</tbody>
</table>

<sup>c</sup>: -x+2, -y, -z
The hydroxyl hydrogen of the host forms a hydrogen bond with the oxygen of the guest. Two rows of host molecules form a bilayer along [010]. The packing of the host framework provides narrow channels along [100] and [010] which are occupied by the DMF guests.

The dimension of the channels down [100] vary from 6.545 Å x 4.788 Å to 7.745 Å x 8.549 Å. The channel down [010] ranges in size from 8.656 Å x 2.736 Å to 8.224 Å x 4.100 Å.

In addition to the hydrogen bonding observed between the host and guest molecules the structure is also stabilised by C–H–π contacts. In particular we have noted distances which range from 3.435 Å from C3G to the centroid of the aromatic ring of the host defined by C7, C8, C9, C10, C11 and C12, to 3.731 Å for the distance between C1G and the C1, C2, C3, C4, C5, C6 aromatic ring of the host. The corresponding C3G–H3G1–π centroid angle was measured as 152.56° and the C1G–H1G2–π centroid is 120.91°.

Figure 3.8 Packing diagram of A1·DMF along [100]
Figure 3.9 Channels of A1•DMF showing voids down [100] and [010].

**Thermal Analysis**

The DSC curve shows one endotherm corresponding to desolvation accompanied by dissolution of the host in the liquid guest.

TG analysis indicated a single mass loss step. The experimental mass loss is 19.7% (calculated=19.4%).

Figure 3.10 TG and DSC curve for A1•DMF.
Kinetics of decomposition

Isothermal methods were used to determine the kinetics of desolvation.

Isothermal Thermogravimetry

A series of isothermal experiments were carried out on a powder of A1•DMF which was grown at 298 K. There was generally good agreement between the experimentally obtained powder patterns and the calculated ones generated from the program LAZYPULVERIX. These are shown in Figure 3.11. The experiments were conducted at selected temperatures ranging from 323 K to 338 K. The mass loss curves were converted into extent of reaction, \( \alpha \), versus time curves. The \( \alpha \)-time curves displayed a fast decomposition step at lower temperatures followed by a slow second step. At higher temperatures the first step controlled the entire reaction and analysis of the first step showed that it followed the deceleratory contracting volume model,

\[
R3: 1 - (1-\alpha)^{1/3} = kt
\]

The resultant Arrhenius plot is shown in Figure 3.12. An activation energy of \( 143(15) \) kJ mol\(^{-1} \) was obtained.

Figure 3.11 Experimental and calculated powder pattern of A1•DMF.
Guest Exchange Reactions

Exchange reactions were performed by exposing crushed crystals of each of the inclusion compounds to the vapours of a different guest as described in Chapter 2. In a typical experiment A1•DIOX was exposed to vapours of dimethylformamide in a sealed container at 298 K and the reaction monitored using DSC. Similar experiments were set up between A1•DIOX and cyclohexane, A1•DMF and dioxane, A1•DMF and cyclohexane, A1•CHEX and dioxane and finally A1•CHEX and dimethylformamide.

The overall exchange reaction can be described by the following equation:

$$A1\cdot G1(s) + G2\ (vapour) \rightarrow A1\cdot G2 + G1\ (vapour)$$

The DSC traces for the complexes are different and thus the reaction was monitored by DSC over a period of 100 min to 2 weeks. The results can be seen in Figures 3.13 to 3.17. The rate of any exchange reaction is generally dependent on particle size and vapour pressure of the incoming guest. The vapour pressures (in mbars)$^8$ of dimethylformamide, dioxane and cyclohexane at 298 K were 4.39, 49.5, and 130 respectively.

For all of the guest exchange experiments an endotherm due to the host melt was observed at $T_{on} = 392$ K. This suggests that the reaction proceeded via a
mechanism which involved loss of the guest to yield desorbed host followed by the uptake of the incoming guest. This can be represented by:

\[
\begin{align*}
A_1\cdot G_1 (s) & \rightarrow A_1 (s) + G_1 \text{ (vapour)} \\
A_1 (s) + G_2 \text{ (vapour)} & \rightarrow A_1\cdot G_2 (s)
\end{align*}
\]

![DSC results of the exchange reaction represented by: A1•CHEX(s) + DIOX (g) -> A1•DIOX(s) + CHEX↑](image)

![DSC result of the exchange reaction: A1•CHEX(s) + DMF (g) -> A1•DMF(s) + CHEX↑](image)
Figure 3.15 DSC results of the exchange reaction represented by:

$$A_1 \cdot \text{DIOX}(s) + \text{DMF} (g) \rightarrow A_1 \cdot \text{DMF}(s) + \text{DIOX}↑$$

Figure 3.16 DSC results of the exchange reaction represented by:

$$A_1 \cdot \text{DMF}(s) + \text{CHEX} (g) \rightarrow A_1 \cdot \text{CHEX}(s) + \text{DMF}↑$$
Figure 3.17 DSC results of the exchange reaction represented by:

\[ \text{A1} \cdot \text{DMF}(s) + \text{DIOX} (g) \rightarrow \text{A1} \cdot \text{DIOX}(s) + \text{DMF} \uparrow \]

**Competition Experiments**

Two component competition experiments were carried out between benzene and 1,4-dioxane guests. A series of 11 vials were made up with mixtures of guests in a host:guest ratio of 1:10, such that the mole fraction of one guest varied from 0 to 1. The mole fraction of a given guest included by the host versus the mole fraction of the guest in the original mother liquor was plotted. The resultant plot is shown in Figure 3.18. The results show that there is a slight preference of A1 for 1, 4-dioxane. The selectivity is not significant and is within experimental error.
Figure 3.18 Results of competition experiments between A1 and guests, benzene and 1, 4- dioxane.
Discussion

The structures A1·CHEX and A1·DIOX are isostructural with respect to the host. The host displays the expected packing motif which was previously reported on for inclusion compounds between A1 and benzene, toluene, the xylene isomers\(^9\) and aniline\(^10\). The host atoms occupy general positions with the guest molecules located on centres of inversion at Wyckoff position \(a\). Two host molecules form a centrosymmetric dimer at Wyckoff position \(a\) (Figure 3.2). The host:guest ratios are typically 1:½ with both the cyclohexane and dioxane guests located in cavities. Stabilisation of the host network occurs via \((\text{Host})-\text{OH} \cdots \text{O} \cdots (\text{Host})\) hydrogen bonding.

For the A1·DMF structure both the host and the guest atoms were found in general positions with a host: guest ratio of 1:1. This structure displays hydrogen bonding between the host and guest molecules of the form \((\text{Host})-\text{OH} \cdots \text{O} \cdots (\text{Guest})\) which is a first for this host. This is illustrated in Figure 3.8. The dimethylformamide molecules are located in interconnected narrow channels running parallel to [100] and [010], Figure 3.9. Both channels exhibit a zigzag arrangement.

Kinetics of desolvation experiments yielded an activation energy range of 133-162 kJ\(\text{mol}^{-1}\) for A1·DIOX and 143(15) kJ\(\text{mol}^{-1}\) for A1·DMF. These values are in the expected ranges for organic inclusion compounds.

The C–H⋯\(x\) distances of A1·CHEX, A1·DIOX and A1·DMF are in expected average ranges as mentioned by Braga et al\(^4\).

\[
d = 2.79(2) \text{ Å} \\
D = 3.69(2) \text{ Å} \\
\text{Angle } C-\text{H} \cdots M = 142(2) ^\circ
\]

where \(M\) is the centroid.
Table 3.5 Summary of thermal analysis data for the structures of A1 studied.

<table>
<thead>
<tr>
<th>Inclusion Compound</th>
<th>A1•CHEX</th>
<th>A1•DIOX</th>
<th>A1•DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>H:G ratio</td>
<td>1:½</td>
<td>1:½</td>
<td>1:1</td>
</tr>
<tr>
<td>TG (calc% mass loss)</td>
<td>12.1</td>
<td>12.6</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>13.7</td>
<td>12.1</td>
<td>19.7</td>
</tr>
<tr>
<td>DSC $T_{on}$/K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endotherm 1</td>
<td>380.2</td>
<td>366.2</td>
<td>331.1</td>
</tr>
<tr>
<td>Endotherm 2</td>
<td>390.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_b$/K</td>
<td>354.2</td>
<td>375.2</td>
<td>426.2</td>
</tr>
<tr>
<td>$T_{on}$/T_b</td>
<td>1.073</td>
<td>0.976</td>
<td>0.777</td>
</tr>
</tbody>
</table>

DSC results for both A1•DIOX and A1•DMF show a single endotherm corresponding to dissolution of the host upon release of the guest. The cyclohexane compound, A1•CHEX, gave two endotherms, the first due to the guest loss and the second due to host melt. This difference is reflected in the TG results which show single steps for the dioxane and dimethylformamide compounds compared to the two steps of the cyclohexane compound. These results suggest that A1•CHEX undergoes a different, more complex mechanism for thermal decomposition than the other two structures. The ratio of the onset of desolvation ($T_{on}$) and the normal boiling point ($T_b$) was used as a measure of thermal stability.
The $T_{on}/T_b$ values as listed in Table 3.5 indicate similar thermal stabilities for A1•CHEX and A1•DIOX which is expected due to their identical packing arrangements and is comparable to that of A1•BENZ clathrate ($T_{on}/T_b = 1.039$). A1•DMF yields a value of $T_{on}/T_b = 0.777$, indicating a less stable structure.

There is no significant selectivity of A1 for either benzene or 1,4-dioxane.
References


CHAPTER 4 A10 AND ITS INCLUSION COMPOUNDS

The host A10 formed inclusion compounds with guests benzene, cyclohexane, cyclohexanone, N,N-dimethylformamide, N,N-dimethylacetamide and 1,4-dioxane. The crystal structures obtained and thermal stability of the inclusion compounds formed will be discussed.

![Chemical structures](attachment:chemical_structures.png)

Figure 4.1 A schematic diagram of the host and guests.

The host, A10, was dissolved in the liquid guests to give dilute solutions. A10 is only slightly soluble in cyclohexane and a co-solvent, ethanol, which does not form an inclusion compound with the host, was added until a clear solution was obtained. The solutions were left to evaporate slowly at room temperature until suitable crystals were formed.
A10·BENZ

C_{20}H_{16}O_{2}·\frac{1}{2}C_{6}H_{6}

Guest: benzene

Space Group: P -1

a = 8.4271(17) Å  \quad \alpha = 99.86(3)°

b = 9.0895(18) Å  \quad \beta = 97.55(3)°

c = 11.870(2) Å  \quad \gamma = 110.19(3)°

Volume = 822.7(3) Å³

Z = 2

Crystal Structure and refinement

The crystal unit cell dimensions were established from the intensity data measured on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-Kα radiation. The A10·BENZ structure was solved successfully in the space group P -1. A host:guest ratio of 1:½ was established by TG and this was confirmed by the crystal structure.

All the non-hydrogen atoms of the host and guest were found in the electron density maps and refined anisotropically. The unit cell contains of two host molecules and one guest molecule (Z=2). The hydroxyl hydrogens were located in the difference electron density maps, and were refined isotropically. The hydroxyl hydrogens were placed in calculated positions based on the relationship between O—H and O···O distances. The remaining hydrogen atoms were geometrically constrained as was described in Chapter 3. The bond lengths and angles of the host molecule are all within accepted ranges.
Table 4.1 Hydrogen bonding details of A10-BENZ.

<table>
<thead>
<tr>
<th>Donor Acceptor</th>
<th>D---A/Å</th>
<th>D-H/Å</th>
<th>H---A/Å</th>
<th>D-H---A/º</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>O1ª</td>
<td>2.864(2)</td>
<td>0.960(1)</td>
<td>1.907(1)</td>
</tr>
</tbody>
</table>

ª: -x, -y-1, -z-1

Crystal Packing

The crystal packing of A10-BENZ is illustrated in Figure 4.2 and is very similar to that observed for A1-CHEX and A1-DIOX. Hydrogen bonding was observed between the hydroxyl oxygen of one host and the ether oxygen of a neighbouring host. The host forms dimers of the form (Host) - OH---O (Host). The host dimers form layers parallel to the [011] direction. The guest molecules lie in cavities formed by the packing of p-methyl phenyl moieties of the host. The cavity were mapped using the program SECTION ³ and size was found to be 5.27 Å x 5.72 Å x 6.78 Å.

The benzene molecule lies on a centre of symmetry at Wyckoff position a. No significant contacts between guest and host molecules were detected, thus this is a true clathrate structure. The closest C-H---n contact between the host and the guest is 3.699 Å. This represents the distance from C19 of the host to the centroid of the benzene ring. The angle C19-H19---benzene was measured as 130(1)º.
Thermal Analysis

The DSC curve shows two endotherms of which the first ($T_{on}=357.4$ K) corresponds to the loss of guest and the second ($T_{on}=420.8$ K) is due to the host melt.

The TG curve showed one single mass loss step. There is a good correlation between the experimental loss which is 11.9% and calculated mass loss which is 12%.
Kinetics of decomposition

Isothermal methods were used to determine the kinetics of desolvation.

Isothermal Thermogravimetry

Samples of A10-BENZ obtained by crushing crystals of the bulk material were analysed by performing a series of isothermal experiments over a temperature range of 323-343 K at intervals of 5K. These are shown in Figure 4.4. The resultant $\alpha$ – time curves best fitted the first order reaction kinetic model, $F1: -\ln (1-\alpha) = kt$ over the range $0 - 0.98$. The resultant Arrhenius plot, Figure 4.5, revealed activation energy of 114(9) kJmol$^{-1}$. 

Figure 4.3 TG and DSC curve for A10-BENZ.
Figure 4.4 Isothermal curves of A10-BENZ.

Figure 4.5 Plot of In $k$ versus $1/T$ for A10-BENZ.
Figure 4.4 Isothermal curves of A10•BENZ.

Figure 4.5 Plot of ln k versus 1/T for A10•BENZ.
A10·CHEX

C_{20}H_{16}O_{2}·\frac{1}{2}C_{6}H_{12}

Guest: cyclohexane

Space Group: P -1

\begin{align*}
a & = 8.5545(17) \text{ Å} & \alpha & = 99.93(3) ^\circ \\
b & = 9.1330(18) \text{ Å} & \beta & = 100.44(3) ^\circ \\
c & = 12.068(2) \text{ Å} & \gamma & = 109.42(3) ^\circ \\
\end{align*}

Volume = 846.5(3) Å³

Z = 2

Crystal Structure and Refinement

A host: guest ratio of 1:½ was established by TG. The crystal structures of A10·CHEX and A10·BENZ are very similar and once again the space group P -1 was assigned. Thus the host molecules were found in general positions with the cyclohexane guest on a centre of inversion (Wyckoff position a) in the chair conformation.

All the non-hydrogen atoms of the host and the guest were obtained by direct methods and refined anisotropically. The hydroxyl hydrogen of the host was located in the difference electron density maps and placed in geometrically calculated positions. The bond lengths and angles of the host molecule were in the expected known ranges.

Table 4.2 Hydrogen bonding details of A10·CHEX.

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>D···A/Å</th>
<th>D–H/Å</th>
<th>H···A/Å</th>
<th>D–H···A°</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>O1b</td>
<td>2.859(2)</td>
<td>0.961(1)</td>
<td>1.956(1)</td>
<td>175(2)</td>
</tr>
</tbody>
</table>

b: -x-1, -y-1, -z-1
**Crystal Packing**

**A10-BENZ** and **A10-CHEX** are isostructural with respect to the host. The host molecules form hydrogen bonded dimers with the guest molecules located in the cavities. The dimensions of the cavity were 6.06 Å x 6.77 Å x 6.89 Å. The structure is also stabilised by aromatic C-H···π interactions between one of the guest C-H bonds and a phenyl group of the host. The C1G–H1G1···π interaction is defined by the following: (a) the distance between C1G and the centroid of the phenyl ring defined by C7, C8, C9, C10, C11 and C12 of the host is 3.881 Å and (b) the angle C1G–H1G1···centroid is 132(1)°.

![Figure 4.6 Packing diagram of A10-CHEX down [100].](image)

**Thermal Analysis**

The TG shows a single mass loss step (calculated mass loss: 12.7%, experimental mass loss: 10.9%).

The DSC curve gave two endotherms of which the first (T_on = 323 K) is due to guest release and the second (T_on = 418, 2 K) is due to the host melt.
Crystal Packing

**A10-BENZ** and **A10-CHEX** are isostructural with respect to the host. The host molecules form hydrogen bonded dimers with the guest molecules located in the cavities. The dimensions of the cavity were 6.06 Å x 6.77 Å x 6.89 Å. The structure is also stabilised by aromatic C-H···π interactions between one of the guest C-H bonds and a phenyl group of the host. The C1G—H1G1···π interaction is defined by the following: (a) the distance between C1G and the centroid of the phenyl ring defined by C7, C8, C9, C10, C11 and C12 of the host is 3.881 Å and (b) the angle C1G—H1G1···centroid is 132(1)°.

Figure 4.6 Packing diagram of **A10-CHEX** down [100].

Thermal Analysis

The TG shows a single mass loss step (calculated mass loss: 12.7%, experimental mass loss: 10.9%).

The DSC curve gave two endotherms of which the first (**T_m = 323 K**) is due to guest release and the second (**T_m = 418, 2 K**) is due to the host melt.
Kinetics of decomposition

Isothermal and non-isothermal methods were used to determine the kinetics of desolvation.

Isothermal Thermogravimetry

Crushed crystals of A10·CHEX were analysed in a series of TG runs over a temperature range of 323-338 K at intervals of 5 K. The resulting α - time curves best fitted the deceleratory first order kinetic model, F1: \(-\ln (1-\alpha) = kt\) over the range 0 to 1. The resultant Arrhenius plot, Figure 4.8, revealed an activation energy of 112(14) kJmol\(^{-1}\).

Figure 4.8 Plot of In k versus 1/T for A10·CHEX.
Non-isothermal kinetics

A series of TG runs were performed over a temperature range of 303-473 K at heating rates 2, 5, 10, 15 and 20 K min\(^{-1}\). The TG curves were analysed at percentage mass losses of 2 % to 10 % using the Flynn and Wall method \(^4\) and converted into plots of – log \(\beta\) vs. 1/T. The activation energy was calculated in the range 80-123 kJmol\(^{-1}\).

![Figure 4.9 Plot of \(-\log \beta\) vs 1/T.](image-url)
A10·CHEXANONE

C_{20}H_{15}O_{2}·C_{6}H_{10}O

Guest: cyclohexanone

Space Group: P -1

a = 9.0694(18) Å   α = 85.80(3)°
b = 9.5026(19) Å   β = 72.97(3)°
c = 12.823(3) Å   γ = 74.75(3)°

Volume = 1019.5(4) Å³
Z = 2

Crystal Structure and Refinement

TG analysis demonstrated a host:guest ratio of 1:1. The structure was solved in the space group P -1.

The non-hydrogen atoms of the host and the guest were found in the electron density maps with both the host and guest atoms situated in general positions. Aromatic hydrogens were fixed at distances of C—H = 0.95 Å. The guest CH₂—hydrogens were fixed with C—H distances of 0.99 Å.

Table 4.3 Hydrogen bonding details of A10·CHEXANONE.

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>D···A/A</th>
<th>D—H/A</th>
<th>H···A/A</th>
<th>D—H···A/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>O1</td>
<td>2.765(2)</td>
<td>0.960(1)</td>
<td>1.829(1)</td>
<td>164(2)</td>
</tr>
</tbody>
</table>

*: 1-x, 1-y, -z

Crystal Packing

Each cyclohexanone molecule possesses only one oxygen atom which is capable of being a hydrogen bond acceptor. In this structure the hydroxyl hydrogen of the host forms a hydrogen bond with the oxygen of the guest. Two rows of host molecules form a bilayer parallel to [010]. The xanthene moieties
point inwards with the hydroxyl groups hydrogen bonded to the guest molecules sandwiched in-between the host bilayers. The cyclohexanone guest exhibits a chair conformation. The guest molecules lie in layers parallel to [010], with each adjacent layer antiparallel to its neighbour.

The packing of the host framework provides interconnected channels down [100] and [010]. The structure is also stabilised by a C–H···π contact. The distance 3.901 Å was measured from C1G to the centroid of the host defined by C1, C2, C3, C4, C5 and C6. The angle C1G-H1G···centroid is 143.24°.

Figure 4.10 Packing diagram of A10-CHEXANONE.

Figure 4.11 Channels of A10-CHEXANONE showing voids down (a) [100] and (b) [010].
Thermal Analysis

A single mass loss step was observed in the TG experiment. The experimental mass loss is 24.9% (calculated = 25.4%).

A single endotherm was observed in the DSC due to the dissolution of the host in the cyclohexanone.

![Diagram](image)

Figure 4.12 TG and DSC curve for A10·CHEXANONE.

Kinetics of decomposition

Non-isothermal methods were used to determine the kinetics of desolvation.

Non-isothermal kinetics

Samples of A10·CHEXANONE were obtained by crushing crystals of the bulk material. A series of TG runs over a temperature range of 303-473 K were performed at heating rates 1, 2, 5 and 10 K min⁻¹. The TG curves were analysed at percentage mass losses of 5% to 25 % using the Flynn and Wall method⁴ and converted into plots of -log β vs. 1/T. The activation energy was calculated in the range 80-90 kJmol⁻¹.
Figure 4.13 Plot of $-\log \beta$ vs $1/T$ for A10-CHEXANONE.
**A10-DIOX**

C$_{20}$H$_{16}$O$_2$·$\frac{1}{2}$C$_4$H$_8$O$_2$

Guest: 1, 4-dioxane

Space Group: P -1

a = 8.0728(16) Å \(\alpha = 87.02(3)^\circ\)

b = 9.6524(19) Å \(\beta = 85.72(3)^\circ\)

c = 10.668(2) Å \(\gamma = 83.97(3)^\circ\)

Volume = 823.6(4) Å$^3$

Z = 2

**Crystal Structure and Refinement**

A host: guest ratio of 1:½ was established by TG and this was confirmed by the crystal structure. The triclinic space group P -1 was assigned. The host was found in general positions with the guest molecules situated on a centre of inversion at Wyckoff position a.

Again the non-hydrogen atoms of the host and guest were obtained by direct methods and refined anisotropically. The hydroxyl hydrogens were located in the difference electron density maps, and were refined isotropically. The hydroxyl hydrogens were then placed in calculated positions based on the O-H distance as a function of the O···O distance$^1$.

**Table 4.4 Hydrogen bonding details of A10-DIOX**

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>D···A/Å</th>
<th>D-H/Å</th>
<th>H···A/Å</th>
<th>D-H···A$^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>O1G</td>
<td>2.868(2)</td>
<td>0.958(1)</td>
<td>1.924(1)</td>
<td>168(1)</td>
</tr>
</tbody>
</table>
Crystal Packing

The crystal packing of A10·DIOX is illustrated in Figure 4.14. Each dioxane molecule is hydrogen bonded to two host molecules with the dioxane in the chair conformation. By comparing the packing of A10·DIOX, as seen in Figure 4.14, with that of A10·CHEX (Figure 4.6) we notice that in the case of the packing of the dioxane compound the host hydroxyl groups are directed towards the guest whereas for the cyclohexane compound the hydroxyl hydrogens are pointed away from the guest forming dimers with adjacent host molecules. The dioxane molecules are situated in cavities which have approximate dimensions of 4.84 Å x 6.66 Å x 6.88 Å. The closest C–H⋯π contact between the host and guest is 2.908 Å. This is the distance from C2G to the centroid of one of the aromatic rings of the host molecule defined by (C1, C2, C3, C4, C5 and C6). The angle C2G–H2G⋯centroid is 131.55°.

![Figure 4.14 Packing diagram of A10·DIOX along [100].](image)

Thermal Analysis

The DSC curve shows three endotherms of which the first (Ton = 327.2 K) is a very small peak compared to the other two endotherms and can be attributed to the commencement of guest release. The loss of dioxane continues at Ton = 384.1 K. The third endotherm (Ton = 399.3 K) is due to the host melt.
The results are consistent with the observations found on the melting point apparatus where the guest loss starts at 333 K and the host is completely melted at 413 K.

A single mass loss curve was observed in the TG experiment. There is a good correlation between the experimental mass loss which is 13.3 % and the calculated mass loss of 13.5 %.

Figure 4.15 TG and DSC curve for A10·DIOX.
A10•DMA

C₂₀H₁₆O₂•C₄H₉ON
Guest: N, N-dimethylacetamide
Space Group: P2₁/n
a =11.135(2) Å  α = 90.00°
b =12.458(3) Å  β = 93.00(3)°
c = 14.407(3) Å  γ = 90.00°
Volume = 1995.8(7) Å³
Z = 4

Crystal Structure and Refinement

TG analysis indicated a host:guest ratio of 1:1. The monoclinic space group P2₁/n was assigned. Both the host and guest molecules were found in general positions.

The crystal structure was solved by direct methods. All the non-hydrogen atoms of the host and guest were refined anisotropically and found in the electron density maps.

Crystal Packing

The host molecules are packed in rows parallel to [010] with the ether oxygen atoms in the same direction. Each adjacent row has their ether oxygens in the opposite direction (Figure 4.17). The crystal structure is stabilized by host–guest hydrogen bonding of the form (Host)–OH⋯O–(Guest) as described in Table 4.5. The shortest contact of the form (Host)–OH⋯O1–(Host) was measured at 3.308 Å which is greater than the sum of the van der Waals radii and cannot be considered as a hydrogen bond. The N,N-dimethylacetamide molecules occupy zigzag channels parallel to [100] and [010].
Table 4.5 Hydrogen bonding details of A10-DMF.

<table>
<thead>
<tr>
<th>Donor (D)</th>
<th>Acceptor (A)</th>
<th>D···A/Å</th>
<th>D–H/Å</th>
<th>H···A/Å</th>
<th>D–H···A/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>O1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.788(2)</td>
<td>0.960(1)</td>
<td>1.833(1)</td>
<td>173(2)</td>
</tr>
</tbody>
</table>

<sup>d</sup>: ½-x, y-½, ½-z

Figure 4.16 Packing diagram of A10-DMF down [100].

**Thermal Analysis**

The DSC curve shows one endotherm ($T_{on} = 411.6$ K). The decomposition of the crystal on the melting point apparatus verified that the host melted in the hot guest.

The TG shows a single mass loss step. The experimental mass loss is 23.1% (calculated= 23.2 %).
Figure 4.17 TG and DSC curve for A10•DMA.
A10-DMF

$C_{20}H_{16}O_2\cdot C_3H_7ON$

Guest: N, N-dimethylformamide

Space Group: P2$_1$/n

- $a = 12.288(3)$ Å, $\alpha = 90.00^\circ$
- $b = 11.010(2)$ Å, $\beta = 102.87(3)^\circ$
- $c = 14.758(3)$ Å, $\gamma = 90.00^\circ$

Volume = 1946.6(7) Å$^3$

$Z = 4$

**Crystal Structure and Refinement**

The host: guest ratio of 1:1 was confirmed by TG analysis. The monoclinic space group P2$_1$/n was assigned. The crystal structure was solved by direct methods.

The host and guest atoms were found in general positions. Again the non-hydrogen atoms of the host were found in the electron density maps and refined anisotropically. The guest atoms were solved isotropically and found to be disordered. The carbon atoms of the guest were refined and found to have the following site occupancy factors C1G: 0.7, C1GA: 0.3, C3GA: 0.3, C3G: 0.7, C2G: 0.7 and C2GA: 0.3 as shown in Figure 4.18. The resultant isotropic temperature factors were acceptable and ranged from 0.02281 Å to 0.09837 Å.

The hydrogen atoms of the guest were omitted from the final refinement model.

![Figure 4.18 Disordered DMF.](image)
Crystal Packing

Figure 4.19 illustrates the packing of A10·DMF. The host molecules are staggered in rows parallel to [001] with adjacent ether oxygens in an anti-parallel relationship. The guest molecules are situated in highly constricted channels parallel to [001], which are effectively cavities. Hydrogen bonding occurs between the hydroxyl hydrogen of the host and the oxygen of the guest (Table 4.6).

Table 4.6 Hydrogen bonding details of A10·DMF

<table>
<thead>
<tr>
<th>Donor (D)</th>
<th>Acceptor (A)</th>
<th>D···A/Å</th>
<th>D—H/Å</th>
<th>H···A/Å</th>
<th>D—H···A°</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>O1G e</td>
<td>2.716(2)</td>
<td>0.960(1)</td>
<td>1.817(1)</td>
<td>155(2)</td>
</tr>
</tbody>
</table>

* e: 1-x, 1-y, -z

Figure 4.19 Packing diagram of A10·DMF down [100].
Thermal Analysis

The DSC curve shows a single endotherm ($T_{on} = 329.9$ K). The TG shows a single mass loss step (experimental mass loss = 19.7% and calculated mass loss = 20.2%).

Figure 4.20 TG and DSC curves for A10·DMF.
Competition Experiments

Two point competition experiments were carried out between benzene and 1,4-dioxane, and N,N-dimethylacetamide and N,N-dimethylformamide. A series of 11 vials were made up with mixtures of guests in a host-guest ratio of 1:10, such that the mole fraction of one guest varied from 0 to 1. The mole fraction of a given guest included by the host versus the mole fraction of the guest in the original mother liquor was plotted. The resultant plots are shown in Figure 4.21 for benzene and 1,4-dioxane and Figure 4.22 for N,N-dimethylacetamide and N,N-dimethylformamide.

Figure 4.21 Results of competition experiments between A10 and guests benzene and 1,4-dioxane.

The results clearly indicate that A10 preferentially includes 1,4-dioxane.
Figure 4.22 Results of competition experiments between A10 and guests N,N-dimethylacetamide and N,N-dimethylformamide.

The results show that A10 does not differentiate between the guests N,N-dimethylacetamide and N,N-dimethylformamide.
Table 4.1 Crystal Data, experimental and refinement parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>A10•BENZ</th>
<th>A10•CHEX</th>
<th>A10•CHEXANONE</th>
<th>A10•DIOX</th>
<th>A10•DMA</th>
<th>A10•DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C_{20}H_{10}O_2\cdot%C_6H_6</strong></td>
<td>327.38</td>
<td>330.41</td>
<td>386.47</td>
<td>332.38</td>
<td>375.45</td>
<td>361.44</td>
</tr>
<tr>
<td><strong>M_{w, g/mol}</strong></td>
<td>173(2)</td>
<td>173(2)</td>
<td>173(2)</td>
<td>173(2)</td>
<td>173(2)</td>
<td>173(2)</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>P(-1)</td>
<td>P(-1)</td>
<td>P(-1)</td>
<td>P(-1)</td>
<td>P2_1/n</td>
<td>P2_1/n</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>a, Å</strong></td>
<td>8.427(17)</td>
<td>8.554(17)</td>
<td>9.0694(18)</td>
<td>8.0728(16)</td>
<td>11.135(2)</td>
<td>12.288(3)</td>
</tr>
<tr>
<td><strong>b, Å</strong></td>
<td>9.0895(18)</td>
<td>9.1330(18)</td>
<td>9.5026(19)</td>
<td>9.6524(19)</td>
<td>12.458(3)</td>
<td>11.010(2)</td>
</tr>
<tr>
<td><strong>c, Å</strong></td>
<td>11.870(2)</td>
<td>12.068(2)</td>
<td>12.823(3)</td>
<td>10.668(2)</td>
<td>14.407(3)</td>
<td>14.758(3)</td>
</tr>
<tr>
<td><strong>α, °</strong></td>
<td>99.86(3)</td>
<td>99.93(3)</td>
<td>85.80(3)</td>
<td>87.02(3)</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td><strong>β, °</strong></td>
<td>97.55(3)</td>
<td>100.44(3)</td>
<td>72.97(3)</td>
<td>85.72(3)</td>
<td>93.00(3)</td>
<td>102.87(3)</td>
</tr>
<tr>
<td><strong>γ, °</strong></td>
<td>110.19(3)</td>
<td>109.42(3)</td>
<td>74.75(3)</td>
<td>83.97(3)</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td><strong>V, Å^3</strong></td>
<td>822.7(3)</td>
<td>846.5(3)</td>
<td>101.95(4)</td>
<td>823.6(3)</td>
<td>1995.8(7)</td>
<td>1946.6(7)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>Absorption coefficient</strong></td>
<td>0.083</td>
<td>0.081</td>
<td>0.081</td>
<td>0.088</td>
<td>0.082</td>
<td>0.078</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>346</td>
<td>352</td>
<td>412</td>
<td>352</td>
<td>800</td>
<td>676</td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>h: ±10; k: ±11,10; l:±14</td>
<td>h:±10; k:±11; l:±14</td>
<td>h:±11; k:±11; l:±15</td>
<td>h:±9; k:±11; l:±15</td>
<td>h:±13; k:±15; l:±17</td>
<td>h:±14; k:±13; l:±17</td>
</tr>
<tr>
<td><strong>Reflections collected/unique</strong></td>
<td>3102/2457</td>
<td>3186/2618</td>
<td>3953/2699</td>
<td>2991/2330</td>
<td>3760/2938</td>
<td>3703/2120</td>
</tr>
<tr>
<td><strong>Data/restraints/Parameters</strong></td>
<td>2457/2/116</td>
<td>2618/2/231</td>
<td>2699/0/118</td>
<td>2330/0/227</td>
<td>2938/2/261</td>
<td>2120/0/247</td>
</tr>
<tr>
<td><strong>Goodness-of-fit</strong></td>
<td>1.049</td>
<td>1.060</td>
<td>1.120</td>
<td>1.186</td>
<td>1.096</td>
<td>1.114</td>
</tr>
<tr>
<td><strong>Final R indices [&gt;2σ(I)]</strong></td>
<td>R₁=0.0592</td>
<td>R₁=0.0373</td>
<td>R₁=0.0420</td>
<td>R₁=0.0529</td>
<td>R₁=0.0575</td>
<td>R₁=0.0704</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R₁=0.0745</td>
<td>R₁=0.0478</td>
<td>R₁=0.0717</td>
<td>R₁=0.0709</td>
<td>R₁=0.0745</td>
<td>R₁=0.0704</td>
</tr>
<tr>
<td><strong>Largest difference peak and hole, eÅ^3</strong></td>
<td>0.662 and -0.460</td>
<td>0.195 and -0.264</td>
<td>0.245 and -0.222</td>
<td>0.835 and -0.904</td>
<td>1.179 and -0.447</td>
<td>0.595 and -0.457</td>
</tr>
</tbody>
</table>
Discussion

All the structures were successfully solved in P \(-1\) except for A10·DMA and A10·DMF which were solved in P2\(_{1}/n\).

(Host)-OH⋯O(Host) hydrogen bonding stabilised both the A10·BENZ and A10·CHEX structures and the packing arrangements were identical to those previously seen for the inclusion compounds formed between A1 and the guests cyclohexane, 1,4-dioxane, benzene\(^6\), the xylene isomers, aniline\(^7\), naphthalene\(^8\), anthracene and phenanthrene.

A summary of the thermal analysis data is shown in Table 4.2. In general the \(T_{on}/T_b\) values for A10·BENZ and A10·CHEX are the highest (1.012 for the benzene compound and 0.910 for the cyclohexane compound) which is indicative of their greater stability. This was also noted in Chapter 3 where the highest \(T_{on}/T_b\) values were recorded for the 1,4-dioxane and the cyclohexane compounds of A1.

<table>
<thead>
<tr>
<th>Inclusion compound</th>
<th>A10·BENZ</th>
<th>A10·CHEX</th>
<th>A10·CHEXANONE</th>
<th>A10·DIOX</th>
<th>A10·DMA</th>
<th>A10·DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>(G) ratio</td>
<td>1:½</td>
<td>1:½</td>
<td>1:1</td>
<td>1:½</td>
<td>1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>(G)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% mass loss</td>
<td>11.9</td>
<td>12.7</td>
<td>25.4</td>
<td>13.3</td>
<td>23.2%</td>
<td>20.2</td>
</tr>
<tr>
<td>% mass loss</td>
<td>12.0</td>
<td>10.9*</td>
<td>24.9</td>
<td>13.5</td>
<td>23.1%</td>
<td>19.7</td>
</tr>
<tr>
<td>SC (T_{on}/K)</td>
<td>357.4</td>
<td>322.5</td>
<td>325.6</td>
<td>327.2</td>
<td>411.63</td>
<td>329.9</td>
</tr>
<tr>
<td>(T_{on}/T_b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(K)</td>
<td>353.2</td>
<td>354.2</td>
<td>428.15</td>
<td>374.0</td>
<td>439.15</td>
<td>426.2</td>
</tr>
<tr>
<td>(T_b)</td>
<td>1.012</td>
<td>0.910</td>
<td>0.760</td>
<td>0.875</td>
<td>0.9373</td>
<td>0.774</td>
</tr>
</tbody>
</table>
The activation energies for the desolvation of the benzene and cyclohexanone compounds were determined as 114 kJmol\(^{-1}\) and 80-90 kJmol\(^{-1}\) respectively. The kinetics of desolvation for the cyclohexane compound was analysed using both isothermal and non-isothermal methods. The resultant activation energies were in good agreement; 112 kJmol\(^{-1}\) (isothermal kinetics) and 80-123 kJmol\(^{-1}\) (non-isothermal kinetics). As was expected similar values were obtained for \(\text{A10-BENZ}\) and \(\text{A10-CHEX}\) which were also higher than that obtained for \(\text{A10-CHEXANONE}\). The activation energies are in the expected ranges for organic compounds of this type\(^6\,\,^7\).

The two point competition experiments between benzene and 1,4-dioxane indicated that the host \(\text{A10}\) prefers 1,4-dioxane, which is unexpected due to the greater stability of the benzene inclusion compound as indicated by the \(T_{on}/T_b\) values. A kinetic effect could explain this type of behaviour and has been reported previously\(^8\). For the competition between \(N,N\)-dimethylformamide and \(N,N\)-dimethylacetamide it was shown that \(\text{A10}\) shows no selectivity even though the \(T_{on}/T_b\) values indicate that \(\text{A10-DMA}\) is the more stable compound.
References:


CHAPTER 5  A1 AND A10 HOST CONFORMATIONS

For host compound A1 five different types of bonds could be distinguished excluding the ones involving hydrogen. These are shown in Figure 5.1. The conformation of the host molecule can be best described by looking at five unique torsion angles which are illustrated in Figure 5.2. The torsion angles \( \tau_1-\tau_4 \) describe the relative position of the xanthenol moiety to the methoxy phenyl group.

Host conformation of A1

Figure 5.1 Classification of bonds for A1.

Table 5.1 Bond length ranges for A1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( a = \text{C}<em>{\text{ar}}-\text{C}</em>{\text{ar}} ) (Å)</th>
<th>( b = \text{C}_{\text{ar}}-\text{O} ) (Å)</th>
<th>( c = \text{C}<em>{\text{ar}}-\text{C}</em>{\text{sp3}} ) (Å)</th>
<th>( d = \text{C}_{\text{sp3}}-\text{O} ) (Å)</th>
<th>( e = \text{C}_{\text{sp3}}-\text{OH} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1·CHEX</td>
<td>1.381(2)</td>
<td>1.374(17)</td>
<td>1.539(2)</td>
<td>1.424(16)</td>
<td>1.454(14)</td>
</tr>
<tr>
<td></td>
<td>1.398(2)</td>
<td>1.393(15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1·DIOX</td>
<td>1.378(2)</td>
<td>1.370(18)</td>
<td>1.528(2)</td>
<td>1.427(19)</td>
<td>1.454(14)</td>
</tr>
<tr>
<td></td>
<td>1.399(2)</td>
<td>1.389(17)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1·DMF</td>
<td>1.376(3)</td>
<td>1.375(3)</td>
<td>1.528(3)</td>
<td>1.423(3)</td>
<td>1.441(2)</td>
</tr>
<tr>
<td></td>
<td>1.400(3)</td>
<td>1.384(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td>1.375(13)</td>
<td>1.375(13)</td>
<td>1.517(16)</td>
<td>1.432(12)</td>
<td>1.432(12)</td>
</tr>
<tr>
<td>values</td>
<td>1.391(13)</td>
<td>1.390(15)</td>
<td>1.539(16)</td>
<td>1.449(12)</td>
<td>1.449(12)</td>
</tr>
</tbody>
</table>

82
Table 5.2 Torsion angles describing A1.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$</td>
<td>38.82°(15)</td>
<td>35.85°(19)</td>
<td>51.33°(17)</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>61.3°(15)</td>
<td>59.10°(18)</td>
<td>58.83°(17)</td>
</tr>
<tr>
<td>$\tau_3$</td>
<td>116.9°(13)</td>
<td>115.3°(15)</td>
<td>119.4°(15)</td>
</tr>
<tr>
<td>$\tau_4$</td>
<td>179.8°(10)</td>
<td>176.8°(12)</td>
<td>178.1°(12)</td>
</tr>
<tr>
<td>$\tau_5$</td>
<td>176.3°(12)</td>
<td>-179.6°(14)</td>
<td>11.10°(12)</td>
</tr>
</tbody>
</table>

A similar analysis of the bond lengths and torsion angles were completed for A10.

Figure 5.3 Classification of bonds for A10.
Table 5.3 Bond length ranges for A10.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a = C_car—C_car (Å)</th>
<th>b = C_car—C_sp³ (Å)</th>
<th>c = C_sp³—O (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A10·BENZ</td>
<td>1.379(3)</td>
<td>1.507(3)</td>
<td>1.388(2)</td>
</tr>
<tr>
<td></td>
<td>1.400(3)</td>
<td>1.525(3)</td>
<td>1.452(2)</td>
</tr>
<tr>
<td>A10·CHEX</td>
<td>1.381(18)</td>
<td>1.512(19)</td>
<td>1.388(15)</td>
</tr>
<tr>
<td></td>
<td>1.396(19)</td>
<td>1.530(18)</td>
<td>1.450(14)</td>
</tr>
<tr>
<td>A10·CHEXANONE</td>
<td>1.374(5)</td>
<td>1.513(5)</td>
<td>1.380(4)</td>
</tr>
<tr>
<td></td>
<td>1.393(4)</td>
<td>1.529(4)</td>
<td>1.441(4)</td>
</tr>
<tr>
<td>A10·DIOX</td>
<td>1.375(3)</td>
<td>1.511(3)</td>
<td>1.377(3)</td>
</tr>
<tr>
<td></td>
<td>1.436(3)</td>
<td>1.532(3)</td>
<td>1.446(2)</td>
</tr>
<tr>
<td>A10·DMA</td>
<td>1.370(4)</td>
<td>1.511(3)</td>
<td>1.373(3)</td>
</tr>
<tr>
<td></td>
<td>1.401(3)</td>
<td>1.527(3)</td>
<td>1.439(2)</td>
</tr>
<tr>
<td>A10·DMF</td>
<td>1.365(6)</td>
<td>1.507(6)</td>
<td>1.378(5)</td>
</tr>
<tr>
<td></td>
<td>1.406(5)</td>
<td>1.521(5)</td>
<td>1.441(4)</td>
</tr>
<tr>
<td>Reference values¹</td>
<td>1.375-1.391(13)</td>
<td>1.517-1.539(16)</td>
<td>1.380-1.442(14)</td>
</tr>
</tbody>
</table>

¹Reference values taken from: 

CH_{3}

CH_{3}
Table 5.4 The torsion angle describing the host A10 conformation.

<table>
<thead>
<tr>
<th>Torsion Angles</th>
<th>A10•BENZ</th>
<th>A10•CHEX</th>
<th>A10•CHEXANONE</th>
<th>A10•DIOX</th>
<th>A10•DMA</th>
<th>A10•DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$</td>
<td>39.30°(3)</td>
<td>40.02° (15)</td>
<td>37.75° (18)</td>
<td>-43.10°(2)</td>
<td>-50.0° (2)</td>
<td>59.80° (3)</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>63.60° (2)</td>
<td>62.91° (14)</td>
<td>64.02° (16)</td>
<td>-73.10°(2)</td>
<td>107.7° (2)</td>
<td>49.30° (3)</td>
</tr>
<tr>
<td>$\tau_3$</td>
<td>-60.20° (2)</td>
<td>-60.37°(14)</td>
<td>-60.01° (16)</td>
<td>49.90°(3)</td>
<td>-130.6° (19)</td>
<td>-72.90°(3)</td>
</tr>
<tr>
<td>$\tau_4$</td>
<td>-178.0° (17)</td>
<td>-178.6°(10)</td>
<td>-175.3° (11)</td>
<td>168.2°(18)</td>
<td>-11.3° (2)</td>
<td>168.5° (2)</td>
</tr>
</tbody>
</table>

Reference:

Concluding Remarks

The compounds, \textbf{A1} and \textbf{A10} are both versatile hosts including a variety of small organic guest molecules. \textbf{A1} prefers to hydrogen bond with itself and form dimers which encapsulate guest molecules. The only exception being the N,N-dimethylformamide compound where for the first time for this host, host-guest hydrogen bonding was observed. \textbf{A10} also exhibits the characteristic host dimer packing motif for the benzene and cyclohexane inclusion compounds. They have proved to be rather stable with relatively high T_{on}/T_b values. Unlike \textbf{A1}, the host compound \textbf{A10} shows more diversity in its packing with various guest molecules. Host-guest hydrogen bonding was observed for the inclusion compounds of \textbf{A10} involving the guests cyclohexanone, 1,4-dioxane, N,N-dimethylformamide and N,N-dimethylacetamide.

The kinetics of desolvation for the 1, 4-dioxane and N, N-dimethylformamide inclusion compounds of \textbf{A1} gave activation energies of 133-162 kJ mol^{-1} and 143(15) kJ mol^{-1} respectively.

Similar kinetic studies were conducted for the inclusion compounds of \textbf{A10} with the guests benzene and cyclohexane. The kinetics of desolvation for \textbf{A10-BENZ} followed the first order rate law, \( -\ln(1-\alpha) = kt \), and gave an activation energy of 114(9) kJ mol^{-1}. Both isothermal and non-isothermal methods were investigated for \textbf{A10-CHEX} and good agreement was obtained between these two methods. The isothermal experiments showed that the desolvation reaction proceeded via the first order rate law with activation energy of 112(14) kJ.mol^{-1} and the non-isothermal experiments gave an activation energy range of 80-123 kJ.mol^{-1}.
Competition experiments were performed for both A1 and A10 compounds with the following pairs of guests included by each host: benzene, and 1,4-dioxane, and N,N-dimethylformamide and N,N-dimethylacetamide. It was found that A1 shows no significant selectivity for 1,4-dioxane or benzene. This is expected as their structures are similar, and similar $T_{on}/T_{b}$ values. The competition experiment of A1 with the guests N,N-dimethylformamide and N,N-dimethylacetamide yielded no crystals or powders thus the competition experiments were not performed. The competition experiments for A10 with the guests benzene and 1,4 dioxane revealed that A10 prefers 1,4 dioxane over benzene. The guests N,N-dimethylformamide and N,N-dimethylacetamide were also included and A10 could not differentiate between the two guests.
Appendix

Supplementary data for all crystal structures are included in the attached CD-ROM in the folder 'Appendix'.

The following files have been included for each crystal structures:

<table>
<thead>
<tr>
<th>Reflection data</th>
<th>HKL file</th>
</tr>
</thead>
<tbody>
<tr>
<td>The visualisation of the structures and packing using the appropriate program X-SEED</td>
<td>RES file</td>
</tr>
<tr>
<td>Crystallographic data</td>
<td>CIF file</td>
</tr>
<tr>
<td>Tables of observed and calculated structure factors</td>
<td>FCF file</td>
</tr>
<tr>
<td>Tables of atomic co-ordination, bond lengths, bond angles, torsion angles and hydrogen bonding details.</td>
<td>LST file</td>
</tr>
</tbody>
</table>

All files can be viewed with a text editor such as WORDPAD or NOTEPAD.