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N,N-Ditritylurea and Analogs As Hosts In Crystalline Host-Guest Complexes

presented by

Kwok-Keung Daniel Ng

has been accepted towards fulfillment
of the requirements for

Chemistry degree in Ph.D

Harold Hart
Major professor

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N,N'-DITRITYLUREA AND ANALOGS AS HOSTS IN CRYSTALLINE HOST-GUEST COMPLEXES

BY

KWOK-KEUNG DANIEL NG

A DISSERTATION

Submitted to

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in partial fulfillment of the requirements

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DOCTOR OF PHILOSOPHY

Department of Chemistry

1986

ABSTRACT

N,N'-DITRITYLUREA AND ANALOGS AS HOSTS
IN CRYSTALLINE HOST-GUEST COMPLEXES

BY

KWOK-KEUNG DANIEL NG

X-ray structures of N,N'-bis(triphenylmethyl)urea (DTU) with different guests were studied. Examination of X-ray structures of DTU complexes with methylene chloride, acetone, acetaldehyde, acetonitrile, ethyl acetate and the DTU complexes already reported in the literature lead to the conclusion conclude that the topological complementarity and bonding interactions between hosts and guests are the primary reasons for the formation of the stable clathrate complexes. Hosts with modified DTU structures have also been prepared and studied. Modifications of the trityl group in DTU included larger end groups, more rigid end groups, smaller end groups and unsymmetrical end groups. Ureas with longer axes and simultaneous variation of the end group and the axis were also examined. Some of these were found to be good

hosts. An X-ray crystal structure of the 3,3,3-triphenylpropanamide-acetone complex was obtained and compared with the X-ray structure of the DTU corresponding complex. Crystal structures of the N-triphenylmethyl-N'-9-triptycylmethyl urea-ether complex and the uncomplexed host were obtained for comparison. Non-urea hosts, including trityl diamines, trityl diamides and trityl diethers were prepared. Some of these complexed with guest molecules. Complex of toluene with the ditrityl ether of ethylene glycol was obtained and its X-ray structure was compared with that of analogs. Selectivity studies with DTU, N,N'-bis[tri-(p-methylphenyl)methyl]urea (BTTMU) and N-tritylurea (NTU) as hosts showed that they can discriminate between guests with different functionalities. In some cases, these hosts can also discriminate between guests with the same functional group but different carbon skeletons.

TO MY PARENTS

ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to Professor Harold Hart for his enthusiasm, encouragement and guidance throughout the course of this study.

Appreciation is extended to Michigan State University, National Science Foundation, and National Institutes of Health for finanacial support in the form of teaching and research assistantships.

I would like to thanks my friends for their love and support over the past few years. Many thanks to my parents, brothers and sisters for their support and constant encouragement during these years.

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INTRODUCTION

INTRODUCTION

This thesis deals with molecular host-guest complexes, with the preparation of some new hosts and with X-ray and selectivity studies of their complexes. Hence it is pertinent, in this introduction, to briefly review some of the history and applications of host/guest chemistry.

Compounds with a molecular cavity are of great interest because of their ability to enclose and bind suitable guest molecules. The complexation of hosts with guests is generally referred to as the inclusion phenomenon. A host is a compound with either an intramolecular void or an intermolecular void in the crystal lattice. A guest is a compound which resides either within the host or within voids created by the host in a crystalline lattice. A molecular host-guest complex is composed of two or more distinct molecules held together by non-covalent forces in a definable structural relationship. The binding can result from any combination of several effects, including hydrogen bonding, ion pairing, metal ion to ligand attractions, acid to base interactions and Van der Waal's attractions.

Host-guest compounds have a wide range of applications. For instance, they may permit the separation of mixtures of substances according to molecular shape and size.[1] Host-guest selectivities may be sufficient to separate aromatic compounds from others in multicomponent hydrocarbon mixtures,[2] to separate branched from normal hydrocarbons,[3] to resolve enantiomers[4] and for many other purposes.[5]

The first inclusion compound was reported in 1823 by Faraday, who prepared a chlorine clathrate hydrate.[6] Other significant examples of inclusion phenomena before 1947 were graphite intercalates,[7] cyclodextrin inclusion compounds,[8] nickel cyanide-ammonia inclusion complexes with benzene,[9] tri-o-thymotide-benzene inclusion compound,[10] clathrates of Dianin's compound,[11] inclusion compounds of the cholic acid clathrates,[12] urea inclusion compounds[13] and amylose inclusion compounds.[14]

At the time of preparation, the nature of these compounds was unknown. Many of these compounds had variable compositions and in some instances the guest molecules could be removed quite easily from the complexes. It was not until 1947 that H.M. Powell showed that many of these compounds were stoichiometric, and he proposed structures and the term "clathrate" to describe novel compounds.[15]

According to their topologies, the host systems can be subdivided into two main types: cavitands, which have intramolecular cavities (i.e., within one molecule) , and clathrands, which have extramolecular cavities (i.e., between

different molecules); see Figure 1a and 1b. In this chapter, I will describe the characteristics of some cavitands studied since 1947 and illustrate them with examples. Afterwards, some clathrate systems will be discussed.

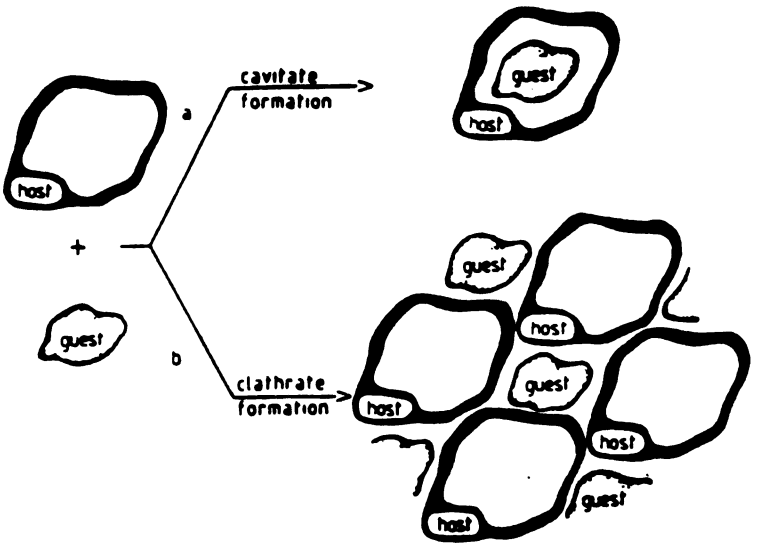


Figure 1. Schematic differences between cavitates and clathrates: (a) conversion of a cavitand into a cavitate by inclusion of the guest in the cavity of a host molecule : (b) inclusion of guest molecules in cavities formed between the host molecules in the lattice : conversion of a clathrand into a clathrate

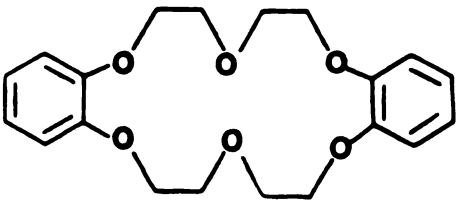
HOST COMPOUNDS WITH INTRAMOLECULAR CAVITIES

1. Crown Ethers

Although metal complexes of naturally occuring macrocyclic ligands have been known for over 50 years (e.g., porphyrins, corrins and phthalocyanines), it is only during the past two decades that a large number of synthetic macrocyclic compounds capable of binding cations or anions have been prepared and investigated.[16] Many of these synthetic macrocyclic polyethers, polyamines, polythioethers, and related molecules possess very interesting and unusual

ion binding properties, and in many cases they undergo marked conformational changes during binding. These novel macrocycles typically contain central hydrophobic cavities ringed with either electronegative or electropositive binding atoms and flexible exterior frameworks that exhibit hydrophobic behavior. Their hydrophobic exterior allows them to solubilize ionic substances in nonaqueous solvents and in membranes. Particularly interesting is the strong affinity shown by polyethers for alkali and alkaline earth metal ions. Their selective binding of specific cations has resulted in their use as models for carrier molecules in the study of active ion transport phenomena in biological systems.

The synthetic polyether, dibenzo[18]crown-6 **1** was the first crown compound to be studied. It exhibited unusual ion



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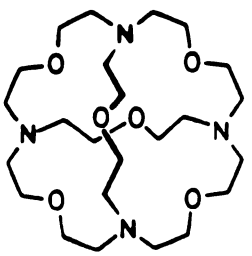
binding properties and complexed sodium ions.[17] Its discovery opened up a new era of synthetic host chemistry and led to the synthesis of many macrocyclic ethers. Today, not only its special ion complexation is studied, but also its complexation with uncharged species.[18,19]

2. Cryptands

Along with two-dimensional monocyclic crown ethers, three- dimensional bicyclic hosts which possess rigid cages of finite diameter were also of interest. The early synthetic three-dimensional bicyclic ethers, called "cryptands", possessed two bridgehead nitrogen atoms joined by three oligooxa chains that differed in length and number of donor atoms. Because of their soccer-ball shape, cryptands are ideal for complexation and show much more specific complexation than crown ethers.[18,19] The tetraprotonated forms of **2** and **3**, for example, are more selective for Cl^- and Br^- than for other halide ions.[20] Figure 2 shows a schematic representation of a chloride anion encapsulated in **2**. The crystal structure of the $2 \cdot 4H^+ \text{-} Cl^-$ complex has been confirmed by X-ray analysis.[21] Many cryptands, with different bridgehead heteroatoms and different shapes, have been reported.[22]



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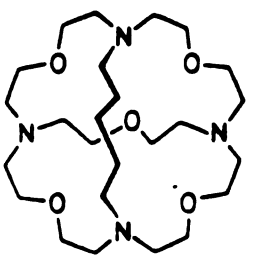

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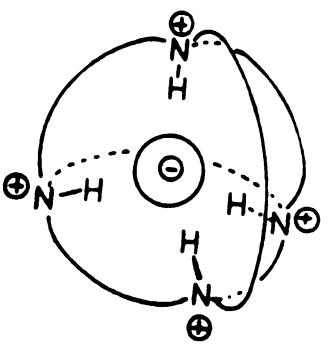
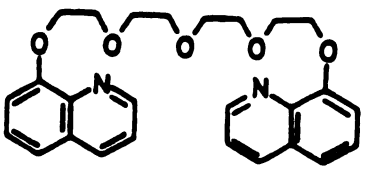


Figure 2. Schematic representation of a chloride anion encapsulated in 2

3. Podants

Podants are noncyclic oligoethers. These acyclic neutral ligands readily complex alkali and alkaline earth metal ions.[18b] In addition, they also complex uncharged molecules.[18a] Podant 4 formed a 1:1 complex with thiourea[23] and 5 has been used as a phase-transfer catalyst in aliphatic and aromatic nucleophilic substitution.[24]



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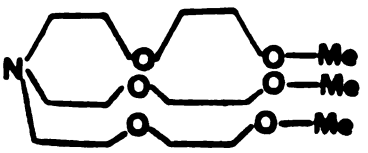

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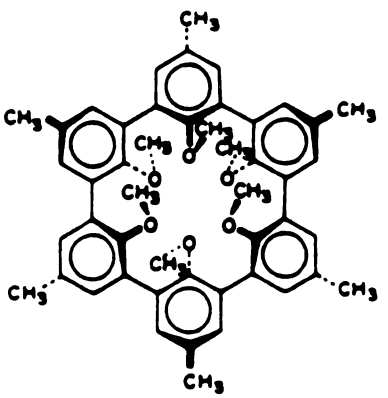
4. Spherands

X-ray structures of uncomplexed crowns, cryptands and natural ionophores do not show the presence of holes, although in their complexes,there are holes filled with metal ions. The unshared electron pairs of their heteroatoms become focussed on the cation during complexation, by conformational reorganization. Potential cavities in the uncomplexed hosts are filled by a folding inward of their parts; these parts then turn outward when "displaced" by guests. Thus the guest conformationally organizes some of the binding sites of the host during complexation, or displaces solvent molecules which may organize the host. "Spherands" are host molecules whose cavities are rigidly preorganized by design, and can only be occupied by spherical entities such as single atoms

or monoatomic ions, and not by parts of the host or by solvent. The cavity is lined with unshared electrons, with the potential for relief of electron-electron repulsion upon complexation.

The first spherand was synthesized by Cram.[25] In 6 a cyclohexametaphenylene system provides a framework which holds the oxygens of the six methoxyl groups in a perfect octahedral array by their attachment to the six convergent positions of the aryl groups. The six methoxyl groups are arranged alternately "up" and "down". The methyls of the methoxyls remain uncompressed by turning away from the center of the system. The diameter of the central hole, between 1.3Å-3.3Å, varies with the dihedral angle between the six aryl groups. Spherand 6 forms complexes with lithium and sodium ions. Extensive studies have been done on complexes of spherands and semi-spherands with metal ions.[26]



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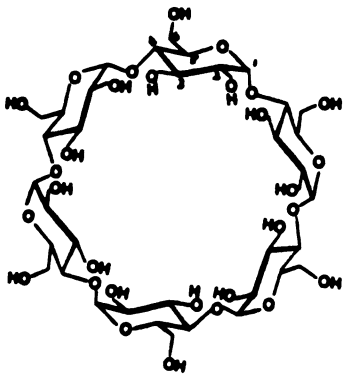
5. Cyclodextrins

Molecular recognition has been significantly pursued and developed in the last decade with crown ethers and cryptands.

These hosts, however, have one particular drawback; they are insoluble in aqueous media. Water-soluble artificial hosts with apolar cavities are of great interest because hydrophobic interactions are a major driving force for binding substrates in biological systems. This is especially true of binding sites of enzymes, as shown by X-ray crystallographic studies. Cyclodextrin is a good miniature of an enzyme in that it has a hydrophobic cavity, sites for the introduction of catalytic groups and satisfactory water solubility. Cyclodextrins are cyclic oligomers of glucose with six (α) 7, seven (β) 8 or more units.



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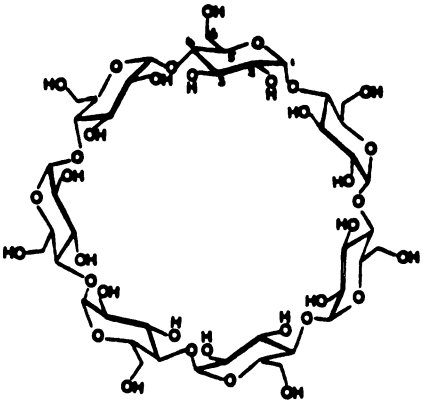

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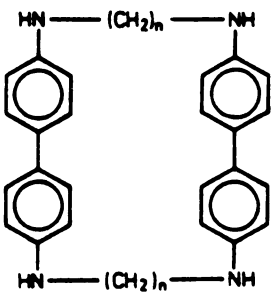
Guests bind to cyclodextrin in aqueous solution,[27] in non-aqueous solvents[27] and in the crystalline form.[28] Despite some examples of enzyme-like recognition,[29] cyclodextrin has a poorer binding site than most enzymes because of the limited hydrophobic surface area with which it can contact the surface of a given guest molecule. One possible improvement is to introduce hydrophobic binding moieties onto

the rim of cyclodextrins. Most of the papers in the current literature deal with this problem[30] and with the search for new applications for cyclodextrin-complexes.[31]

6. Macrocyclic Cyclophanes

Another unique class of compounds, macrocyclic cyclophanes, has been developed recently to expand the area of artificial water-soluble hosts and catalysts. Bridged aromatic compounds are called "phanes". The inclusion phenomenon by a macrocyclic cyclophane was first observed by Stetter and Roos in 1955. They reported that the cyclic tetramine **9b** (n=3) or **9c** (n=4) forms a stable 1:1 complex with benzene or dioxane,[32] whereas no similar complex was observed for **9a** (n=2), which has a smaller ring . This discovery was followed by many synthetic and structural studies of macrocyclic cyclophanes, by Stetter and others.[33]

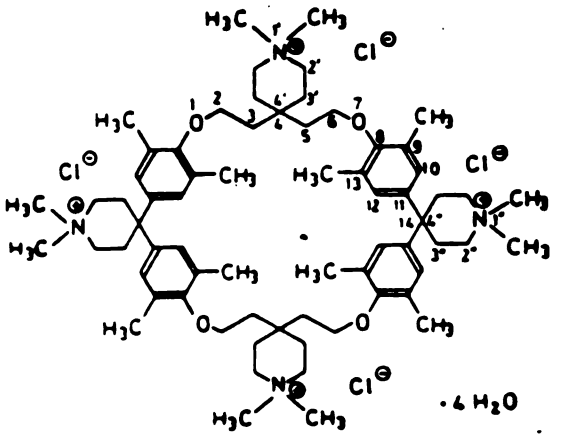


9 *a-c*

(n = 2, 3, 4)

These early synthetic macrocyclic cyclophanes were water insoluble. However, water-soluble macrocyclic cyclophanes have been developed recently and used as artificial hosts with a hydrophobic cavity that acts as a selective binding site for apolar guests. Complexes of cyclophanes in aqueous

solution have been extensively studied.[34] An example is 10, which forms many complexes with neutral aromatic guests in aqueous solution.[35]



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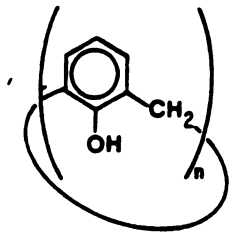
7. Other Cavitands

The area of cavitands is very broad. One important class are the "calixarenes" with the general structure 11.[36,18c] A simple example is 12. Calixerenes form complexes in the solid state and in solution. Other examples of new hosts include 13[37] and 14,[38] with large intramolecular cavities designed to complex ions and neutral molecules. Other examples of new host systems are carcerand (i.e. 15),[39] macrooligocyclic (i.e. 16),[40] speleand (i.e. 17)[41] and carbomacrocyclic (i.e. 18)[42].

HOSTS WITH EXTRAMOLECULAR CAVITIES

Unlike cavitands which form complexes in solution or in the solid state, clathrates can form complexes only in the crystalline state. Guest molecules are either incorporated



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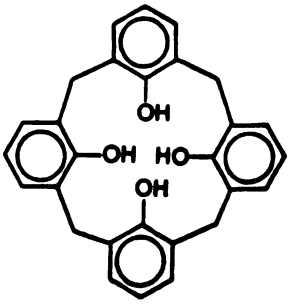

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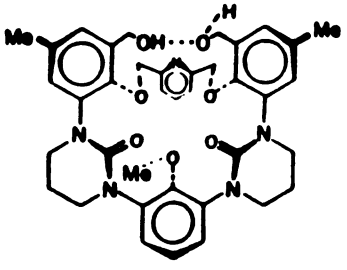

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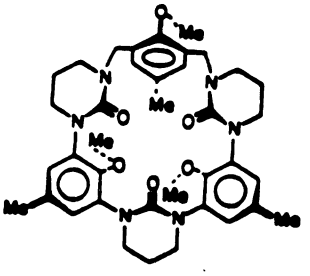

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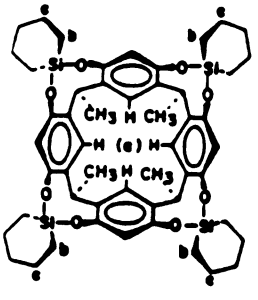

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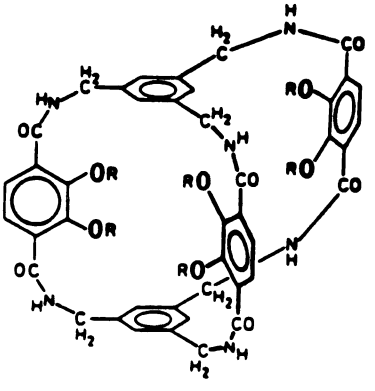
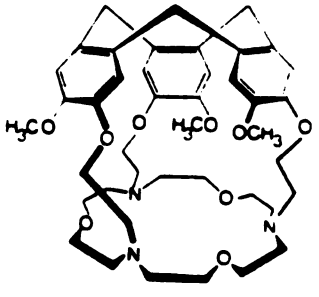


16 a : R = CH_3 b : R = H



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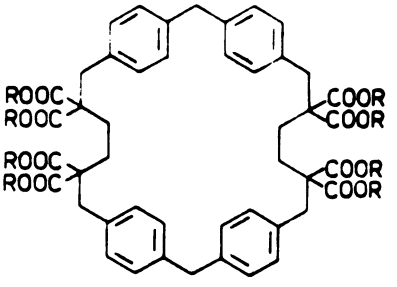


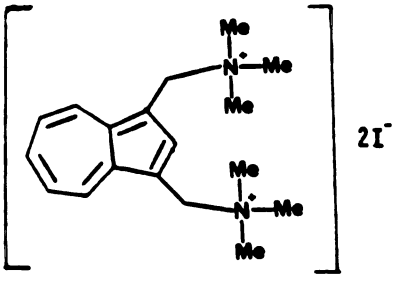
18 a R = C_2H_5
b R = H

into extramolecular cavities already present in the lattice or, during crystallization, they induce a host-lattice structure with guest-specific vacancies.

Interest in clathrate host-guest chemistry arises in part from the search for hosts capable of separating similar guests (i.e. enantiomers[4] or other isomers[3]). Other interests include the photochemistry of inclusion compounds[43] and the stabilization of unstable species.[44]

8. Onium ions

Onium clathrate hosts have been recently reported. They are unique in their versatile inclusion ability probably because of the conformational mobility of the ammonium side branches. Their ready availability facilitates their study. At present, 30 different stoichiometric inclusion compounds of azulenylene-bis-ammonia host **19** with guest molecules have been reported.[45] Moreover, structural modification of **19** lead to further clathrates of this type, with similar extensive inclusion capacities.[46]



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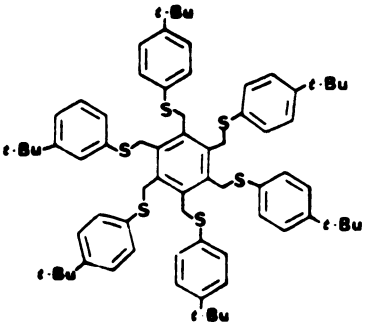
9. Hexahosts

Hexahosts are six-armed benzene derivatives that form stoichiometric inclusion compounds.[18a] In typical hexasubstituted benzenes, the side arms are displaced alternately upwards and downwards from the plane of the central benzene ring. This results in three-dimensional intermolecular cavities in the crystal lattice. Guest molecules are embedded into these cavities in a stoichiometric ratio. Hexahosts **20**[47] and **21**[48] function as hosts for neutral organic molecules like benzene, toluene, tetrahydrofuran and cyclohexane. Numerous hexahosts with donor centers, **22** for example, show marked phase-transfer properties towards metal ions.[49] A phane-like cage hexahost **23** that was synthesized recently opens up the possibility for a new type of hexahost that has guest molecules in intra- and intermolecular cavities.[50] The six-fold bridging, particularly with longer bridges, provides molecules with large cavities that are suitable for the encapsulation of organic guest molecules.



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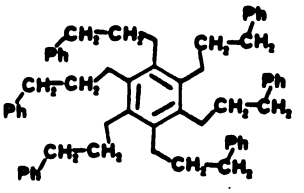

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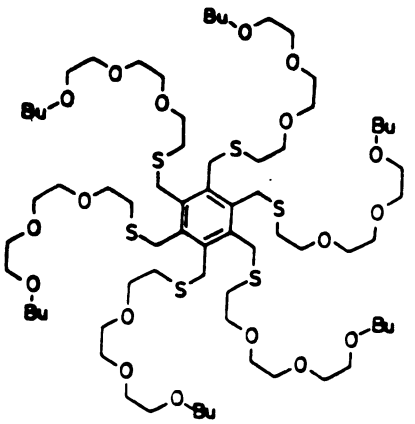

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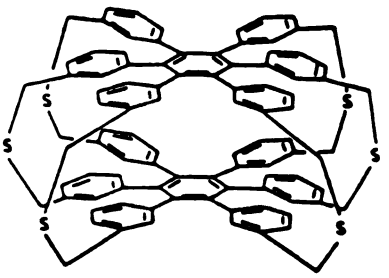

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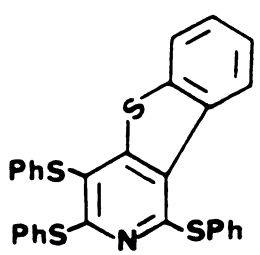
10. Other clathrates

Many other clathrate-forming hosts are known, though they are not easily categorized into groups. Examples includes 24,[51] 25,[52] 26,[53] and 27.[54]



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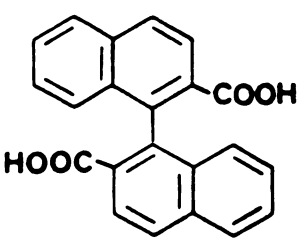

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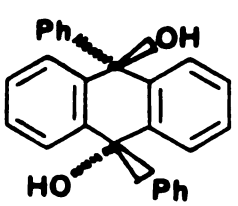

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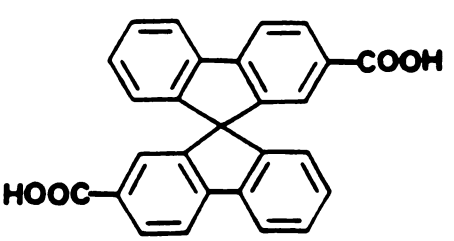

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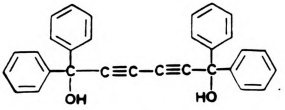
Discovery of Wheel and Axle Compounds

Compound **28** (1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol) was reported by Toda in 1968 to form well-defined crystalline complexes with a great variety of small organic molecules including carbon tetrachloride, chloroform, methylene chloride, alcohols, amines, ketones and sulfoxides.[55]



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An x-ray study on the complex of **28** with two acetone molecules showed that it was of the channel type (Figure 3).[56] The host molecules are aligned roughly parallel to the long molecular axis, and the acetone guest lies in channels roughly parallel to the long axis of the hosts.

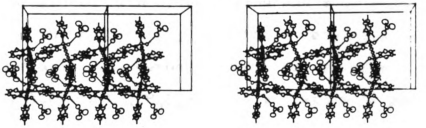
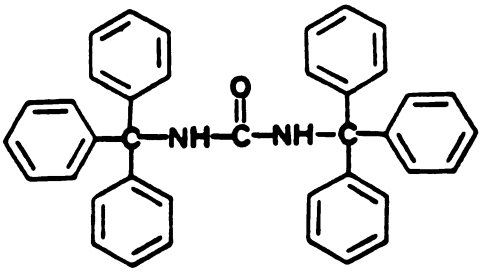


Figure 3. Stereoview of crystal structure of the 1:2 1,1,6,6-tetraphenyl-2,4,-hexadiyne-1,6-diol-acetone complex

Compound **28** is referred to as a 'wheel and axle' compound. The end groups, which consist of an sp^3 carbon with its attached groups, is somewhat like a wheel and the connecting chain can be likened to an axle. Due to the

geometry of **28**, the wheels act as spacers to prevent close packing, and the axle establishes the spacing between the wheels. These two effects may contribute to the ease with which **28** forms so many well-defined channel crystalline complexes. Many known clathrates in the literature are bulky and have limited degrees of comformational changes. The concept of wheel and axle design seems to have such characteristics and may be a good design for molecular recognition. With this idea in mind, hosts with trityl or triptycyl groups as spacers, and with long or short intervening carbon chains, or chains containing both carbon and heteroatoms were prepared. Hosts such as R-(C≡C-)$_n$-R (n=2, 3), R-(CH$_2$)$_n$-R (n=4, 6), R-CH$_2$-CH=CH-CH$_2$R, RCO-CH$_2$-CH$_2$-COR, R-CH=N-N=CHR and R'-CH=N-N=CH-R', where R=trityl or R'=triptycyl, were studied.[57] The results supported the validity of the wheel and axle concept, since these hosts formed a variety of complexes with hydrocarbons and simple chlorinated hydrocarbons. The possibility that these complexes can be used for separation was demonstrated. For example, recrystallization of R-(CH$_2$)$_6$-R from a mixture of para and meta xylene gave crystals containing p-xylene only.

To improve the host design to include both polar and non-polar guests, the urea moiety was incorporated into the axle. It could act as a donor or acceptor in hydrogen bonds. Triphenylmethyl end groups were still used as spacers to create voids and to prevent intermolecular hydrogen bonding among hosts. N,N'-bis(triphenylmethyl)urea **29** (DTU) was



29

prepared from trityl isocyanate and trityl amine.[58] It had been reported earlier by Helferich et al that one DTU formed a complex with two molecules of ethanol.[59] More than 35 DTU-guest complexes were formed, the guests being amines, ethers, alcohols, aromatic hydrocarbons, esters of amino acids, amides and ketones.[60] These inclusion studies with DTU further supported the concept of wheel and axle design for molecular recognition. Moreover, guests with different functionalities were not equally bound to DTU;[61] that is, DTU can selectively form a complex with one guest in the presence of another. The ratio of some guests incorporated in DTU are shown below.

Et_2O : $nPrOCH_3$,	3.5 :1.0
Et_2NH : $nPrNHCH_3$,	4.6 :1.0
2-PrOH : 1-PrOH,	4.0 :1.0
Et_2O : Et_2NH	>25 :1.0

These selectivities may be attributed to different degrees to which the various guests stabilize the complex structures.

It was the purpose of this thesis to explore structural variations on DTU as a host, with the hope of discerning the structural features that are important in complexation. It was the intention that such studies would lead to hosts with improved selectivity, and possibly also to chiral hosts.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

I. Preparation of hosts

A. Preparation of reaction intermediates

This investigation was directed towards the preparation of different disubstituted and monosubstituted ureas, amides, diamides, diamines, ethers and carbamates as potential hosts for studying inclusion phenomena.

The investigation began with the preparation of different intermediates for urea synthesis. The amines were prepared by bubbling ammonia gas into a methylene chloride solution of the appropriate halide (see Table 1).[62]

$$Ar_3CCl + 2NH_3 \longrightarrow Ar_3CNH_2 + NH_4^+Cl^- \qquad (1)$$

Isocyanates were prepared by three different methods: (a) reaction of tertiary chlorides with potassium cyanate or silver isocyanate[63] in refluxing acetone (see Table 2).[58] (b) reaction of amines with phosgene in toluene solution (see Table 3).[64] (c) thermal decomposition and rearrangement of an acyl azide. The latter method was used to prepare triptycyl isocyanate 59.[65]

Table 1

REACTIONS OF HALIDES WITH AMMONIA

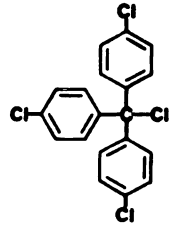
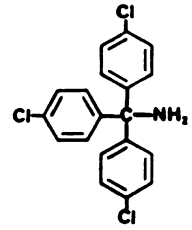
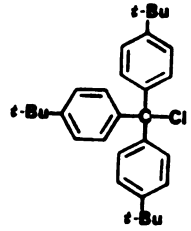
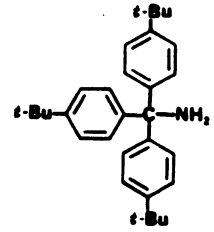
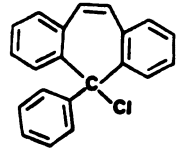
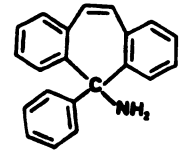
Substrates		Products		m.p. (°C) (Yield)
30		31		96-100 (80%)
32		33		238-240 (90.6%)
34		35		170-171.5 (68.8%)

Table 1 (continued)

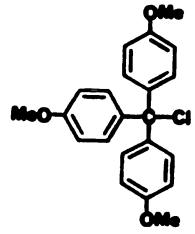
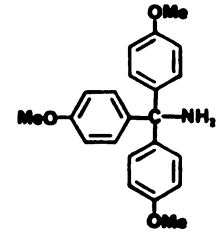
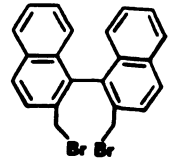
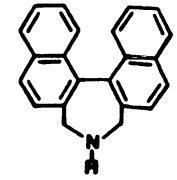
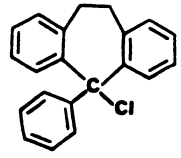
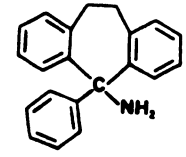
36		37		110-112 (71.3%)
38		39		149-151 (52.1%)
40		41		155-156.5 (64.1%)

Table 2

REACTIONS OF TERTIARY HALIDES WITH POTASSIUM CYANATE

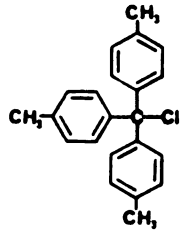
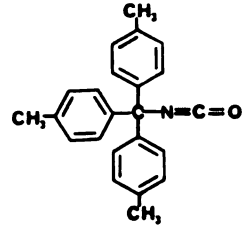
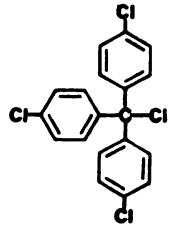
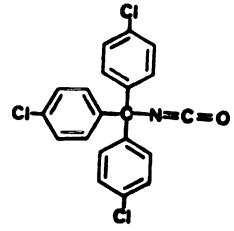
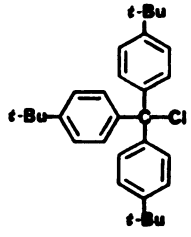
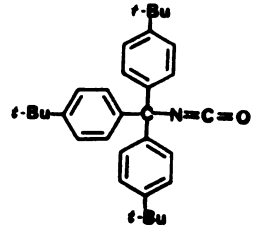
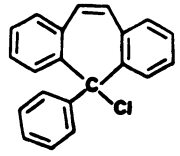
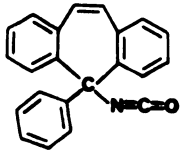
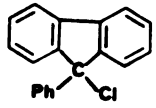
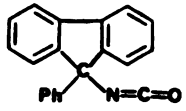
Substrates	Products	m.p. (°C) (Yield)
42		43  125-129 (65.3%)
30		44  -- (41.5%)
32		45  245-250 (70.9%)

Table 2 (continued)

34		46		107-117 (68.5%)
47		48		-- * (90%)

*Silver isocyanate was used instead of potassium isocyanate

Table 3

REACTIONS OF AMINES WITH PHOSGENE

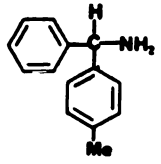
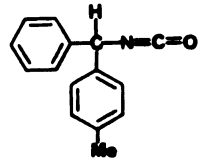
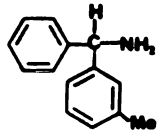
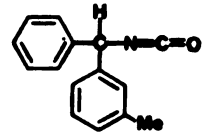
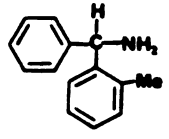
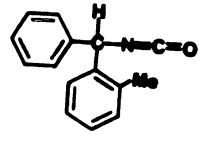
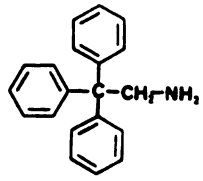
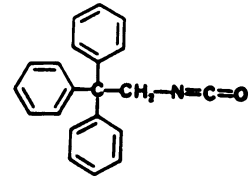
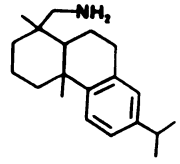
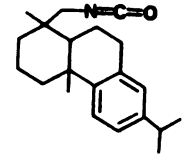
Substrates		Products		Yield (%)
49		50		84.4%
51		52		88.3%
53		54		93.6%

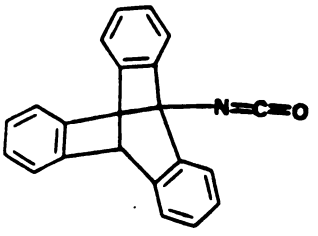
Table 3 (continued)

55		56		86.7%
57		58		94.7%

$$Ar_3CCl \xrightarrow[\text{or AgOCN}]{\text{KCNO}} Ar_3C\text{-}N{=}C{=}O \qquad (2)$$

$$RNH_2 + COCl_2 \xrightarrow{\text{toluene}} R\text{-}N{=}C{=}O + 2HCl \qquad (3)$$

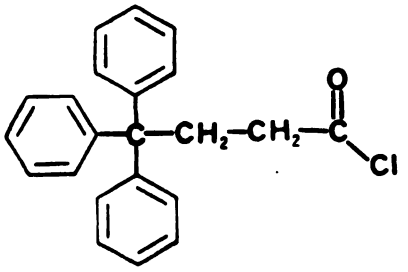
$$R_3CCON_3 \longrightarrow R\text{-}C\text{-}N{=}C{=}O + N_2 \qquad (4)$$



59

Acyl chlorides used as intermediates for the synthesis of amides and diamides were prepared from the appropriate carboxylic acids by reaction with thionyl chloride,[66] for example in the preparation of 4,4',4''-triphenyl-1-butanoyl chloride 60.

$$R_3CCOOH + SOCl_2 \longrightarrow R_3CCOCl + SO_2 + HCl \qquad (5)$$



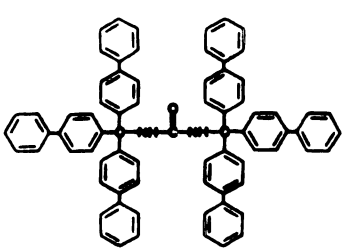
60

B. Preparation of urea hosts

The synthesis of the urea hosts was conducted in the following manner. Disubstituted ureas were prepared from the reaction of triarylmethyl chlorides with urea.[59]

$$Ar_3Cl + H_2NCONH_2 \xrightarrow{\text{pyridine}} Ar_3C\text{-}NHCONH\text{-}CAr_3 + 2HCl \quad (6)$$

This method could only be employed to prepare ureas with symmetrical substituents. For example, the procedure used to prepare N,N'-bis[(tri-4-biphenyl)methyl]urea **61** was as follows. A suspension of 1 equiv. of urea and 2 equiv. of tri(4-biphenyl)methyl chloride in dry pyridine was refluxed for 8 hours. The reaction mixture was poured into a 10% solution of dilute hydrochloric acid. Filtration gave **61**.



61

Both symmetrical and unsymmetrical ureas were prepared by the reaction of isocyanates with amines.[59] This method was easy to carry out as indicated in the following synthesis of N,N'-bis[(triphenyl)methyl]urea **29**. A solution of 1 equiv. of tritylamine and 1 equiv. of trityl isocyanate was heated at reflux in t-butanol for 8 hours. The product **29** was isolated

$$Ar_3CNH_2 + Ar_3C\text{-}N{=}C{=}O \longrightarrow Ar_3C\text{-}NHCONH\text{-}CAr_3 \quad (7)$$

after the usual workup in 63 % yield. The preparation of other N,N'-bis(disubstituted)ureas by this method is summarized in Table 4.

This method was used for sterically hindered amines. Milder reaction conditions, however, could be used in the case of less sterically hindered amines. For example, to a suspension of 1 equiv. of diphenylmethylamine hydrochloride and 1 equiv. of triethylamine in dry methylene chloride, was added dropwise 1 equiv. of diphenylmethyl isocyanate in dry methylene chloride. After being stirred at room temperature for 8 hours, the reaction mixture was worked up as usual to afford N,N'-bis(diphenylmethyl)urea **74** in 95 % yield. Other ureas prepared by this procedure are listed in Table 5.

The methods described above require nitrogens in the ureas or amines that are sufficiently nucleophilic to react with tertiary chlorides or isocyanates. For some unreactive tertiary amines, only starting materials were recovered by these procedures. To overcome this difficulty, a modification of the previous methods was used. Anions of the tertiary amines were used instead of the amines themselves. To a stirred solution of 1 equiv. of tri(p-t-butylphenyl)methylamine in dry THF at $-78^{o}C$ under argon atmosphere, was added dropwise 1 equiv. of n-butyllithium. After the solution was stirred for 10 minutes, 1.1 equiv. of

Table 4

REACTIONS OF STERICALLY DEMANDING AMINES WITH ISOCYANATES

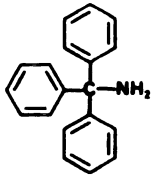
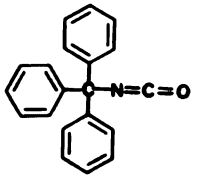
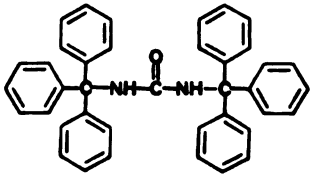
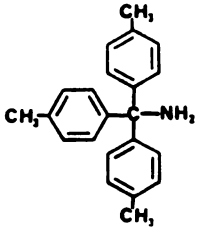
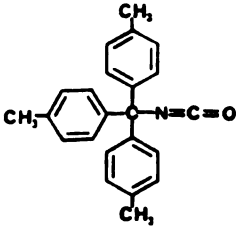
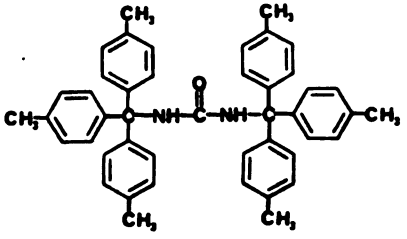
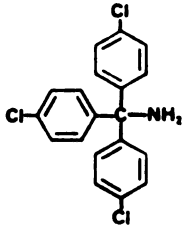
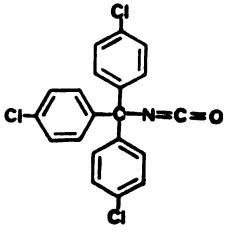
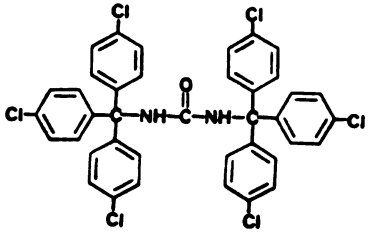
	Substrates			Products	m.p. (°C) (Yield)
62		63		29		260-261 (63%)
64		43		65		229-230 (41.9%)
31		44		66		267-269 (38.9%)

Table 4 (continued)

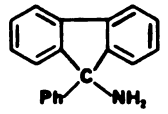
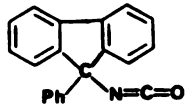
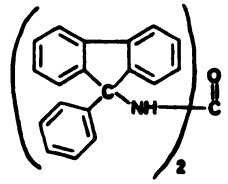
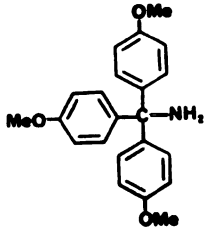
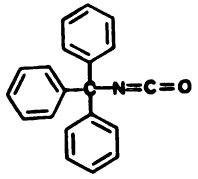
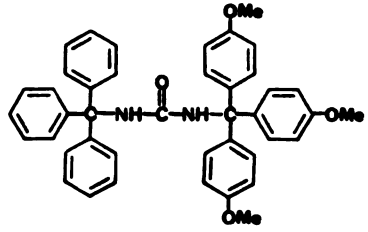
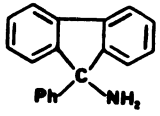
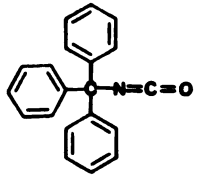
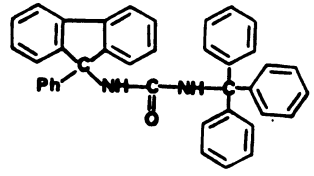
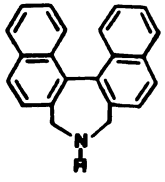
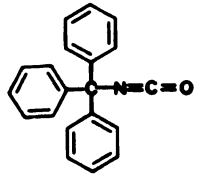
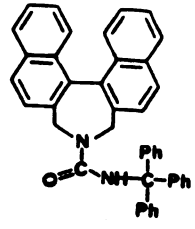
67		48		68		253-254 (60.3%)
37		63		69		215-216 (84.5%)
67		63		70		235-237 (57.2%)
39		63		71		263-265 (52.5%)

Table 5

REACTIONS OF AMINES WITH ISOCYANATES AT ROOM TEMPERATURE

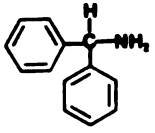
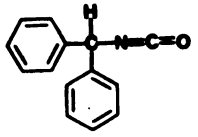
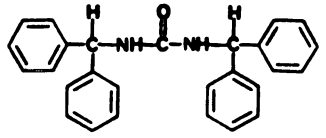
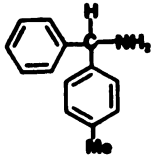
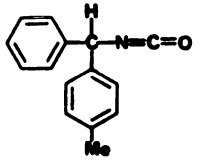
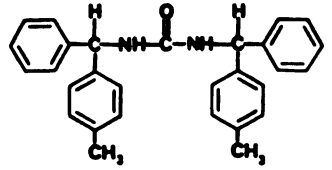
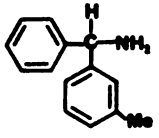
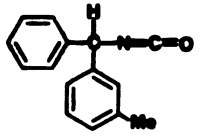
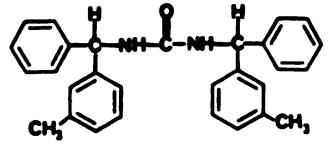
	Substrates		Products	m.p. (°C) (Yield)
72		73		74		272-273 (95.7%)
49		50		75		261-262 (91.7%)
51		52		76		251-252 (76.4%)

Table 5 (continued)

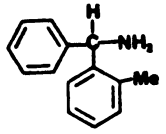
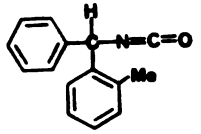
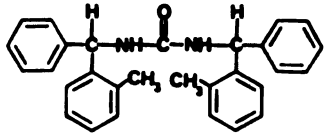
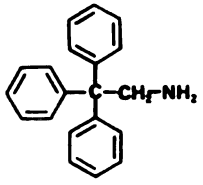
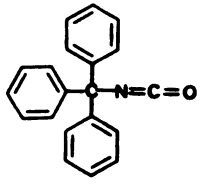
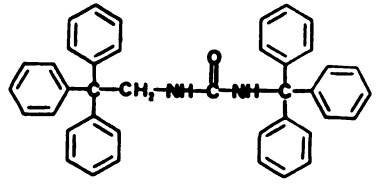
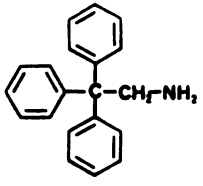
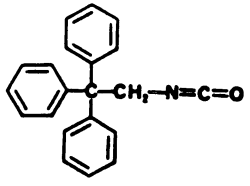
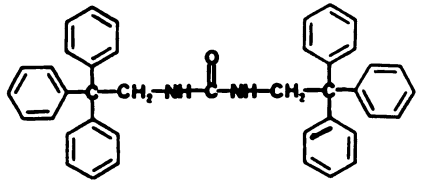
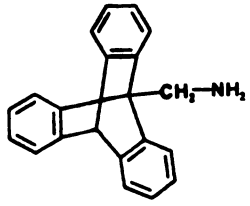
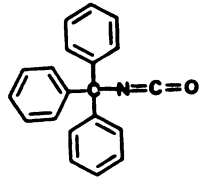
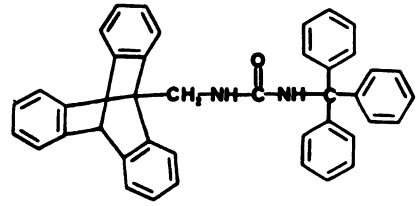
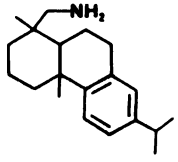
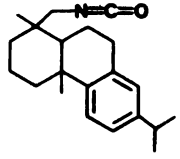
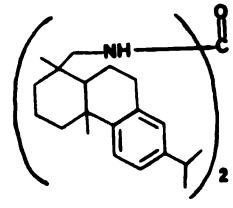
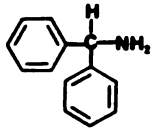
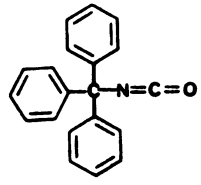
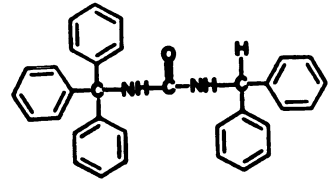
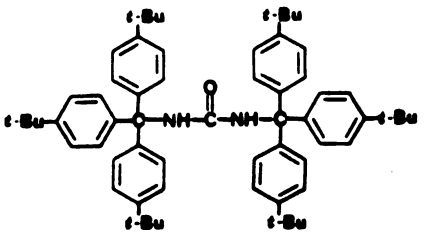
53		54		77		266-267 (72.8%)	
55		63		78		225-226 (75.2%)	
55		56		79		240-241 (78.6%)	

Table 5 (continued)

59		63		80		264-266 (80.3%)	
57		58		81		169-171 (64.7%)	
73		63		82		229-230 (69.7%)	

the corresponding isocyanate in dry THF was added dropwise. Work-up gave N,N'-bis[tri(p-t-butylphenyl)methyl]urea **83** in 58 % yield.

$$Ar_3CNH^-Li^+ + Ar_3C\text{-}N{=}C{=}O \longrightarrow Ar_3C\text{-}NHCONH\text{-}CAr_3 \qquad (8)$$



83

A summary of the ureas prepared using this method is listed in Table 6.

Certain monosubstitued ureas were also prepared for host-guest studies. The typical method used was to bubble ammonia gas into a solution of an isocyanate in methylene chloride over 3 hours.[59]

$$R_3C\text{-}N{=}C{=}O \xrightarrow{NH_3} R_3C\text{-}NHCONH_2 \qquad (9)$$

Workup as usual gave the desired monosubstituted urea (see Table 7 for examples).

C. Preparation of non-urea hosts

Although ureas exhibited superior inclusion properties, certain non-urea host molecules were also prepared to study

Table 6

REACTIONS OF AMIME ANIONS WITH ISOCYANATES

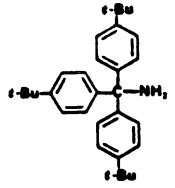
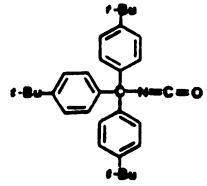
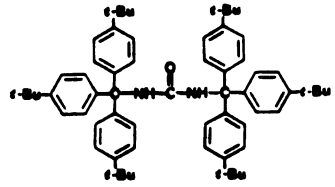
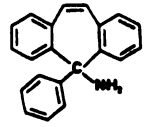
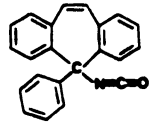
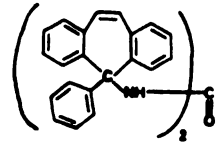
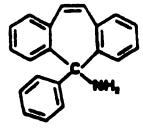
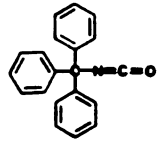
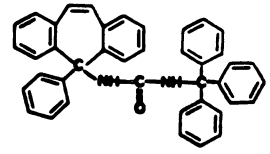
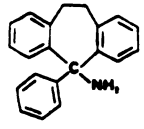
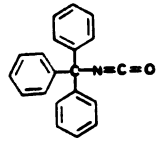
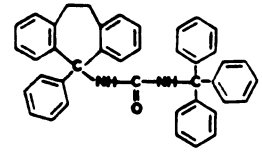
	Substrates			Products	m.p. (°C) (Yield)
33		45		83		272-273 (58.2%)
35		46		84		266-268 (42.2%)
35		63		85		238-240 (53.7%)
41		63		86		225-227 (30%)

Table 7

MONOSUBSTITUTED UREAS VIA THE REACTION OF ISOCYANATES WITH AMMONIA GAS

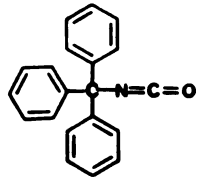
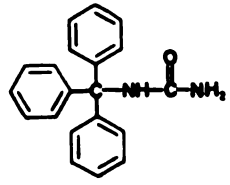
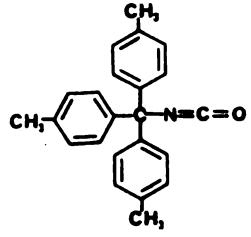
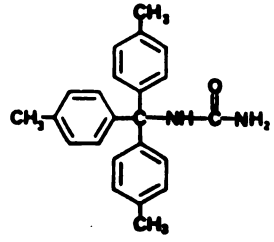
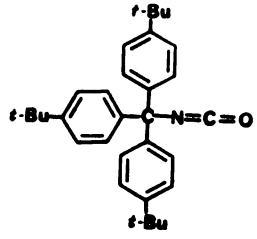
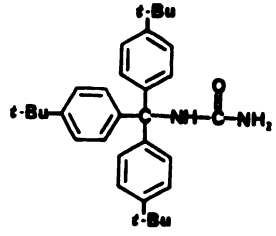
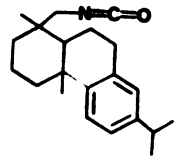
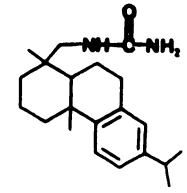
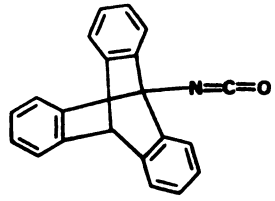
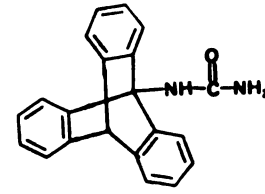
	Substrates		Products	m.p. (°C) (Yield %)
63		87		251-252 (91.2%)
43		88		235-236 (97.8%)
45		89		252-254 (85.9%)

Table 7 (continued)

58		90		190-191 (97.2%)
59		91		314-315 (94.5%)

their host-guest chemistry. These simple diamides and amides were extremely interesting because they possess rigid, polar axles capable of hydrogen bond formation. Several diamides were prepared from the reaction of tritylamine with diacyl chlorides in THF.[67]

$$Ar_3CNH_2 + ClCO(CH_x)_yCOCl \longrightarrow Ar_3C\text{-}NHCO(CH_x)_yCONH\text{-}CAr_3 + 2HCl \qquad (10)$$

Simple amides were prepared similarly from tritylamines and acyl chlorides. These results are summarized in Table 8.

Chiral tartaric acid diamides were contemplated for our studies. Instead of preparing optically pure tartaric acid diamide, racemic N,N'-ditrityltartaric diamide **103** was obtained from the oxidation of fumaric diamide with tetrabutylammonium permanganate.[68]

$$Ar_3C\text{-}NHCOCH{=}CHCONH\text{-}CAr_3 \xrightarrow{(C_4H_9)_4N^+MnO_4^-} Ar_3C\text{-}NHCOCH(OH)CH(OH)CONH\text{-}CAr_3 \qquad (11)$$

103

The diamide had poor solubility in most organic solvents and so these studies were abandoned.

The rigid and polar carbamate system was also studied. To test the possibility of a new host system, O-2-naphthyl-N-triphenylmethyl carbamate **104** was prepared from the reaction of the anion of 2-naphthol with triphenylmethyl isocyanate.[69]

Table 8

REACTIONS OF TRITYLAMINE WITH ACYL CHLORIDES

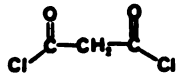
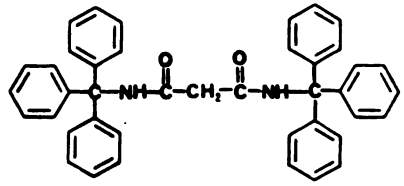
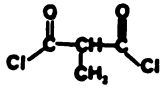
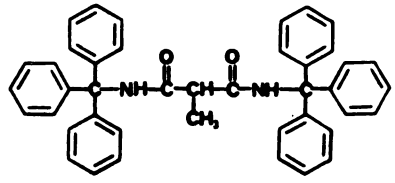
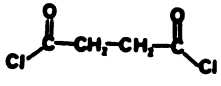
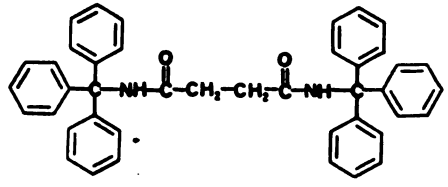
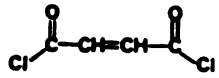
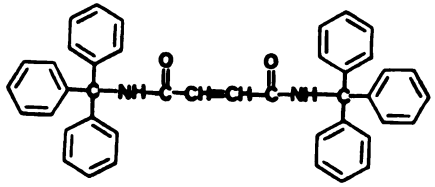
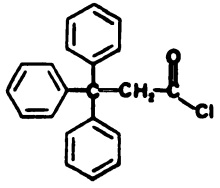
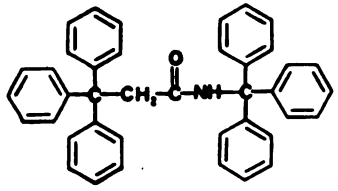
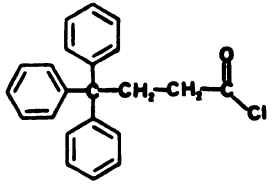
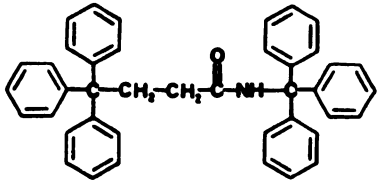
	Substrates	Products	m.p. (°C) (Yield %)
92		93 	293-294 (32%)
94		95 	299-300 (48.8%)
96		97 	302-303 (11.6%)

Table 8 (continued)

98		99		307-308 (64.8%)
100		101		169-171 (76.7%)
60		102		263-265 (47.3%)

$$C_{10}H_7O^- + Ar_3C\text{-}N{=}C{=}O \longrightarrow C_{10}H_7O\text{-}CONH\text{-}CAr_3 \quad (12)$$

104

So far, only the polar compounds that were synthesized and tested have been described. Some less polar compounds, i.e. trityl ethers and amines, were also examined as potential hosts for non-polar guests. The diamines were prepared by the reactions of diaminoalkanes with trityl chloride in methylene chloride.[70] The diethers were obtained from the reaction of diols with trityl chloride in dry pyridine.[70]

$$Ar_3CCl + NH_2(CH_2)_nNH_2 \xrightarrow{CH_2Cl_2} Ar_3CNH(CH_2)_nNHCAr_3 + 2HCl \quad (13)$$

$$2Ar_3CCl + HO(CH_2CH_2O)_nCH_2CH_2OH \longrightarrow Ar_3CO(CH_2CH_2O)_nCH_2CH_2OCAr_3 + 2HCl \quad (14)$$

Examples of the preparation of these diamines and diethers are given in Table 9.

II. X-ray Studies of DTU Complexes

The ability of DTU to form complexes with many organic compounds containing various functionalities led us to carry out an intensive x-ray study of their crystal structures. DTU was designed with large, rigid, end groups that would prevent the formation of intermolecular hydrogen bonds between host molecules. Thus, the stablity of the clathrate complex came

Table 9

REACTIONS OF DIAMINES AND DIOLS WITH TRITYL CHLORIDE

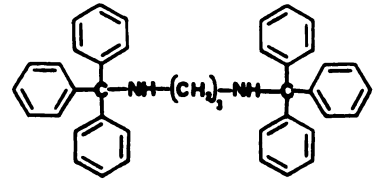
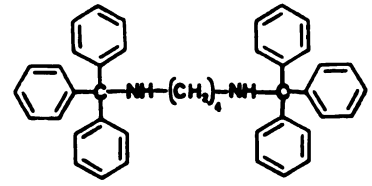
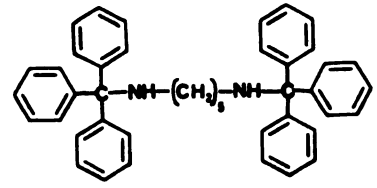
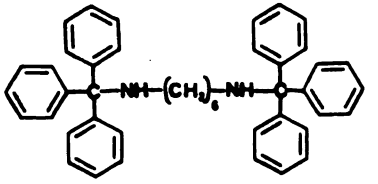
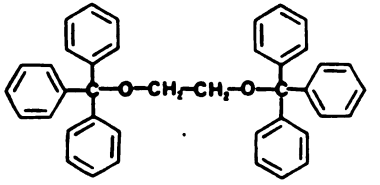
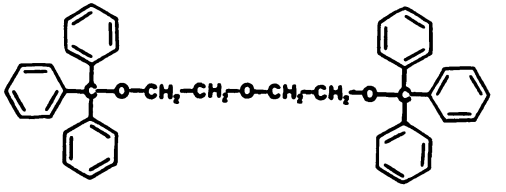
	Substrates	Products	m.p. (°C) (Yield %)
105	$NH_2-(CH_2)_3-NH_2$	106 	179-181 (59.4%)
107	$NH_2-(CH_2)_4-NH_2$	108 	154-155 (51.8%)
109	$NH_2-(CH_2)_5-NH_2$	110 	148-149 (68.4%)

Table 9 (continued)

111	$NH_2-(CH_2)_6-NH_2$	112		188-189 (59.8%)
113	$HO-CH_2-CH_2-OH$	114		188-189 (49.3%)
115	$HO-CH_2-CH_2-O-CH_2-CH_2-OH$	116		157-158 (56%)

from the van der Waals' interactions between host molecules and the bonding interactions between host and guest. To achieve further thermodynamic stability, the clathrate complex also had to be densely packed. The topological complementarity and the bonding interactions between hosts and guests as well were responsible for the dense packing in DTU.[71] This may account for the success of DTU and explain why it forms so many clathrate complexes.

Of the four DTU clathrate complexes previously reported from our research group or the new complexes reported within this thesis, four different types of crystal packing diagrams were recognized. The inclusion complexes of DTU are numbered as follows I. DTU-propanamide,[60] II. DTU-diethylamine, III. DTU-diethyl ether, IV. DTU-methylene chloride, V. DTU-acetone, VI. DTU-acetaldehyde, VII. DTU-2,2-dimethylpropanamide,[72] VIII. DTU-acetonitrile, IX. DTU-ethyl acetate, X. DTU-ethyl N-acetylglycinate.[60] They are classified as type A (I to VI), type B (VII and VIII), type C (IX) and type D (X) according to their stereopacking diagrams. The unit cell constants are summarized in Table 10.

Hart and his coworkers reported in 1984 the X-ray structure of the DTU complex with propanamide (type A) (see Figure 4).[60] It is a channel type clathrate. The host molecules are closely stacked on one another along the a-axis of the unit cell. They form layers along the c-axis. Each host molecule is surrounded by six other hosts. Such six-fold coordination is regarded as one of the most

Table 10

SUMMARY OF CRYSTAL DATA FOR TYPE A, B, C, AND D STRUCTURES

Compounds	I	II	III	IV	V	VI	VII	VIII	IX	X
formula weight	617.8	616.84	618.82	629.64	602.78	588.75	617.78	626.80	632.81	689.8
space group	C_2/C	C_2/C	C_2/C	C_2/C	C_2/C	C_2/C	$P2_1/n$	$P2_1/c$	$P2_1/n$	P1
Z	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	2.0
a, Å	15.839	16.926	16.707	16.287	15.581	16.111	9.471	8.763	12.175	9.010
b, Å	9.088	8.740	8.790	8.887	9.450	8.861	17.596	22.838	15.945	10.800
c, Å	25.584	24.404	24.376	24.772	24.575	24.834	22.311	18.517	19.198	19.810
α, deg	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	105.29
β, deg	111.05	106.99	106.94	111.35	110.37	110.89	89.99	111.12	107.84	94.33
γ, deg	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	93.03
R	0.070	0.077	0.066	0.053	0.038	0.046	0.047	0.042	0.050	0.084
R_w	0.093	0.073	0.055	0.046	0.036	0.047	0.046	0.041	0.054	0.119

I to X are referred as I. DTU-propanamide, II. DTU-diethylamine, III. DTU-diethyl ether, IV. DTU-methylene chloride, V. DTU-acetone, VI. DTU-acetaldehyde, VII. DTU-2,2-dimethylpropanamide, VIII. DTU-acetonitrile, IX. DTU-ethyl acetate, X. DTU-ethyl N-acetylglycinate. I to VI are referred to as type A, VII to VIII as type B, IX as type C, and X as type D.

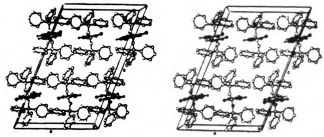


Figure 4. Stereoview of the crystal structure of the 1:1 DTU-propanamide complex : for clarity, only one orientation of the disordered guest is shown at each site.

efficient crystal packings. A hydrophobic interaction among the aromatic moieties of the host molecules constitutes a major stabilizing force for the clathrate structure. The propanamide guest resides in a void formed by four surrounding host molecules. Two host molecules, one above and one below the plane of the guest, form hydrogen bonds with the guest. The other two lie on the opposite sides of the guest molecule. There is an extensive network of hydrophilic interactions formed among the amides of alternating hosts and guests along the b-axis of the unit cell (Figure 5). The C=O and N-H groups of all molecules

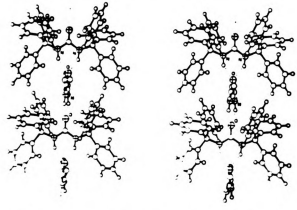


Figure 5. Stereoview of the hydrogen-bonding association of the guest to two adjacent hosts in the DTU-propanamide crystal structure

point in opposite directions, providing a complementary geometric arrangement for forming such an extensive network of hydrogen bonding that contributes to the stability of the clathrate complex. The hydrophobic alkyl residue of the guest molecules lies parallel to the molecular axis of the host surrounded by the benzene rings of the host molecules. This arrangement avoids steric repulsion between host and guest. At the same time, it strengthens the bonding interactions between them.

Two similar packing diagrams for the DTU-diethylamine (II) and DTU-diethyl ether (III)complexes were also reported.[61] The host molecules packed in a similar manner to the hosts in the DTU-propanamide (I) complex. Hydrogen bonds, however, were only formed between individual host-guest pairs. These hydogen bonds had lengths of 2.95Å and 3.23Å in the diethyl ether and diethylamine complexes respectively. These are weaker hydogen bonds than those in the DTU-propanamide complex, which had a length of 2.86Å.

These preliminary observations indicated that topological complementarity between hosts and guests, and hydrogen-bonding interactions between host and guest are responsible for the formation of such packing patterns. Small guests like to form type A structures with DTU because in these structures host molecules maximize their van der Waals' interactions and the host-guest pairs maximize their bonding interactions.

X-ray structures of DTU-acetone, DTU-acetaldehyde and DTU-methylene chloride complexes were obtained (Figures 6, 7,and 8) and consolidate our assumption that DTU likes to form type A structures with very small organic guests. These complexes are channel type clathrates (Figures 9, 10, and 11) that are isostructural with the DTU-propanamide, DTU-diethyl ether and DTU-diethylamine complexes.

Not surprisingly, acetone and acetaldehyde guests form hydrogen bonds with individual hosts because they have only one electron donor group, the carbonyl, in their molecules. Figures 12 and 13 showed the host-guest bonding relationship. The interaction in the DTU-acetone complex in Figure 12 is described by the following parameters: 2.965(4)Å, 2.19(2)Å and 152(2)^{o} for the N...O and H...O distances, and the N-H...O angle respectively. The bonding parameters in the DTU-acetaldehyde complex (Figure 13) are 3.034(8)Å, 2.25(4)Å and 152(3)^{o} for the N...O and H...O distances, and the N-H...O angle respectively. These hydrogen bonds were somewhat weaker than the hydrogen bonds formed between amide host-guest bonds in DTU-propanamide, where the bond length is 2.86 Å. The dihedral angles between the plane that contains the urea molecular axis of the host and the plane that contains the molecular axis of the acetone or acetaldehyde are 61.5^{o} and 66^{o} respectively. The two pairs of lone-pair electrons on the carbonyl oxygen atom in the acetone or acetaldehyde guests can be represented as approximately sp^2 hydridized orbitals.[73] Thus, these two pairs of lone-pair electrons and

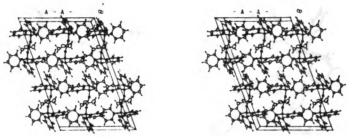


Figure 6. Stereoview of the crystal structure of the 1:1 DTU-acetone complex : for clarity, only one orientation of the disordered guest is shown at each site.

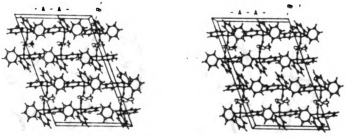


Figure 7. Stereoview of the crystal structure of the 1:1 DTU-acetaldehyde complex : for clarity, only one orientation of the disordered guest is shown at each sites.

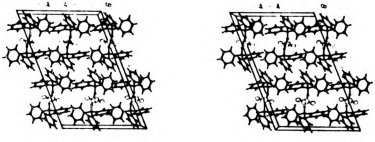


Figure 8. Stereoview of the crystal structure of the 1:1 DTU-methylene chloride complex

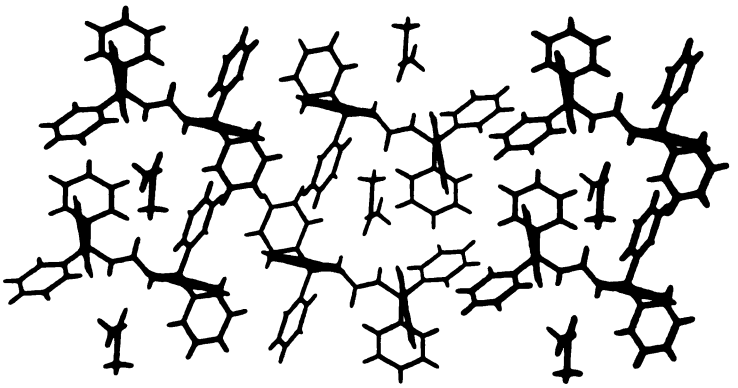


Figure 9. Picture of the DTU-acetone molecular packing, showing channels occupied by acetone molecules

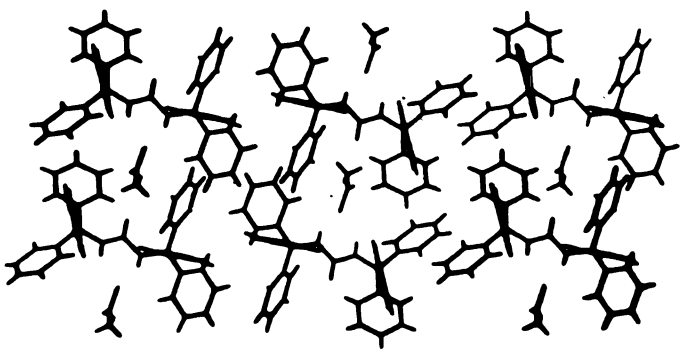


Figure 10. Picture of the DTU-acetaldehyde molecular packing, showing channels occupied by acetaldehyde molecules

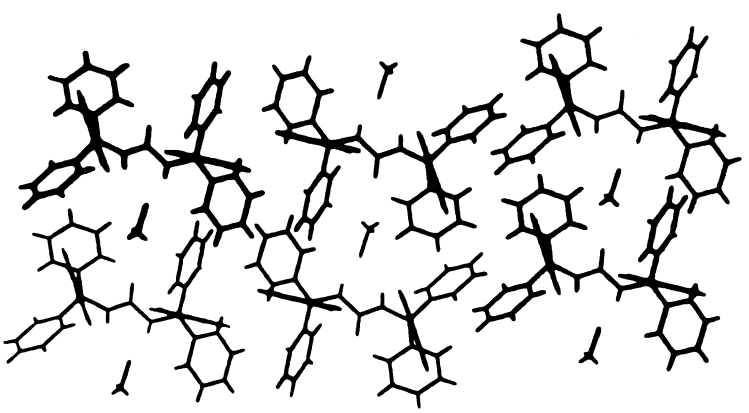


Figure 11. Picture of the DTU-methylene chloride molecular packing, showing channels occupied by methylene chloride molecules

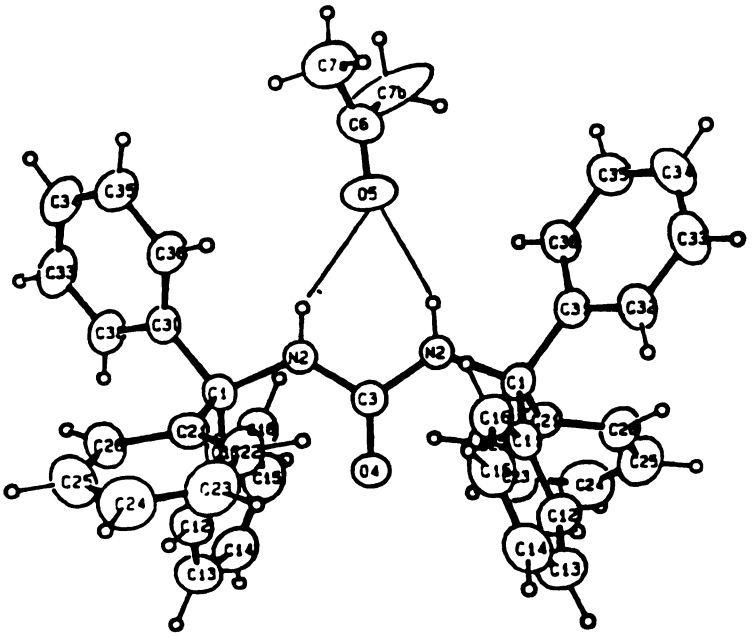


Figure 12. Hydrogen bonding interactions of the guest with the host in the DTU-acetone complex.

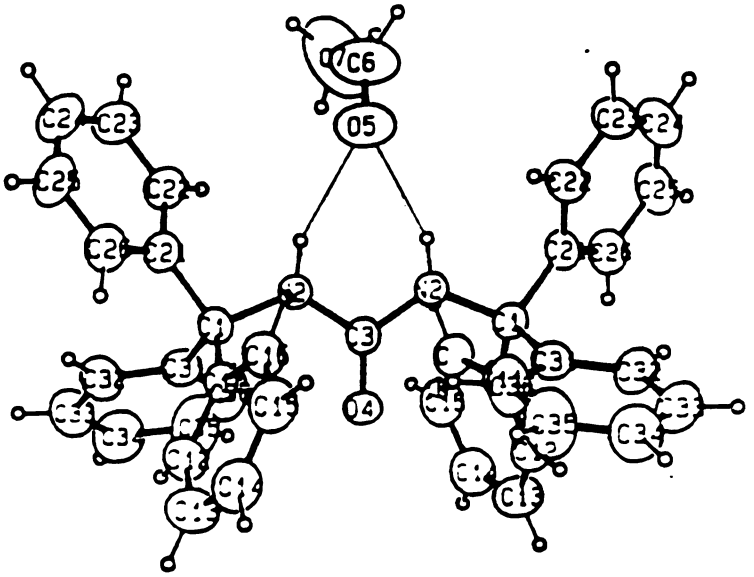


Figure 13. Hydrogen-bonding interactions of the guest with the host in the DTU-acetaldehyde complex.

the bonding pair of electrons of the oxygen atom constitute a plane which overlaps with the molecular plane of the guest molecule. Maximum overlap of the hydrogen orbital of the DTU N-H group and the lone pair orbitals of the oxygen atom in the guest can be achieved if the plane containing the urea molecular axis bisects the plane containing the oxygen lone pair orbitals.

The dimensions of the void formed by the four neighboring hosts is approximately 6.5Å, 3.4Å, and 4.2Å with respect to the x, y, and z axes (see appendix for void dimensions determination). The best orientation of the guest molecule, to avoid any steric repulsion, is to arrange its bulky group along the x-axis (a-axis in the crystallographic sense). Thus the molecular plane of the guest lies almost perpendicular to the plane containing the urea molecular axis. The combination of these bonding and steric requirements which results in dihedral angles of 61.5^{o} in the acetone complex and 66^{o} in the acetaldehyde complex is not totally unexpected. The large thermal motion (standard deviation more than $10Å^{2}$) and the disorder of the guest suggests that there is still some additional space inside the void.

In the DTU-methylene chloride complex, the host molecules pack themselves similarly to the host in the DTU-propanamide complex (Figure 8). A network of bonding interactions between host and guest molecules was observed. The bonding relationship between DTU and methylene chloride

is described in Figure 14. The bonding parameters are as follows: a, 3.619(2)Å, 2.94(2)Å, 144(2)°; b, 3.682(2)Å, 2.97(2)Å, 149(2)° for Cl...N, Cl...H distances and N-H...Cl angle respectively; c, 2.850(7)Å, 2.46(4)Å and 121(4)° for the O...C, O...H distances and the C-H...O angle respectively. Hydrogen bonding occurs between the hydrogen atoms in methylene chloride and the carbonyl group of DTU. The bonding distances for the O(host)...H(guest) and O...C

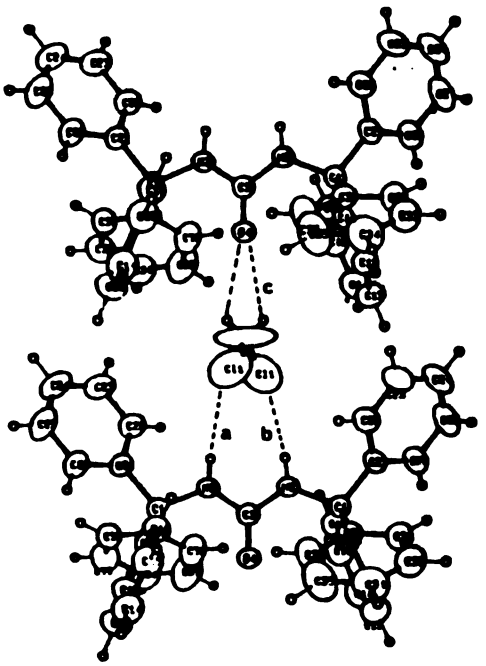


Figure 14. Bonding associations of the guest with the host in the DTU-methylene chloride complex.

are shorter than the sum of their van der Waals' radii, 2.72Å and 3.22Å respectively for the O...H and O...C distances. This suggests hydrogen bond formation.[74] The amide hydrogen atom of the host and the chlorine atoms of the guest surprisingly do not a form hydrogen bond. They

interact weakly through a slightly long 3.61Å NH(host)...Cl(guest) bond distance which is longer than the reported N-H...Cl hydrogen bond distances, which ranged in length from 2.91-3.52Å.[75] The 86° dihedral angle of the planes containing the Cl-C-Cl and the urea molecular axis is strictly due to the steric requirement to avoid repulsion between host and guest. Such an arrangement was also observed in the DTU complexes with diethyl ether, diethylamine, acetone and acetaldehyde.

For the small acetonitrile guest molecule, we expected that a type A structure would form. An NMR spectrum indicated that one DTU molecule is complexed with two acetonitrile molecules, quite different from the 1 to 1 DTU-guest ratio in the other complexes. An X-ray determination revealed the structure (Figure 15). The packing diagram of DTU-2 acetonitrile showed that the complex is of the channel type, but it has a different host structure (type B) from that of the DTU-propanamide complex. Viewing down the a-axis of the unit cell, the host molecules are stacked on top of each other along the c-axis. Each host is surrounded by six neighouring hosts. The hosts form layers along the b-axis. A void which is formed between two parallel host molecules in the same layer includes two molecules of acetonitrile. An alternating arrangement of the two acetonitrile molecules with hosts was also found in this complex. Figure 16 shows the orientation of the two acetonitrile molecules with respect to the host. The two acetonitrile molecules are arranged in a specific way. One molecule lies midway

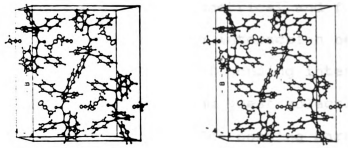


Figure 15. Stereoview of the crystal structure of the 1:2 DTU-acetonitrile complex

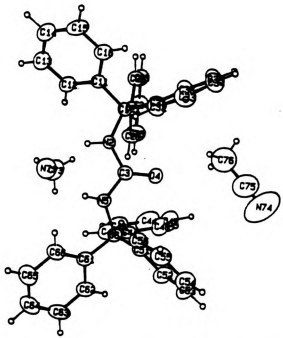


Figure 16. Orientation of two acetonitrile molecules with respect to the DTU host

between two parallel hosts and also between the planes that contain the urea molecular axis. The acetonitrile molecule, which is linear, lies almost perpendicular between two planes that contain the urea molecular axes of the hosts. Thus, the C≡N group of the guest is almost at a 90° angle to the N-H group of the host. Similarily, the CH_3 group of the

guest and the C=O group of the host are almost perpendicular to each other. These provide a geometrical and functional relationship for effective bonding interaction between the complex constitutents. A network of bonding interaction is formed between alternating host and guest molecules. Figure 17 summarizes this relationship. The bonding parameters are: a. 3.188(5)Å, 2.420(2)Å, 137.8(4)^{o} for the C...O, H...O distances and C-H...O angle; b. 3.179(5)Å, 2.414(3)Å, 154.3(2)^{o}; c. 3.252(5)Å, 2.507(3)Å, 142.4(2)^{o} for the N...N, N...H distances and N-H...N angle respectively. Although the 3.18Å C...O bond distanceis shorter than the reported 3.23Å C...O possible hydrogen bond distance, no hydrogen bond is formed. The acetonitrile molecule is only well packed inside the cavity of the host. The nitrogen atom of the acetonitrile molecule forms weak hydrogen bonds with the amide hydrogen atoms.

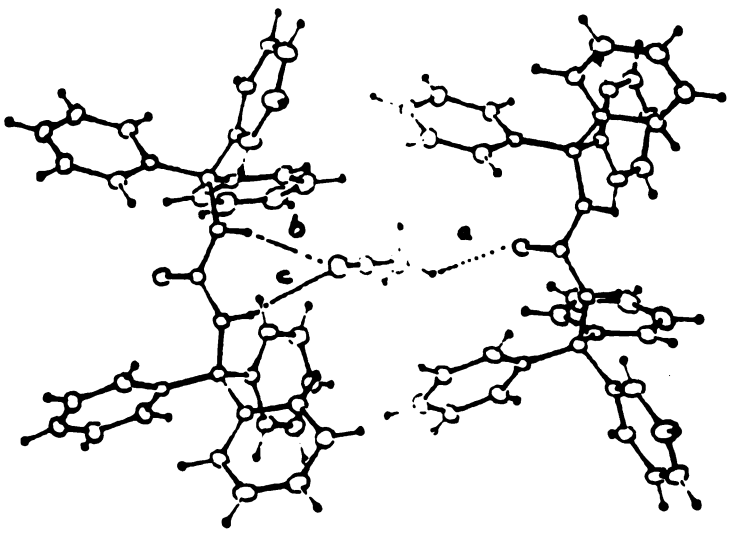


Figure 17. Hydrogen bonding interactions of the guest with two adjacent hosts in the DTU-acetonitrile complex.

The second acetonitrile molecule lies in the void formed between two layers of hosts that are stacked on top of each other. This acetonitrile interacts weakly with the aromatic moieties and the carbonyl oxygen of the hosts, as indicated by the 3.284Å C(guest)...O(host) bond distance. The large thermal motion of this acetonitrile molecule in the crystal complex indicates that there is still some empty space inside the void.

With this information in hand, we may try to ascertain why some of these DTU complexes are of type A and some are of type B. The available space between the two hosts along the C_2 axis in type A and type B complexes had length approximately from 3.4Å to 4.5Å and from 4.7Å to 6.0Å respectively (Figure 18). The dimensions of the void along

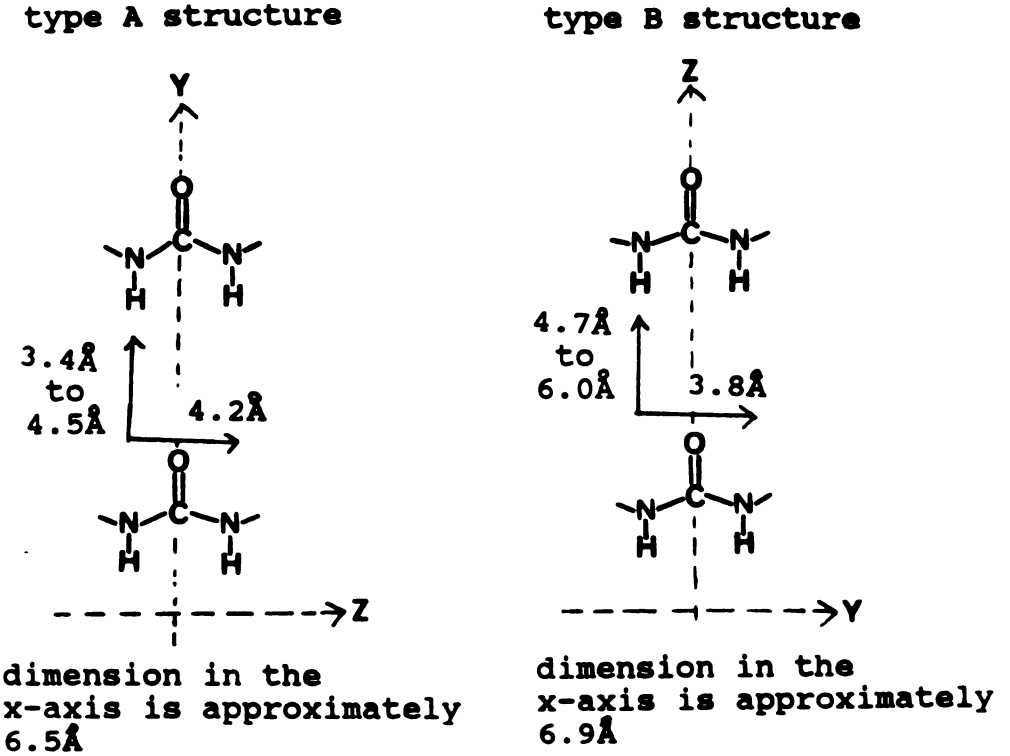


Figure 18. Schematic representation to show the dimension of the voids in type A and type B complexes

the C_2 axis will limit the size of the guest molecule enclosed in the cavity, especially for those guests that form hydrogen bonds with the host along the C_2 axis. For acetone, acetaldehyde, propanamide, methylene chloride, diethyl ether and diethylamine molecules, the molecular plane of the guests ranged from 60° to 86° with respect to the molecular plane that contained the urea molecular axis. Presumably this arrangement avoids any steric congestion in the void along the C_2 axis of the hosts. Simultaneously, hosts and guests had their maximum bonding interactions in all directions.

For some guests, larger dimensions may be required along the C_2 axis of the hosts. Sometimes the type A structure does not give a complex with the thermodynamically most stable structure. For example, acetonitrile is a linear molecule that forms a network of hydrogen bonds with the DTU along the C_2 axis of the host. The space required along the C_2 axis is more than 5.5Å. Not surprisingly, acetonitrile forms a type B structure rather than type A structure. The second acetonitrile molecule, which interacted with the host and filled up the void, also added to the stabilization of this structure.

The question arises whether a large guest molecule will form the type B structure or some other type of structure. In searching for an answer, the X-ray structure of the DTU complex with 2,2-dimethylpropanamide was studied (Figure 19).[72] A packing diagram like that of the DTU-2 acetonitrile complex was found. The carbonyl groups of neighboring hosts

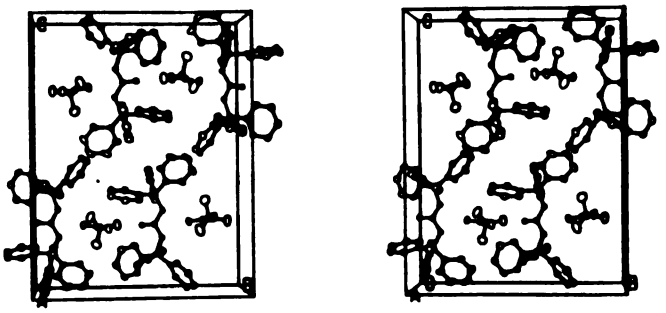


Figure 19. Stereoview of the crystal structure of the 1:1 DTU-2,2-dimethylpropanamide complex

in the same layer are almost perpendicular to each other, providing a good geometrical arrangement for interacting with the guest. The guest resides in the void formed between two parallel hosts, along the b-axis. An extensive network of hydrogen bonds is formed between the amide moieties of alternating host and guest along the b-axis of the unit cell (Figure 20). The interaction is described by the following bonding parameters: a. 2.895(5)Å, 2.04(3)Å, 153(3)^{o}; b.

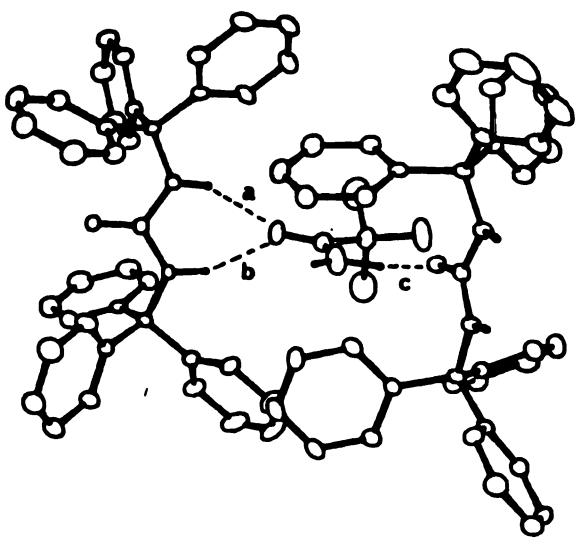


Figure 20. Hydrogen-bonding associations of the guest with two adjacent hosts in the DTU-2,2-dimethylpropanamide complex.

2.903(5)Å, 2.10(3)Å, 151(3)°; c, 2.867(5)Å, 1.73(9)Å, 161(6)° for the N...O and O...H distances and N-H...O angle respectively. The two amide hydrogen atoms in the host form unequal hydrogen bonds with the carbonyl group of the guest. However, only one amide hydrogen atom of the guest forms a hydrogen bond with the carbonyl group of the host. The topological complementarity of the bulky group of the guest with the hosts may be responsible for the formation of only one hydrogen bond between the amide of the guest and carbonyl of the host. The bulky alkyl group, which is not involved in the hydrophilic interactions with the host, lies almost perpendicular to the molecular axis of the host and also interacts weakly with the benzene moieties of the host.

The packing diagram of the DTU-ethyl acetate complex was also studied. It was astonishing to find that this complex was not a channel type clathrate. It is classified as a type C structure (see Figure 21). The four hosts in the unit cell lie in two diagonal planes that are almost perpendicular to each other. The hosts in the same plane are inversely related through the inversion center of the unit cell. The guest molecule resides in a void formed by the four surrounding hosts. The carbonyl group of the guest forms unequal hydrogen bonds with the amide hydrogens of a single host molecule (see Figure 22). The bonding interaction in Figure 22 is described by the following parameters: a. 2.943(8)Å, 2.13(6)Å, 158.1(6)°; b. 2.962(8)Å, 2.16(5)Å, 163.0(5)° for the N...O, H...O

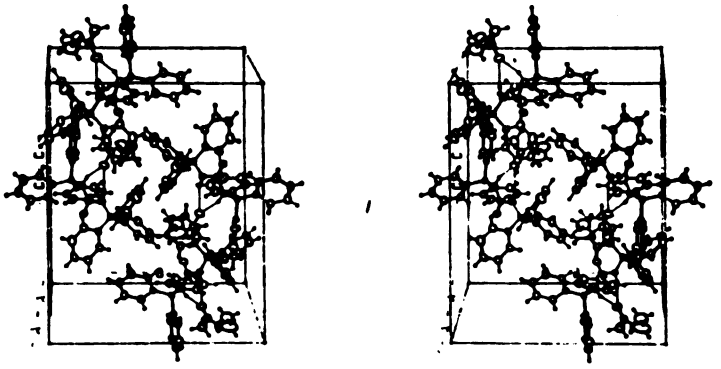


Figure 21. Stereoview of the crystal structure of the 1:1 DTU-ethyl acetate complex

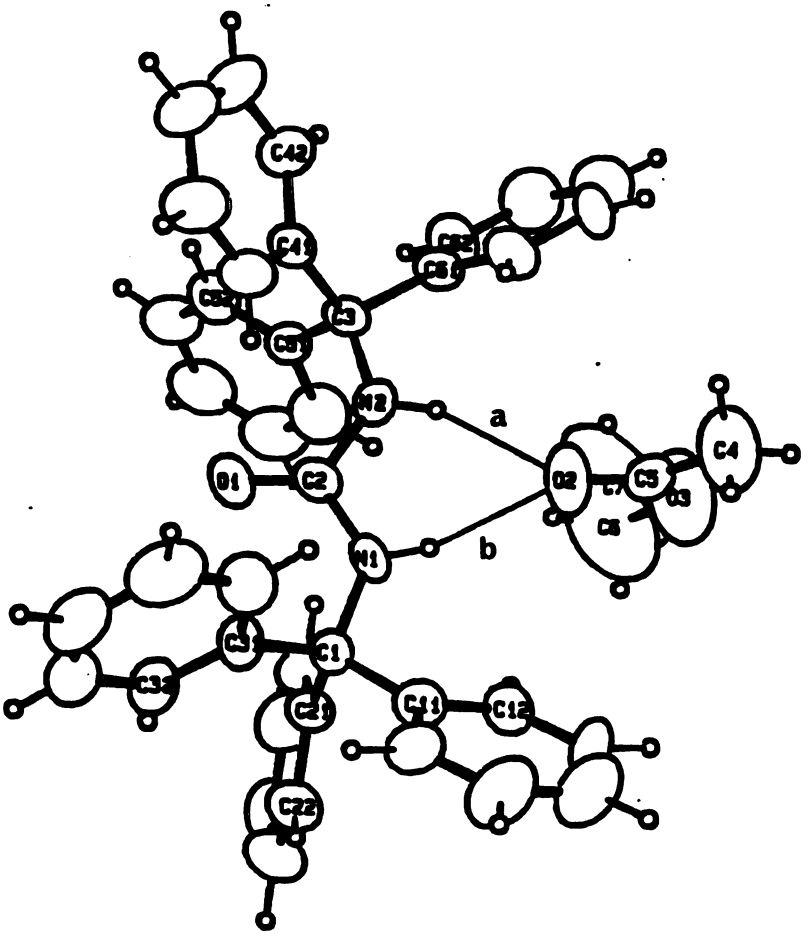


Figure 22. Hydrogen-bonding interactions of the guest with the host in the DTU-ethyl acetate complex.

distances and N-H...O angle respectively. The alkyl group in the ester portion of the guest lies almost perpendicular to the urea molecular axis of the host to which it is hydrogen bonded. This alkyl group interacts hydrophobically with the benzene rings of the surrounding host. The long ester group of ethyl acetate, which is too long to be accomodated in the void of a type A or type B structure might explain the formation of the type C structure for this complex.

Structure types other than those I have described have also been reported. The DTU-ethyl N-acetylglycinate structure is labelled as a type D, in which the host and guest molecules form a network of hydrogen bonds between amide moieties (Figures 23 and 24).[60] It is a channel type complex. A layer of host molecules stacks above another layer along the a-axis, to increase the efficiency of this dense packing. The bulky ester group of the amino acid, which was not involved in any hydrophilic interaction, lies along the molecular axis of the host to avoid steric interaction with the host.

Some important information has been gained through these studies of DTU clathrate complexes. The molecules in these complexes try to pack as densely as possible to achieve the maximum van der Waals' and hydrogen bonding interactions, and at the same time to avoid any steric repulsion. The type of complex that DTU forms with a particular guest molecule depends on the size of the guest molecule and on the orientation of the molecular axis of the guest with respect

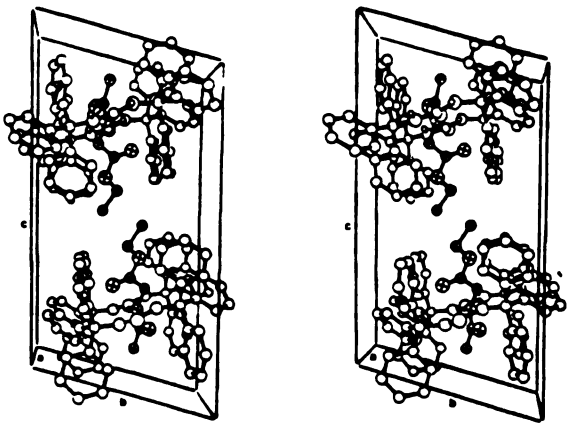


Figure 23. Stereoview of the crystal structure of the 1:1 DTU-ethyl N-acetylglycinate complex

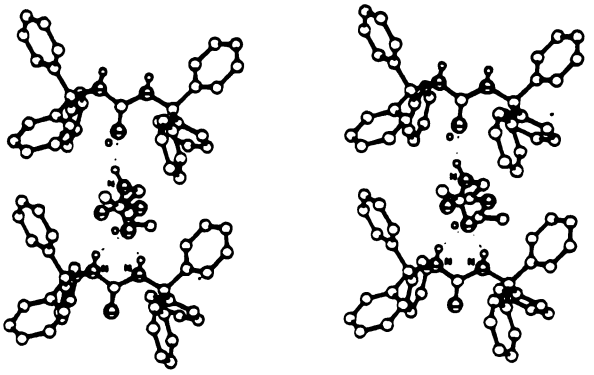


Figure 24. Stereoview of the hydrogen-bonding association of the guest to two adjacent hosts related by translation along a in the DTU-ethyl N-acetylglycinate complex.

to the host. Thus, topological complementarity is also a major factor in determining the packing patterns of these host-guest complexes.

III. Hosts with Modified DTU structures

With important information learned from DTU clathrate structures, I started to design hosts that had specific cavity sizes. Hopefully, in this way one could gain better control over clathrate formation. The logical approach was to modify the DTU moieties. Two possible ways existed (a) modification of the wheel and (b) modification of the axle.

It has not yet been possible to determine many X-ray structures on these new complexes, except for a few instances. Hence the discussion of the effect of these structural variations on the complexing capacity of the resulting hosts can at present only be qualitative and must be considered as preliminary. Nevertheless, the structural changes are grouped in a systematic way and are summarized briefly.

(a) Modification of the wheels

1. Urea hosts with larger end groups

It was thought that an increase in the size of the end groups in DTU may increase the size of the voids. This change might favor the formation of complexes with large guest molecules, according to the idea of topological complementarity. A number of DTU-type hosts with larger end

groups than trityl were prepared. Their inclusion studies with some guests are given in Table 11. The results indicate that the capacity of the hosts to form inclusion compounds actually decreased as the size of the wheel was increased. Compounds **65** and **66** formed some complexes with guests, but almost no guest molecules were included by compounds **83** and **61**. The increase in the wheel size may allow the host to form a larger void, but the bonding interaction between host and guest may no longer be at a maximum. In fact, the host molecules may pack more densely than in DTU, and therefore have cavities that are not big enough to accommodate the larger guests. Thus, compounds **65** and **66** formed some complexes, but **83** and **61** formed few or none. Although the ureas with larger end-groups than DTU were poorer hosts than DTU, they were more selective. For example, compound **65** did not form complexes with less polar, small organic compounds such as methylene chloride and toluene. Methanol was not included in compound **66**. This lack of complex formation was expected from the design. Compound **65** also did not form complexes with allyl alcohol and t-butanol, which did form complexes with DTU.

2. Urea hosts with rigid end groups

The three phenyl rings on each wheel of DTU are free to rotate. This may be important for the host in adapting to conformations in the crystal. By decreasing the number of conformational degrees of freedom of the wheel, the host

Table 11

COMPLEXATION STUDIES OF UREA HOSTS WITH LARGER END GROUPS THAN TRITYL[a]

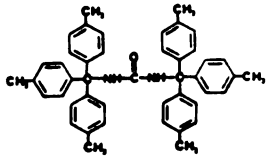
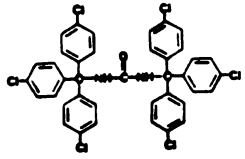
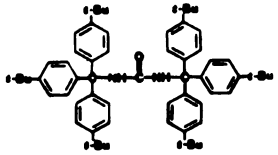
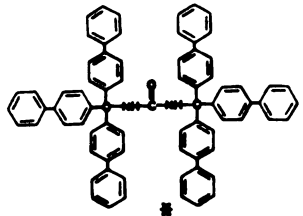
Guests \ Hosts	 65	 66*	 83	 61*
acetone	1:1 (110-112) [238-240]	1:1 (225-240) [267-269]	X	X
diethyl ether	1:1 (152-159) [234-235]	1:1 (176-180) [249-250]	X	X
toluene	X			X
methylene chloride	X			X

Table 11 (continued)

methanol	1:1	(137-140) [225-227]	X		X		X	
DMF	1:1	(--) [239-243]	1:1	(205-210) [265-267]		1:2	(185-190) [274-275]	

*66 also forms 1:1 complexes with 2,2-dimethylpropanamide [207-215], methylpropylamine, (158-165) [238-240] acetamide [231-234], 1-propanol (125-130) [244-245], diethylamine (178-182) [246-248], isopropanol (132-140) [237-238], acetonitrile (120-124) [234-236], ethanol (136-141) [235-236] but did not form a complex with allyl alcohol, ethyl acetate, t-butanol or isopropylamine.

*61 also formed no complex with ethanol or THF.

(a) Vacant entries do not necessarily mean that no complex is formed; not all host-guest combinations were tried; X = no complex; all ratios are expressed as host : guest; ( ) = temperature at which the crystals crumbled; [ ] = melting point of the compound (--) = no break-up of the crystals was observed; all temperatures are measured in °C.

might form complexes with guests more selectively. The phenyl rings were tied up in two ways to reduce the number of conformational degrees of freedom: (a) direct connection of two phenyl rings, i.e. in compound **68** (b) connecting two phenyl rings by a rigid bridge, as in **84**.

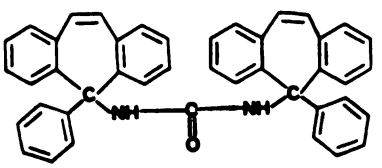
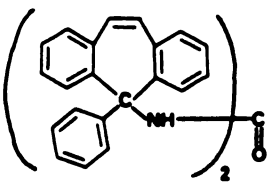
The inclusion studies of **84** and **68** with different small organic compounds are summarized in Table 12. The results indicated that **84**, which had a less rigid wheel than **68**, formed more complexes. The decrease of the conformational degrees of freedom and the irregular shape of the end groups increased the difficulty for the hosts to arrange themselves in an orderly pattern. The number of possible spatial arrangements for the hosts decreased. Thus, **84** and **68** were more selective than DTU in forming complexes with guests.

3. Urea hosts with smaller end groups

If an increase in the size of the end groups increases the size of the void, a reduced size of the end groups may have the opposite effect. Small guests may form better complexes with ureas having smaller wheels. Several hosts with smaller end groups were prepared and the results of inclusion studies are given in Table 13. The poor inclusion properties of **74**, **75**, **76**, and **77** were unexpected. One possible explanation is that replacement of one phenyl ring in the end group by a hydrogen atom may allow the end group of a neighboring host molecule to pack closely to its internal cavity from the less sterically hindered side, thus diminishing the dimensions of the void.

Table 12

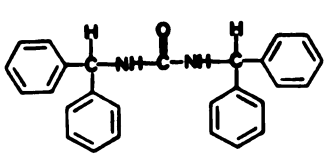
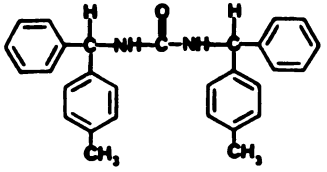
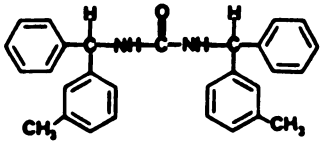
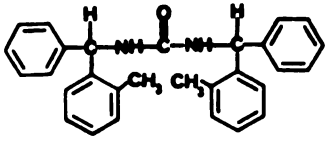
COMPLEXATION STUDIES OF UREA HOSTS WITH MORE RIGID END GROUPS THAN TRITYL[a]

Guests \ Hosts	 **84**	 **68**
acetone	1:1 (198-202) [198-202]	X
DMF	1:2 (132-139) [184-186]	4:3 (181-185) [252-254]
acetonitrile	3:1 (183-189) [240-245]	X
ether	2:1 (171-185) [230-231]	X
ethyl acetate	X	X

(a) Vacant entries do not necessarily mean that no complex is formed; not all host-guest combinations were tried; X = no complex; all ratios are expressed as host : guest; ( ) = temperature at which the crystals crumbled; [ ] = melting point of the compound (--) = no break-up of the crystals was observed; all temperatures are measured in °C.

Table 13

COMPLEXATION STUDIES OF UREA HOSTS WITH SMALLER END GROUPS THAN TRITYL

Guests \ Hosts	 74	 75	 76	 77
acetone	X	X	X	X
methanol	X	X	X	X
DMF	X	X	X	X

4. Urea hosts with unsymmetrical structures

The ureas mentioned so far are symmetrical, in that they have identical end groups. Ureas, with two different end groups may pack themselves in either of two simple fashions: (a) head to tail (b) head to head and tail to tail. The topologies of such packings may be useful in controlling the cavity size. In particular, complexes might form with unsymmetric guests that may fit into the cavity from one end but not from the other. Some unsymmetrical hosts were prepared and the results of complexation studies are listed in Table 14.

When both end groups were quite similar in structure, they fitted well in either fashion. Voids were easily formed. Thus compounds **69**, **70**, **85** and **86** included some guests. Complexation of small guests were in some instances poor, however, possibly due to the difficulty of filling up uneven spaces in the void. Thus unsymmetrical hosts had problems in forming complexes with methanol and acetonitrile.

When the end groups were quite different in structure (as in **71** and **82**) the efficient packing of the host became more difficult because of the uneven ends. The number of possible spatial arrangements was therefore limited and so were the inclusion capabilities. The results with compound **71** were not surprising. The poor complexation capability of **82** compared with DTU despite the relatively small structural change may be attributed to the fact that the voids were too small for the guest.

Table 14

COMPLEXATION STUDIES OF UREA HOSTS WITH UNSYMMETRICAL END GROUPS[a]

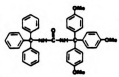
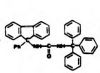
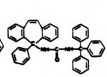
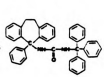
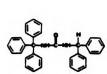
Guests \ Hosts	 69*	 70	 85	 86	 71	 82
diethyl ether	1:1 (117-125) [130-140]	3:2 (110-115) [229-230]	3:2 (168-171) [231-232]	3:2 (176-183) [224-226]	X	X
DMF	2:1 (147-150) [195-205]	1:1 (132-133) [236-237]	1:1 (102-105) [102-105]	1:1 (188-193) [229-230]	X	X
acetamide	1:1 (--) [189-190]	3:1 (--) [218-225]	2:1 (--) [242-244]	1:1 (--) [254-255]		
DMSO	1:1 (188-190) [200-210]	1:1 (188-189) [188-189]	1:1 (--) [245-248]	1:1 (--) [249-251]		
acetone	1:1 (135-140) [215-216]	3:1 (190-200) [236-237]	X	1:1 (162-170) [232-233]		X

Table 14 (continued)

methanol		X	X	X	2:1 (146-150) [232-233]	X	X
acetonitrile	2:1	(127-133) [212-214]	X	X	X		
diethylamine	1:1	(121-126) [215-216]			1:1 (161-164) [227-228]		
ethanol	1:1	(122-128) [122-128]				X	
toluene		X			X		

(a) Vacant entries do not necessarily mean that no complex is formed; not all host-guest combinations were tried; X = no complex; all ratios are expressed as host : guest; ( ) = temperature at which the crystals crumbled; [ ] = melting point of the compound (--) = no break-up of the crystals was observed; all temperatures are measured in °C.

• 69 forms 1:1 complex with nitromethane (128-133) [187-204], but did not form a complex with 2,2-dimethylpropanamide, 1-propanol, methyl propyl ether, diisopropylamine or methylene chloride.

(b) Modification of the axle

5. Urea hosts with longer axes

Up to now, we have been concerned only with the effect of the end group on the crystal packing. The axle may also affect the packing of the host. Ureas with a one carbon extension on one side or both sides of the urea axis were prepared. Their complexation studies are shown in Table 15.

The extension of one carbon unit on one side of the urea axis as in compound **78** did not seem to affect complexation capability. The end-group spacers still kept neighbouring hosts away from one another. Thus, voids were still present in the crystal lattices. When one carbon unit was introduced on each end of the axle, however, the packing of the host became much less efficient. Thus, a host structure without voids big enough to enclose guests was preferred. This was consistant with our experimental results that **79** did not form many molecular complexes.

6. Simultaneous variation of the wheel and the axle in urea and non-urea hosts

Variations of both the wheel and the axle of DTU were explored to see whether a new host could be found. Compounds with such combined features, and the crystallization studies of these compounds are shown in Table 16. Some were found to include guest molecules.

An X-ray structure of the 1:1 complex of **80** with diethyl ether was studied (Figure 25). Viewing down the b-axis of the unit cell, the hosts form layers along the

Table 15

COMPLEXATION STUDIES OF UREA HOSTS WITH LONGER AXES[a]

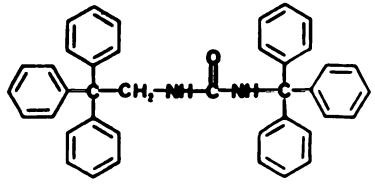
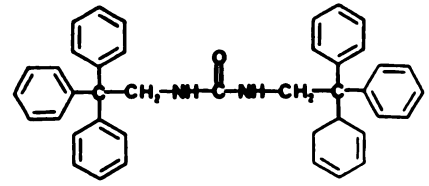
Guests \ Hosts	 **78**[*]	 **79**
acetone	1:1 (182-189) [227-228]	X
methanol	1:1 (110-115) [225-226]	X
DMF	1:1 (135-145) [220-221]	1:1 (211-214) [243-244]
diethyl ether	1:1 (--) [228-229]	X
ethanol	1:1 (112-115) [227-228]	X

Table 15 (continued)

acetonitrile	2:3	(150-155) [227-228]	X
nitromethane	1:2	(152-160) [235-236]	X
acetamide	1:1	(207-211) [207-211]	X
THF	1:1	(--) [226-227]	

(a) Vacant entries do not necessarily mean that no complex is formed; not all host-guest combinations were tried; X = no complex; all ratios are expressed as host : guest; ( ) = temperature at which the crystals crumbled; [ ] = melting point of the compound (--) = no break-up of the crystals was observed; all temperatures are measured in °C.

* Compound **78** did not form a complex with ethyl acetate, 2-propanol, diethylamine, toluene, 2,2-dimethylpropanamide or thioacetamide.

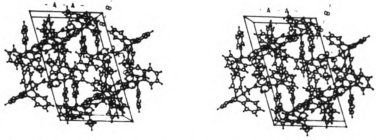


Figure 25. Stereoview of the crystal structure of the 1:1 N-triphenylmethyl-N'-9-triptycylmethyl urea — diethyl ether complex

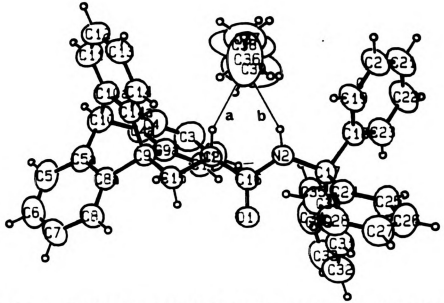


Figure 26. Hydrogen bonding associaton of the guest with the host in N-triphenylmethyl-N'-9-triptycylmethyl urea-diethyl ether complex

Table 16

COMPLEXATION STUDIES OF HOSTS WITH DIFFERENT END GROUPS AND AXES[a]

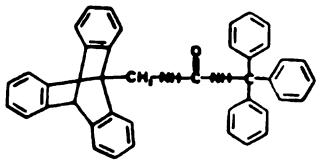
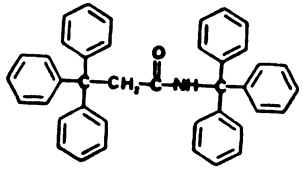
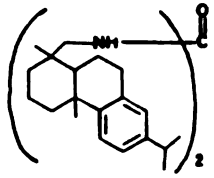
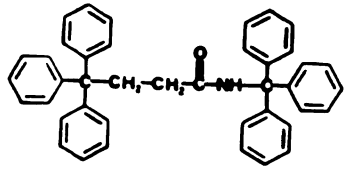
Guests \ Hosts	 80	 101	 81	 102
ethyl acetate	X	X	4:1 (--) [174-175]	X
acetone	1:1 (117-123) [263-265]	1:1 (100-105) [172-173]	X	X
methanol	1:1 (136-141) [263-265]	3:1 (95-97) [95-97]	2:1 (--) [171-172]	X
acetonitrile	X	2:3 (90-95) [170-171]	X	X

Table 16 (continued)

diethyl ether	1:1	(170-175) [268-268]	1:1	(102-104) [102-104]	X
methylene chloride	1:1	(105-110) [257-259]	2:1	(96-100) [169-170]	
THF	1:1	(139-143) [265-267]			X
ethanol	1:1	(161-164) [267-268]			
toluene				X	X
nitromethane					X

(a) Vacant entries do not necessarily mean that no complex is formed; not all host-guest combinations were tried; X = no complex; all ratios are expressed as host : guest; ( ) = temperature at which the crystals crumbled; [ ] = melting point of the compound (--) = no break-up of the crystals was observed; all temperatures are measured in °C.

a-axis in a head to tail fashion. The triptycene end groups in each layer are stacked above the triptycene and below a triphenylmethyl end or vice versa. The void is formed by four surrounding hosts. Hydrogen bonds unite individual host and guest entities. The bonding and spatial relationship between host and guest are described in Figure 26. The parameters of the hydrogen bonds shown are: a. 3.036(4)Å, 2.24(2)Å, 155(2)^{o} ; b. 3.042(4)Å, 2.25(2)Å, 157(2)^{o} for the N...O, H...O distances and N-H...O angle respectively. As with analogous DTU complexes, the molecular plane of the guest lies perpendicular to the plane containing the molecular axis of the host. The complex structure revealed that the rigid triptycyl group had a limited degree of conformational freedom. Only the bond between the tertiary carbon of the wheel and the urea nitrogen could freely rotate to allow conformational changes. Such a restriction on the wheel severely restricted the number of possible spatial arrangements among the hosts, thus, damaging the capability of the host to form complexes with guests. This proved to be true in our complexation studies. Only a few complexes of **80** with guests were formed.

An X-ray structure of uncomplexed **80** host showed a different structure from the **80**/diethyl ether crystal complex (Figure 27) (for comparision of some structural data for complexed and uncomplexed **80**, see table 17). No cavity large enough to enclose any small organic compounds was present. The amide hydrogen atoms of the host point in opposite,

Table 17

SUMMARY OF CRYSTAL DATA FOR COMPLEXES XI AND XII

Compounds	**XI**	**XII**
formula weight	642.85	568.73
space group	$P2_1/n$	$P2_1/n$
Z	4	4
a, Å	12.614	13.655
b, Å	15.665	13.693
c, Å	19.562	15.970
α, deg	90.0	90.0
β, deg	107.48	101.33
γ, deg	90.0	90.0
R	0.045	0.042
R_w	0.042	0.044

XI. is referred as N-triphenylmethyl-N'-9-triptycylmethyl urea-diethyl ether and XII. is referred as N-triphenylmethyl-N'-9-triptycylmethyl urea.

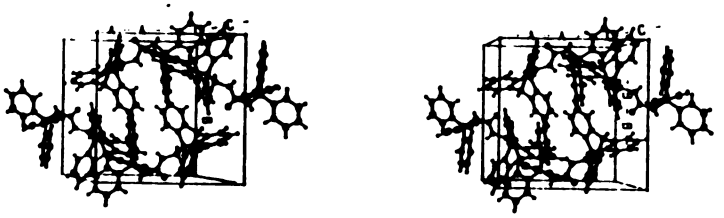
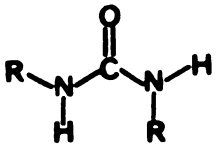


Figure 27. Stereoview of the crystal structure of N-triphenylmethyl-N'-9-triptycylmethyl urea



directions thus allowing the phenyl rings in the end groups, now free from any steric interaction with a guest, to occupy space in the internal cavity of the host.

Replacement of one NH group in the urea axis of DTU by a methylene group gave amide **101** which was found to enclose guests. A crystal structure of the 1:1 complex of **101** with acetone showed the same packing pattern as the analogous DTU complex (Figure 28). The complexes also have similar strutural data (see Table 18). Figure 29 shows the channels occupied by the guest molecules in this complex. The NH and CH_2 groups of the host were indistinguishable in the crystal structure. Compound **101** formed fewer complexes with guests than did DTU. This may be due to the fact that the two hydrogen bonding interactions possible for DTU are stronger than the one hydrogen bond possible with **101**. For similar reasons, nitromethane formed a complex with DTU but not with **101**.

The bonding and spatial relationship between **101** and acetone are described in Figure 30. The bonding interaction is described by the following parameters: 2.931(6)Å, 2.10(3)Å and 163(2)^{o} for the N...O, H...O distance and N-H...O angle respectively.

The dehydroabietyl urea **81**, which has a more bulky end group than the triphenylmethyl group, did not seem a promising host as indicated by the results of the inclusion

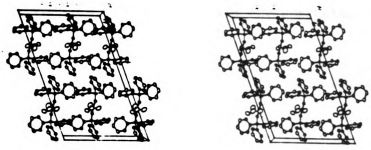


Figure 28. Stereoview of the crystal structure of the 1:1 N-trityl-3,3,3-triphenylpropanamide : acetone complex

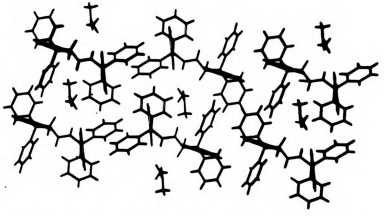


Figure 29. Picture of the N-trityl-3,3,3-triphenylpropanamide-acetone molecular packing, showing the channels occupied by acetone molecules

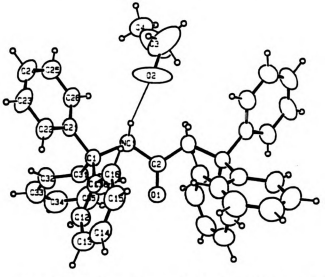


Figure 30. Hydrogen bonding interaction of the guest with the host in the N-trityl-3,3,3-triphenylpropanamide-acetone complex.

Table 18

SUMMARY OF CRYSTAL DATA FOR COMPLEXES V AND XIII

Compounds	**V**	**XIII**
formula weight	602.78	601.80
space group	C2/c	C2/c
Z	4.0	4.0
a, Å	15.581	15.615
b, Å	9.450	9.443
c, Å	24.575	24.963
α deg	90.0	90.0
β deg	110.37	110.76
γ deg	90.0	90.0
R	0.038	0.044
R_w	0.036	0.040

V is referred as DTU-acetone and XIII is referred as N-triphenyl-3,3,3-triphenylpropanamide-acetone.

studies. The irregular shape of the end group may account for the difficulty that this host has in lining up in an organized pattern to form voids where the guest molecules could reside. It was tried, however, because the amine moiety is chiral.

Amide **102** which has an axle one carbon unit longer than **101**, and a similar structure to urea **78**, did not include any guests in our studies. The decreased binding of guests might be due to the presence of only one electon accepting NH group, and also to the increased length of the axis, thus increasing the dimensions of the void and reducing the number of spatial arrangements that could include a guest.

7. Monosubstituted ureas

The concept of wheel and axle may also be applied to monosubstituted ureas. An X-ray study[60] of the 2:1 N-triphenylmethylurea (NTU) complex with dimethylformamide illustrates a completely different relationship between host and guest (Figure 31). With only one end-group present, host-

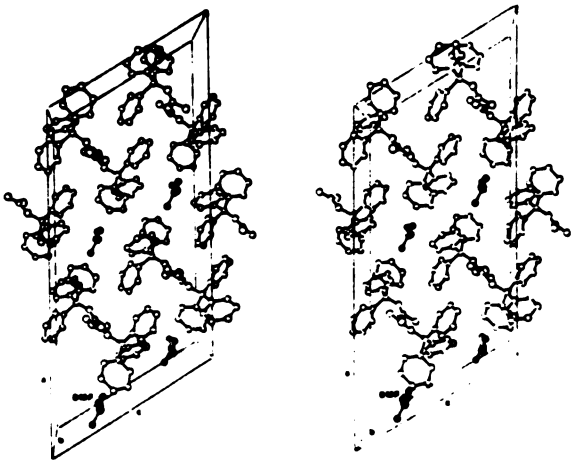


Figure 31. Stereoview of the crystal structure of 2:1 NTU-DMF

host hydrogen bonding was now possible. The guest was enclosed in the external hydrophobic cavity formed by four neighbouring hosts. No significant bonding interaction between host and guest was observed. Therefore, the topological complementarity of the external cavity with the guest may be the primary reason for host-guest complexation.

Monosubstituted ureas with different sized end-groups, and hopefully different cavity sizes, were prepared and their studies are summarized in Table 19. The results indicated that the increase in end-group size decreased the complexation capability of the hosts. Compound **88** formed a few complexes, but no host-guest complexes were observed with **89** and **90**. The increased size of the wheel may make the external cavity too small to enclose a guest. However, urea **91**, with a small triptycl end-group which closely resembles NTU, formed complexes readily.

8. Other hosts

Polar compounds other than the ureas and its analogs have not been previously investigated. N,N'-dirityldiamides with a polar and rigid axis capable of hydrogen bond formation, might also be good hosts. Several diamides were prepared and their complexation studies are shown in Table 20. Only a few complexes were formed. Host-host intermolecular hydrogen bonds were suspected of forming to prevent formation of a void for complexation. This may also explain the poor solubility of these diamides in most organic

Table 19

COMPLEXATION STUDIES OF MONOUREA HOSTS[a]

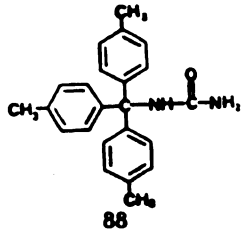
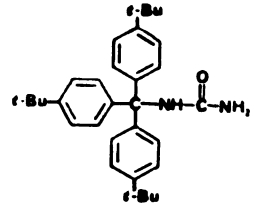
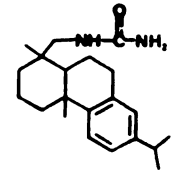
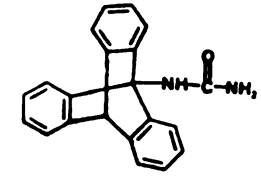
Guests \ Hosts	 88	 89	 90	 91
acetone	3:1 (--) [235-236]	X	X	3:1 (140-145) [317-318]
ethyl acetate	3:1 (--) [236-237]	X	X	2:1 (150-160) [314-315]
acetonitrile	X	X	X	1:1 (155-160) [321-322]
DMF		X	X	3:1 (--) [331-333]

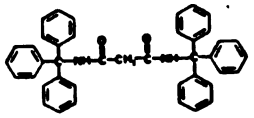
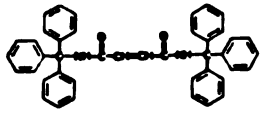
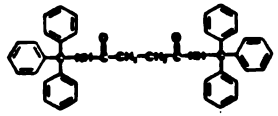
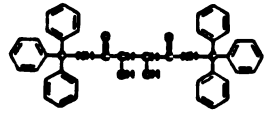
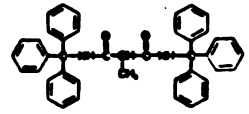
Table 19 (continued)

methanol	X	X	X
ether	X	X	X
ethanol			X

(a) Vacant entries do not necessarily mean that no complex is formed; not all host-guest combinations were tried; X = no complex; all ratios are expressed as host : guest; ( ) = temperature at which the crystals crumbled; [ ] = melting point of the compound (--) = no break-up of the crystals was observed; all temperatures are measured in °C.

Table 20

COMPLEXIATION STUDIES OF DIAMIDE HOSTS[a]

Guests \ Hosts	 93	 99	 97	 103	 95
methanol	X	X	X	X	X
methylene chloride	X	X	X	X	X
acetonitrile	2:1	X	X	X	X
acetone	X	3:1	X	3:1	X

[a] all ratios are expressed as host : guest.

solvents. O-2-naphthyl-N-triphenylmethyl carbamate was also studied, but the results proved unsuccessful. It formed a complex with acetonitrile but not with acetone, methanol, toluene and ethyl acetate.

So far, only quite polar hosts have been described. Non-polar compounds with similar topologies may be good hosts for non-polar guests. Hart and his coworkers reported some symmetrical ditrityl diacetylenes that formed complexes with non-polar aromatic solvents. Diamines and diethers may also form such complexes with guests. Several diamines and diethers were examined and their complexation studies are presented in Table 21 and 22. Hosts with a short axis had better inclusion ability than hosts with a longer axis. The dense packing of the long axis host resulted in the formation of a structure in which the cavity was not big enough to enclose a guest molecule. Therefore, hosts with long axes have poorer complexation capabilities than hosts with short axes.

An X-ray structure of the 1:1 complex of diether **114** with toluene was obtained (Figure 32). The hosts stack on top of each other along the b-axis of the unit cell. Layers of host molecules are found along the c-axis. Viewing down the a-axis, a channel is observed in which the guests reside (Figure 33). The toluene guests align themselves in one direction in a given layer and in the opposite direction in neighboring layers.

The 1:1 complex of diether **114** with toluene is different from the 1:1 complexes of **117** and **118** with toluene. The

Table 21

COMPLEXATION STUDIES OF DIAMINE HOSTS.[a]

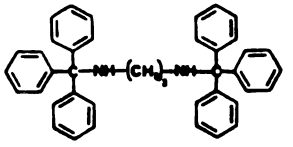
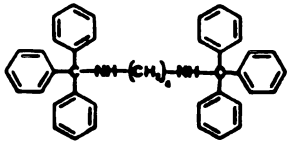
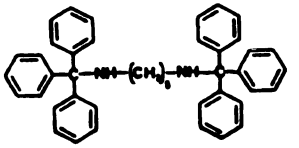
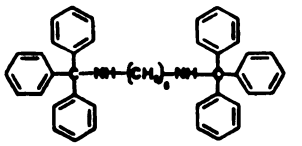
Guests \ Hosts	 107	 109[a]	 111[a]	 113
acetone	X	3:1 (135-137) [157-158]	X	X
THF	1:1 (147-150) [147-150]	1:1 (142-144) [151-153]	X	1:1 (--) (190-191)
p-xylene	1:1 (137-145) [137-145]	1:1 (136-144) [136-144]	X	X
toluene	X	2:1 (137-140) [157-158]		X

Table 21 (continued)

methylene chloride		2:1	(144-147) [157-158]	X
methanol	X		X	X

(a) Vacant entries do not necessarily mean that no complex is formed; not all host-guest combinations were tried; X = no complex; all ratios are expressed as host : guest; ( ) = temperature at which the crystals crumbled; [ ] = melting point of the compound (--) = no break-up of the crystals was observed; all temperatures are measured in °C.

* Compound 109 did not form a complex with acetonitrile.

* Compound 111 did not form a complex with acetonitrile cyclohexanone or cyclopentanone.

Table 22

COMPLEXATION STUDIES OF DIETHER HOSTS[a]

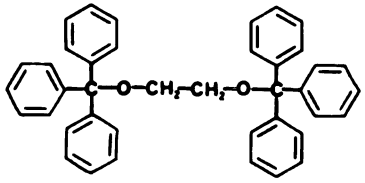
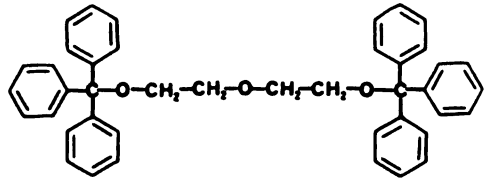
Guests \ Hosts	 114	 116
acetone	X	X
methanol	X	
toluene	1:1	X

Table 22 (continued)

p-xylene	X	X
m-xylene	X	
2-propanol		X

(a) Vacant entries do not necessarily mean that no complex is formed; not all host-guest combinations were tried; X = no complex; all ratios are expressed as host : guest.

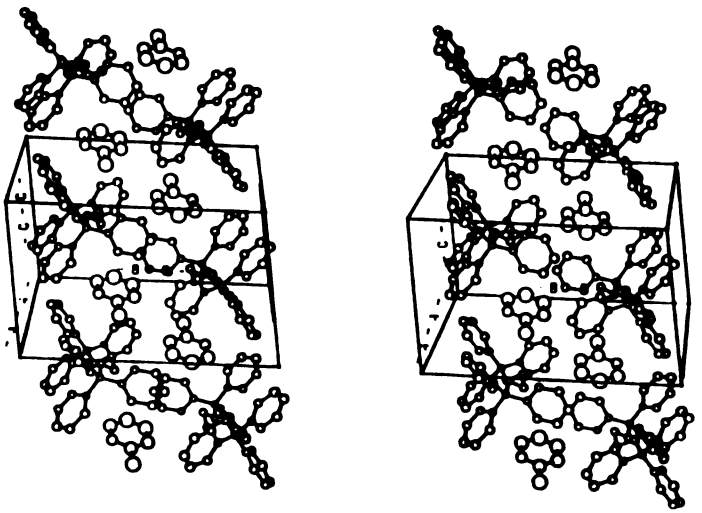


Figure 32. Stereoview of the crystal structure of the 1:1 ethylene glycol-di-trityl ether-toluene complex

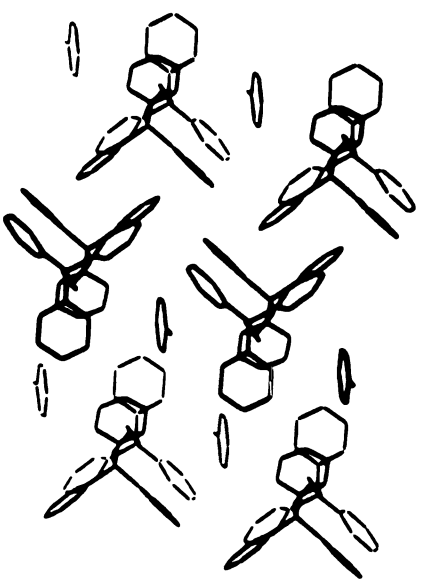
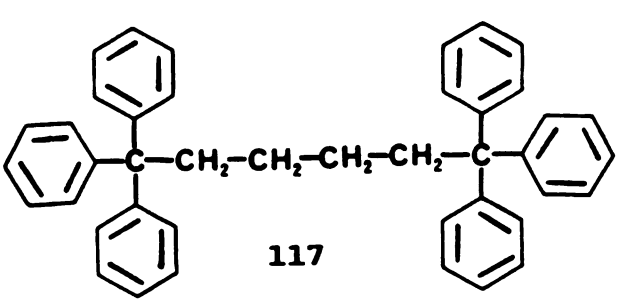
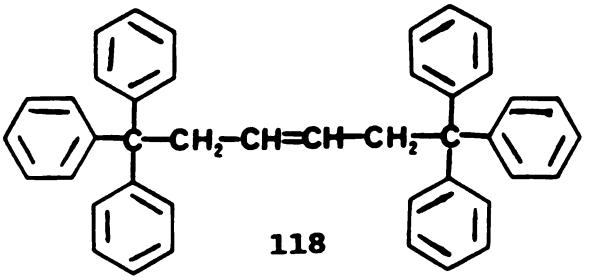


Figure 33. Picture of the ethylene glycol-Di-trityl ether-toluene molecular packing shows channels occupied by toluene



117



118

toluene molecules in **117** and **118** complexes lie in the extramolecular cavities of the hosts (see Figures 34 and Table 23 for comparision structures and structural data). The toluene molecules in the complexes of **117** and **118** can occupy two possible orientations in the same layer; the methyl group of some toluene molecules lies in one direction, and the others lie in the opposite direction. The possible explanation for this disorder is due to the non-directional bonding interactions of toluene with the surrounding benzene rings of the hosts. In the **114**-toluene complex, a more directional bonding interactions between the host and the guest forces the toluene molecules to line up uniformly in one direction only.

INCLUSION AND SELECTIVITY STUDIES

(a). With DTU

DTU was shown to include amides, aromatic hydrocarbons, alcohols, ketones, esters of amino acids and halogenated hydrocarbons stoichiometrically. Other guest molecules, for example, nitro compounds, aldehydes, thiols, epoxides, and difunctional compounds were also studied. Examples are

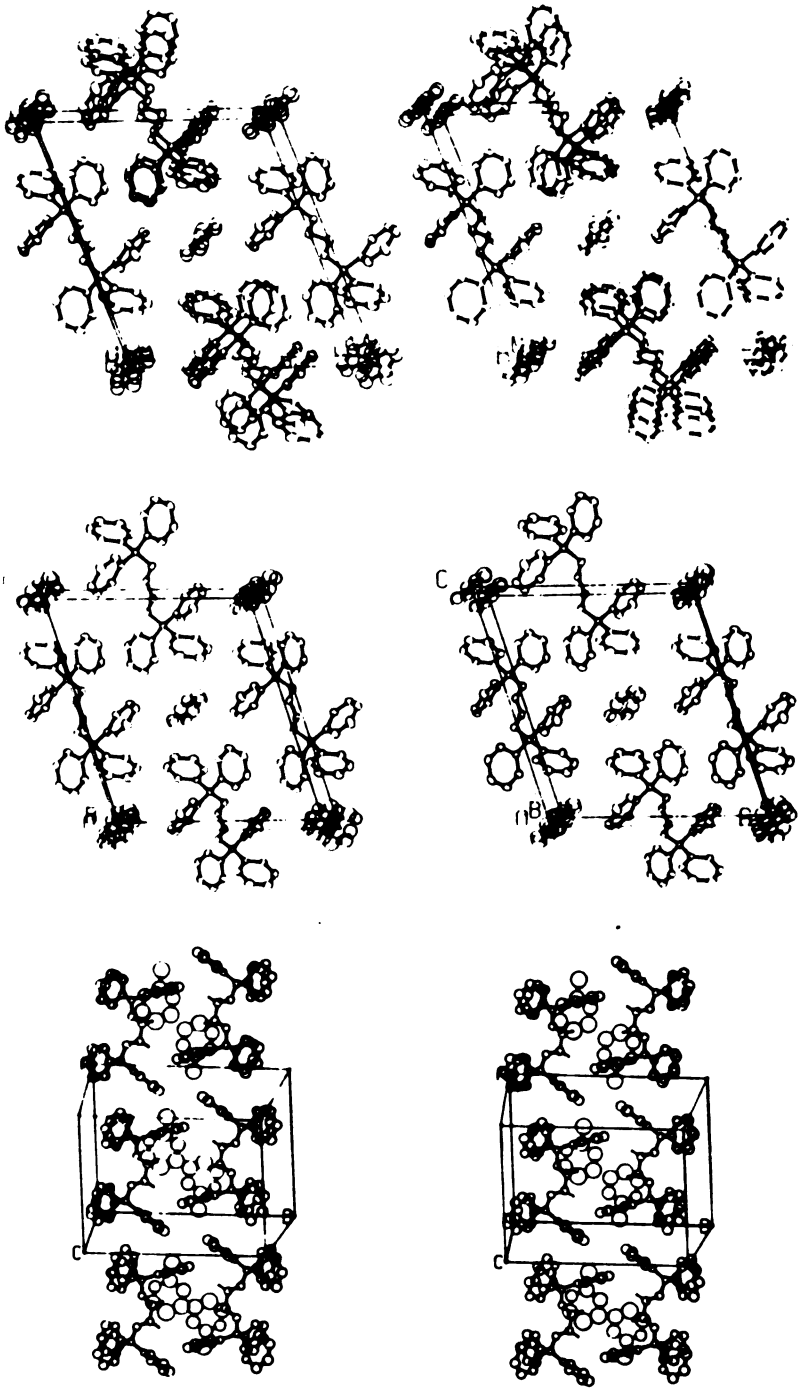


Figure 34. Comparison of the stereoview of the crystal structures of 1,1,1,6,6,6-hexaphenylhexane-toluene complex (a), 1,1,1,6,6,6-hexaphenyl-3-hexene-toluene complex (b), and ethylene glycol-ditrityl ether-toluene complex (c)

Table 23

SUMMARY OF CRYSTAL DATA FOR XIV, XV AND XVI COMPLEXES

Compounds	**XIV**	**XV**	**XVI**
formula weight	683.85	634.90	632.89
space group	P_1	$P2_1$	$P2_1/n$
Z	2	2	2
a, Å	12.329	16.685	14.786
b, Å	16.254	7.915	7.525
c, Å	9.925	14.772	17.063
α, deg	97.56	90.0	90.0
β, deg	113.11	110.98	107.98
γ, deg	93.39	90.0	90.0
R	0.121	0.090	0.130
R_w	0.088	0.079	0.143

XIV. to XVI. are referred as XIV. $Ph_3CO\text{-}CH_2\text{-}CH_2O\text{-}CPh_3$-toluene.

XV. $Ph_3C(CH_2)_4CPh_3$-toluene XVI. $Ph_3CCH_2\text{-}CH{=}CH\text{-}CH_2CPh_3$-toluene.

listed in Table 24. In most cases, these clathrate compounds were stable at a temperature well above the boiling point or the melting point of the guest without decomposition.

The host lattice of DTU enclosed guest molecules selectively. Selectivity is defined as the amount of a particular guest included in the host lattice when the host was crystallized from an equimolar amounts of two guests. The term selectivity in this thesis is an arbitrary selectivity because it refers to the inclusion of the guest in the host lattice in a specific concentration of the host and specific concentration of guest. The general procedure for selectivity studies of DTU was as follows. DTU (0.2 g) was dissolved in 3 mL of hot ethyl acetate. Then 20 mole equivalents of the guests were added in a closed system. The resulting crystalline complexes were dried at room temperature under 0.5 to 1.5 torr for 10 hours. The stoichiometric ratio of the guests in the complexes was determined by NMR intergrations of signals derived from the host and the guests (for details, see experiment section).

These selectivities varied with the concentration of the host in the inert solvent. The dilution effect is illustrated in Tables 25 and 26 in the selectivity studies of DTU with diethyl ether : methyl propyl ether mixtures and with methyl propyl ether : N-methyl propylamine mixtures. The results show that a decrease in the concentration of the host increases its selectivity. For example, in the selectivity studies on DTU with mixtures of diethyl ether and

Table 24

INCLUSION COMPLEXES OF DTU WITH DIFFERENT GUESTS[a]

Entry	Guest	Host : Guest Ratio
1	nitromethane	2 : 1
2	acetaldehyde	1 : 1
3	acetonitrile	1 : 2
4	m-xylene	1 : 1
5	benzene	1 : 1
6	anisole	1 : 1
7	ethylene glycol	2 : 1
8	ethanolamine	2 : 1
9	dimethoxyethane	1 : 1
10	2-methoxyethanol*	2 : 1
11	N-Methylethylenediamine	3 : 2
12	N,N'-dimethylurea	1 : 1

(a) DTU did not form a complex with benzenethiol, nitrobenzene, diethyl sulfide, benzenesulfonamide, 1,4-diaminobutane, cyclohexene oxide, 4-picoline, pyridine or ephedrine.

* the crystal crumbled between 217-224°C.

Table 25

SELECTIVITY STUDIES ON DTU WITH MIXTURES OF DIETHYLAMINE AND DIETHYL ETHER*

Weight of Et_2O: Et_2NH in 1 mL of ethyl acetate \ Weight of DTU in 2 mL of ethyl acetate	80 mg	40mg	20 mg	13.3 mg	10 mg
200 mg:100 mg (2 equiv.) : (1 equiv.)	7.3:1 7.1:1	8.0:1 8.1:1	9.4:1 9.6:1	10.8:1 9:1	13.3:1 13.7:1
100 mg:100 mg (1 equiv.) : (1 equiv.)	3.5:1 3.3:1	4.1:1 4.2:1	4.4:1 4.4:1	5.1:1 4.8:1	6.7:1 6.2:1
100 mg:200 mg (1 equiv.) : (2 equiv.)	1.8:1 2.0:1	2.2:1 2.2:1	2.3:1 2.4:1	2.3:1 2.6:1	2.7:1 3.0:1
Selectivity	3.6±.2	4.2±.2	4.6±0.2	4.8±0.1	6.4±0.4

*The ratio is diethyl ether : diethylamine

Table 26

SELECTIVITY STUDIES ON DTU WITH MIXTURES OF DIETHYL ETHER AND METHYL PROPYL ETHER

Weight of Et_2O: CH_3OPr in 1 mL of ethyl acetate \ Weight of DTU in 2 mL of ethyl acetate	57 mg	40mg	20 mg	13.3 mg
200 mg:100 mg (2 equiv.) : (1 equiv.)	12.3:1 12.0:1	14.7:1 15.6:1	17.0:1 16.7:1	19.0:1 19.3:1
100 mg:100 mg (1 equiv.) : (1 equiv.)	7.6:1 8.2:1	8.2:1 8.8:1	9.9:1 11.1:1	12.1:1 11.5:1
100 mg:200 mg (1 equiv.) : (2 equiv.)	4.4:1 4.2:1	4.9:1 4.3:1	4.8:1 5.4:1	6.7:1 6.6:1
Selectivity	8.3±0.4	8.8±0.4	10.3±0.3	12.5±0.7

*The ratio is diethyl ether : methyl propyl ether

diethylamine (Table 25), when 10 mg of DTU was dissolved in equimolar amounts of diethyl ether and diethylamine in ethyl acetate solution, DTU preferentially included diethyl ether to diethylamine in 6.4 to 1 ratio. However, when the amount of DTU was increased to 80 mg, the ratio decreased to 3.6 to 1.

A comparison of the results obtained from a 1:2, 1:1 and 2:1 mole ratio of diethyl ether and diethylamine with DTU showed that the selectivity of the host toward the guests was reproducible. For instance, a two-fold increase in the diethyl ether concentration in the guest mixtures does not change the selectivity of the host, as indicated in Table 25. In Table 26, experimental errors exist in the ratio of diethyl ether and methyl propyl ether in the complexes due to the error in measuring the NMR integrations of the methyl propyl ether protons at low concentration. Thus, the selectivity of DTU toward diethyl ether and methyl propyl ether is best represented by considering the results from 1:1 and 1:2 mole ratios of diethyl ether to methyl propyl ether. The selectivity of the host in Table 26, thus, is also nearly constant regardless of the concentration of the guest mixtures.

The results from the selectivity studies on DTU with diethyl ether : diethylamine and diethyl ether : methyl propyl ether mixtures show the reproducibilty of these experiments. Thus, for the rest of the selectivity studies of DTU and other hosts, all experiments were performed in duplicate for one specific concentration of the host and

guest. With liquid guests, twenty or twenty-five to one mole ratios of the guests to host were used. With solid guests, two mole equivalents of guest to one mole equivalent of host were used.

Selectivity results of different guests with DTU are summarized in Table 27. These selectivities were attributed to the topological fit and the bonding interactions between hosts and guests. In some cases, there is almost 100% discrimination in favor of one guest. Guests that can form strong bonding interactions with DTU form complexes preferentially. DTU formed complexes preferentially with diethyl ether over diethylamine and with methyl propyl ether over N-methyl propylamine. Oxygen forms a stronger hydrogen bond than nitrogen, which may explain the guest discrimination in these cases. The extensive network of hydrogen bonding of DTU with acetamide accounts for the formation of the DTU-acetamide complex over DTU-N,N-dimethyl formamide and DTU-diethylamine complexes. The π electron cloud of the allyl alcohol can interact with the host leading to preferential complexation of allyl alcohol over 1-propanol. A better topological fit of acetone with the host, compared to acetaldehyde, is due to the extra methyl group and leads to selective complexation. Examples of guest discriminations from a steric point of view is found in the selectivity studies of members in the same homologous series and of geometrical functional isomers. For example, DTU preferably complexed with methanol over ethanol and with 2-propanol over

Table 27

STUDIES OF GUESTS BINDING TO THE HOST (DTU) IN A TWO-COMPONENT SYSTEM

Entry	Mixture of Guests in Equal Molar Ratio			Guests Ratio in the Complexes
1	allyl alcohol	:	1-propanol	3.1 : 1
2	acetamide	:	DMF	20> : 1
3	methanol	:	ethanol	2.3 : 1
4	acetone	:	acetaldehyde	15 : 1
5	methyl n-propyl ether	:	methyl propylamine	2.1 : 1
6	acetamide	:	diethylamine	20> : 1
7	acetamide	:	2,2-dimethylpropanamide	20> : 1

1-propanol. The full formation of an extensive network of hydrogen bonds between the amide groups of the host and guests in the DTU-acetamide complex, rather than the partial hydrogen bonding in DTU-2,2-dimethylpropanamide (see Figure 20) due to the steric complement of the host with the guest, favors the formation of a complex with acetamide over 2,2-dimethyl propanamide.

(b) With BTTMU

N,N'-Bis(tri-p-tolylmethyl)urea (BTTMU) which included some guest molecules and probably formed a bigger void in the lattice than DTU, was subjected to selectivity studies. The results are given in Table 28. Again, methanol was preferred over ethanol, acetamide over 2,2-dimethylpropamide, and acetone over acetaldehyde. This is due to the steric complement among host and guests. The stronger bonding interactions of the guests with the host account for the preferred complexation of a particular guest. Thus, BTTMU selectively formed complexes with acetamide rather than DMF, with diethyl ether rather than diethylamine and with allyl alcohol over 1-propanol. Surprisingly, there was no guest discrimination between 2-propanol and 1-propanol in these complexation studies. A comparision of the selectivity capability of DTU with BTTMU in two component guest mixtures shows that DTU in general is more selective than BTTMU, except for the selectivity toward methanol and ethanol mixtures. The larger voids in the BTTMU lattice may allow the host to enclose guests more easily but less selectively.

Table 28

STUDIES OF GUESTS BINDING TO THE HOST (BTTMU) IN A TWO-COMPONENT SYSTEM

Entry	Mixture of Guests in Equal Molar Ratio			Guests Ratio in the Complexes
1	allyl alcohol	:	1-propanol	1.5 : 1
2	acetamide	:	DMF	20> : 1
3	methanol	:	ethanol	2.6 : 1
4	acetone	:	acetaldehyde	8.1 : 1
5	2-propanol	:	1-propanol	1 : 1
6	diethyl ether	:	diethylamine	1.3 : 1
7	acetamide	:	2,2-dimethylpropanamide	20> : 1

(c) With NTU

The extramolecular cavity in NTU was reported to trap DMF.[60] The formation of complexes of NTU with guests is primarily due to the steric complementarity. NTU may be as useful as DTU for separating one guest from another. The complexation of NTU with a mixture of guests which had similar sizes but different functionalities was studied (Table 29). As expected, the topological complementarity is the main reason for NTU complexing with one guest but not another. Strong supporting evidence came from the selectivity studies of acetamide and DMF mixtures. Acetamide was expected to form a network of hydrogen bonds with NTU. However, NTU preferentially complexed with DMF over acetamide, which suggested that steric fit rather than bonding interaction was the driving force for complexation. For a similar reason, NTU preferentially formed complexes with acetonitrile over nitromethane and with DMF over acetonitrile.

CONCLUSION

Experimental results from my studies of host-guest complexes indicates that bonding interactions and toplogical complementarity between host and guest control the formation of the complex. By careful design of the host, the host lattice can be made more selective towards specific kinds of guests. Host-guest chemistry undoubtedly will be explored further for more applications.

Table 29

STUDIES OF GUESTS BINDING TO THE HOST (MTU) IN A TWO-COMPONENT SYSTEM

Entry	Guest Mixture in Equal Molar Ratio	Guest Ratio in the Complexes
1	acetonitrile : nitromethane	1.6 : 1
2	DMF : acetonitrile	10 > : 1
3	DMF : acetamide	10 > : 1

EXPERIMENTAL

EXPERIMENTAL

General Procedures

NMR spectra (^{1}H and ^{13}C) were recorded on either a Bruker WM 250 MHz or a Varian T-60 Nuclear Magnetic Resonance Spectrometer using tetramethylsilane (TMS) as the internal standard. IR spectra were recorded on a Perkin-Elmer Model 167 and Model 599 spectrometer. Mass spectra were measured at 70 eV by Mr. Ernest Oliver and Mr. Rick Olsen using a Finnigan 4000 spectrometer with the INCOS data system. Melting points were determined using a MEL TEMP apparatus, or a Thomas Hoover Unimelt apparatus, and are uncorrected. Silica gel for chromatography was either 230-400 or 60-200 mesh. Analyses were performed by either Spang Microanalytical Laboratory, Eagle Harbor, Michigan or Guelph Chemical Laboratories, Ltd., Guelph Ontario, Canada.

1. N,N'-Bis(triphenylmethyl)urea 29

A suspension of 4 g (15.4 mmol) of trityl amine[62a] and 4.40 g (15.4 mmol) of trityl isocyanate[58] in 100 mL of t-butanol was heated at reflux for 24 h under argon. Vacuum removal of the solvent gave an oily residue which was triturated with ether to give 5.41 g (64.4%) of **29**. Recrystallization of the product from ethyl acetate gave white crystals; m.p. 260-261°C. (lit.[58] 252°C)

2. Tri(p-chlorophenyl)methylamine 31

Into a stirred solution of 0.5 g (1.31 mmol) of tri-(p-chlorophenyl)methyl chloride,[77] was bubbled anhydrous ammonia gas over 3 h. A 10% sodium hydroxide solution (100 mL) was added and the aqueous layer was extracted two times with methylene chloride. The combined organic layers were washed with water, saturated NaCl solution and dried over $MgSO_4$. Vacuum removal of the solvent gave crude product. Column chromatography of this crude product over silica gel, eluting with 7:3 methylene chloride/hexane gave 0.38 g (80%) of 31; m.p. 96-100°C; mass spectrum: m/e (relative intensity) 362 (M^+, 2), 361 (5), 347 (3), 345 (7), 252 (61), 250 (100), 140 (13), 139 (17), 138 (37), 111 (16); ^1H NMR ($CDCl_3$) : δ 2.22 (broad s, 2 H), 7.17 (dd, 12 H); IR (KBr) 3472, 3399 cm^{-1}.

3. Tri(p-t-butylphenyl)methylamine 33

In a procedure similar to that used for 31, 0.3 g (0.67 mmol) of tri(p-t-butylphenyl)methyl chloride[78] in 50 mL of dry methylene chloride was treated with anhydrous ammonia gas for 1.5 h to give 0.26 g (90.6%) of 33, m.p. 238-240°C; ^1H NMR ($CDCl_3$) : δ 1.30 (s, 27 H), 2.21 (broad s, 2 H), 7.22 (dd, 12 H); mass spectrum, m/e (relative intensity) 427 (M^+, 6), 411 (6), 295 (25), 294 (100); IR (KBr) 3447, 3285 cm^{-1}.

4. 5-Amino-5-phenyl-5H-dibenzo[a,d]cycloheptene 35

In a procedure similar to that used for 31, 0.7 g (2.31 mmol) of 5-chloro-5-phenyl-5H-dibenzo[a,d]cycloheptene[79] in

50 mL of dry methylene chloride was treated with ammonia for 1.5 h to give a crude product. Chromatography of this crude product over silica gel, eluting with 1:1 CH_2Cl_2/hexane gave 0.45 g (68.8%) of 35, m.p. 173-174° C (lit.[80] m.p. 170-171.5°C); ^1H NMR ($CDCl_3$) : δ 1.95 (broad s, 2 H), 6.47-6.53 (m, 2 H), 6.68 (s, 2 H), 6.96-7.09 (m, 3 H), 7.03-7.32 (m, 4 H), 7.45-7.52 (m, 2 H), 8.08 (d, 2 H); mass spectrum, m/e (relative intensity) 283 (M^+, 100), 282 (30), 267 (16), 254 (20), 206 (28), 178 (16), 105 (34), 104 (51), 77 (22); IR (KBr) 3451, 3391 cm^{-1}.

5. Tri(p-methoxyphenyl)methylamine 37

In a procedure similar to that used for 31, 3.7 g (10 mmol) of tri(p-methoxyphenyl)methyl chloride[81] in 150 mL of dry methylene chloride was treated with anhydrous ammonia gas for 3 h to give a crude product. Chromatography of this crude product over silica gel, eluting with 7:3 hexane/ethyl acetate gave 2.5 g (71.3%) of 37, m.p. 110-112°C. ^1H NMR ($CDCl_3$) : δ 2.19 (broad s, 2 H), 3.78 (s, 9 H), 6.97 (dd, 12 H); mass spectrum, m/e (relative intensity) 349 (M^+, 25), 334 (15), 333 (36), 318 (11), 243 (23), 242 (100), 134 (14); IR (KBr) 3374, 3300 cm^{-1}.

6. 2,7-Dihydrodinaphtho[2,1-c:1',2'-e] azepine 39[82]

A stirred solution of 6.3 g (14.3 mmol) of 2,2'-bisbromoethyl-1,1-dinaphthyl[83] in 200 mL of methylene chloride and 150 mL of methanol mixture was treated with

anhydrous ammonia gas for 3 h. A 10% sodium hydroxide solution (50 mL) was added and the organic layer was washed with water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Vacuum removal of the solvent gave an oily product. Chromatography of this oily product over silica gel, eluting with 7:3 ethyl acetate/methanol gave solid which was extracted with ether to give 2.2 g (52.1%) of **39** as white needles, m.p. 149-151°C. ^1H NMR ($CDCl_3$) : δ 2.41 (broad s, 1 H), 3.52 (d, 2 H, J=12.2 Hz), 3.85 (d, 2 H, J=12.2 Hz), 7.23-7.29 (m, 2 H), 7.43-7.49 (m, 4 H), 7.56-7.59 (m, 2 H), 7.92-7.98 (m, 4 H) ; ^{13}C NMR ($CDCl_3$) : δ 46.01, 126.37, 126.46, 127.28, 127.55, 128.46, 129.19, 129.69, 131.25, 133.96, 135.31; mass spectrum, m/e (relative intensity) 295 (M^+, 21), 294 (11), 267 (26), 266 (100), 265 (35), 252 (12); IR (KBr) 3335 cm^{-1}.

7. 5-Amino-5-phenyl-dibenzo[a,d][1,4]-cycloheptane **41**

Into a stirred solution of 8.3 g (30 mmol) of 5-phenyl-dibenzo[a,d][1,4]cycloheptadien-5-ol[84] in 150 mL of anhydrous ether, was bubbled dry hydrogen chloride gas for 1.5 h. Vacuum removal the of solvent gave a solid which was dissolved in 150 mL of methylene chloride. Into this stirred solution, was bubbled anhydrous ammonia over 3 h. Removal of the solvent under reduced pressure gave a residue. Chromatography of this residue over silica gel, eluting with 1:1 hexane/methylene chloride gave 5.3 g (64.1%) of **41**, m.p. 155-156.5°C. ^1H NMR ($CDCl_3$) : δ 2.01 (broad s, 2 H), 2.64-

2.91 (m, 4 H), 6.91-6.95 (m, 2 H), 7.05-7.09 (m, 2 H), 7.16-7.28 (m, 7 H), 7.91-7.94 (m, 2 H); mass spectrum, m/e (relative intensity) 285 (M^+, 70), 284 (56), 268 (27), 209 (15), 208 (100), 191 (19), 178 (15), 165 (16), 106 (30), 105 (49), 104 (50), 77 (26); IR (KBr) 3325, 3296 cm^{-1}.

8. Tri(p-tolyl)methyl isocyanate **43**

A suspension of 1.5 g (4.68 mmol) of tri(p-tolyl)methyl chloride[77] and 1.5 g (18.5 mmol) of potassium cyanate in 75 mL of dry acetone was refluxed for 1.5 h under argon. The resulting white precipitate was filtered and washed three times with acetone. The combined organic solvents were dried over anhydrous Na_2SO_4. Vacuum removal of the solvent gave 1.0 g (65.3%) of **43**, m.p. 125-129°C; Mass spectrum: m/e (relative intensity) 327 (M^+, 58), 312 (11), 286 (26), 285 (100), 237 (12), 236 (61), 211 (30), 182 (13), 178 (12), 119 (50), 91 (52); IR (KBr) 2262 cm^{-1}.

9. Tri(p-chlorophenyl)methyl isocyanate **44**

In a procedure similiar to that used for **43**, a suspension of 0.5 g (1.30 mmol) of tri(p-chlorophenyl)methyl chloride[77] and 0.5 g (6.16 mmol) of potassium cyanate in 50 mL of dry acetone was refluxed for 3 h to give 0.21 g (41.5%) of **44** as a semi-solid; Mass spectrum: m/e (relative intensity) 389 (38), 387 (M^+, 46), 345 (100); IR (neat) 2253 cm^{-1} .

10. Tri(p-t-butylphenyl)methyl isocyanate **45**

In a procedure similar to that used for **43**, a suspension of 2.5 g (5.6 mmol) of tri(p-t-butylphenyl)methyl chloride[78] and 2.5 g (3.07 mmol) of potassium cyanate in 100 mL of dry acetone was refluxed for 3 h to give 1.8 g (70.9%) of **45**, m.p.245-250^{o}C; mass spectrum, m/e (relative intensity) 453 (M^{+}, trace), 411 (13), 320 (6), 43 (100); ^{1}HNMR ($CDCl_3$) : δ 1.31(s, 27 H), 7.21 (dd, 12 H); IR (KBr) 2388 cm^{-1}.

11. 5-Phenyl-5H-dibenzo[a,d]cycloheptenyl-5-isocyanate **46**

In a procedure similar to that used for **43**, a suspension of 1 g (3.3 mmol) of 5-chloro-5-phenyl-5H-dibenzo[a,d]cycloheptene[79] and 1.2 g (14.8 mmol) of potassium isocyanate in 75 mL of dry acetone was refluxed for 3 h to give 0.7 g (68.5%) of **46** as a yellow solid, m.p. 107-117^{o}C; mass spectrum, m/e (relative intensity) 309 (M^{+}, 75), 284 (12), 267 (24), 232 (10), 178 (42), 43 (100); IR (KBr) 2342 cm^{-1}

12. 9-Phenyl-9-fluorenyl isocyanate **48**

In a procedure similar to that used for **43**, a suspension of 1 g (6.68 mmol) of silver isocyanate[85] and 1.9 g (6.67 mmol) of 9-chloro-9-phenyl fluorene[86] in 100 mL of anhydrous acetone was refluxed for 3 h to give 1.71 g (90%) of **48** as a yellow oily material; mass spectrum, m/e (relative intensity) 283 (M^{+}, 82), 242 (22), 241 (100), 206 (20), 181 (12); IR (neat) 2241 cm^{-1}.

13. Phenyl-p-tolylmethyl isocyanate **50**

To a stirred solution of phenyl-p-tolylmethylamine[87] (0.9 g, 4.57 mmol) in 75 mL of dry toluene under argon atmosphere, was added 0.90 g (9.14 mmol) of phosgene in 15 mL of dry toluene over 10 min. After being stirred for 8 h at room temperature, the reaction mixture was maintained at 50°C for an additional 2 h. Vacuum removal of the solvent gave 0.86 g (84.4%) of **50** as an oily material; mass spectrum, m/e (relative intensity) 223 (M^+, 100), 208 (68), 194 (24), 181 (79), 180 (22), 166 (31), 165 (41), 146 (31), 91 (33), 77 (34); IR (neat) 2248 cm^{-1}.

14 . Phenyl-m-tolylmethyl isocyanate **52**

In a procedure similar to that used for **50**, reaction of 0.25 g (1.27 mmol) phenyl-m-tolylmethylamine[87] in 25 mL of dry toluene with 0.25 g (2.45 mmol) of phosgene in 10 mL of dry toluene gave 0.25 g (88.3%) of **52** as an oily material; mass spectrum, m/e (relative intensity) 223 (M^+, 100), 194 (13), 181 (46), 180 (20), 166 (20), 165 (27), 146 (15), 91 (20), 77 (21); IR (neat) 2253 cm^{-1}.

15. Phenyl-o-tolylmethyl isocyanate **54**

In a procedure similar to that used for **50**, reaction of phenyl-o-tolylmethylamine[87] (0.67 g, 3.4 mmol) in 75 mL of dry toluene with 0.67 g (6.8 mmol) of phosgene in 15 mL of toluene gave 0.71 g (93.6%) of **54** as an oily material; mass

spectrum, m/e (relative intensity) 223 (M^+, 15), 208 (22), 194 (10), 181 (40), 180 (100), 179 (32), 165 (37), 146 (18), 91 (25), 77 (34); IR (neat) 2252 cm^{-1}.

16. Isocyanate of Dehydroabietylamine 58[64a]

In a procedure similar to that used for 50, reaction of 1.7 g (5.95 mmol) of dehydroabietylamine[88] in 50 mL of dry toluene with 1.18 g (11.9 mmol) of phosgene in 30 mL dry toluene gave 1.7 g (11.9 mmol) of 58 as an oily material; mass spectrum, m/e (relative intensity) 311 (M^+, 4), 296 (20), 223 (10), 92 (66), 91 (100); IR (neat) 2264 cm^{-1}.

17. 4,4',4''-Triphenyl-1-butanoyl chloride 60

4,4',4''-Triphenyl-1-butanoic acid[89] (0.175 g, 0.55 mmol) in 5 mL of thionyl choride was refluxed for an hour. Vacuum removal of the solvent gave 0.14 g (75.5%) of 60 as a semi-solid. ^1H NMR ($CDCl_3$) : δ 2.71 (t, 2 H), 3.01 (t, 2 H), 7.19-7.33 (m, 15 H); mass spectrum, m/e (relative intensity) 334 (M^+, 1), 299 (2), 243 (100), 165 (36); IR (neat) 1796 cm^{-1}.

18. N,N'-Bis[tri(4-biphenyl)methyl]urea 61

The solution of 4.88 g (9.63 mmol) of tri(4-biphenyl)methyl chloride[90] and 0.25 g (4.16 mmol) of urea in 200 mL of dry pyridine was refluxed for 10 h. The reaction was quenched with 500 mL of 10 % dilute hydrochloric acid and extracted three times with 100 mL of methylene chloride.

The combined organic solvents were washed twice with 50 mL of 10% dilute hydrochloric acid, water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Vacuum removal of the solvent gave 1.6 g (38.4%) of **61** which was recrystallized from acetone; m.p. 277-278°C; ^{1}H NMR ($CDCl_3$) : δ 5.67 (s, 2 H), 7.25-7.55 (m, 54 H); ^{13}C NMR (DMSO-d_6) : δ 68.26, 125.54, 126.36, 127.24, 128.77, 129.01, 137.89, 139.48, 144.71, 155.88; mass spectrum, m/e (relative intensity) 513 (M^+ -487, 12), 487 (12), 471 (54), 334 (100); IR (KBr) 3412, 1671 cm^{-1}. Anal. Calcd. for $C_{75}H_{56}N_2O$: C, 89.97; H,5.64. Found: C, 89.98; H, 5.82

19. N,N'-Bis[tri(p-methylphenyl)methyl]urea **65**

In a procedure similar to that used for **29**, reaction of 0.9 g (2.75 mmol) of **43** and 0.8 g (2.66 mmol) of tri(p-methylphenyl)methylamine[91] in 50 mL of t-butanol was refluxed for 36 h. Vacuum removal of the solvent gave an oily residue. Trituration of the residue with ether gave a solid product, **65**; m.p. 220-227°C. Recrystallization of the crude product from acetonitrile gave 0.71 g (41.9%) white crystals, m.p. 229-230°C (dec); ^{1}H NMR ($CDCl_3$) : δ 2.29 (s, 18 H), 5.36 (s, 2 H), 6.99-7.02 (m, 24 H), ^{13}C NMR ($CDCl_3$) : δ 20.93, 69.29, 128.55 (overlap), 136.34, 141.93, 155.86; mass spectrum (30 eV), m/e (relative intensity) 628 (M^+, trace), 344 (30), 343 (100), 285 (40), 210 (45); IR (KBr) 3419, 1666 cm^{-1}. Anal. Calcd. for $C_{45}H_{44}N_2O$: C, 85.95; H, 7.05. Found: C, 86.01; H, 7.14

20. N,N'-Bis[tri-(p-chlorophenyl)methyl]urea **66**

In a procedure similar to that used for **29**, reaction of **44** (0.2 g, 0.51 mmol) with **31** (0.2 g, 0.55 mmol) in 35 mL of t-butanol was refluxed for 8 h to give 0.15 g (38.9%) of **66**, which was recrystallized from acetone; m.p. 267-269°C (dec); ^{1}H NMR ($CDCl_3$) : δ 5.51 (s, 2 H), 6.94 (d, 12 H, J=8.5 Hz), 7.20 (d, 12 H, J=8.5 Hz) ; ^{13}C NMR ($CDCl_3$) : δ 68.89, 128.29, 129.79, 133.41, 142.38, 155.53; mass spectrum (30 eV), m/e (relative instensity) 405 (M^+-343, 35), 403 (40), 347 (37), 345 (33), 278 (19), 276 (29), 252 (55), 250 (100), 139 (31), 138 (28), 111 (13); IR (KBr) 3395, 1632 cm^{-1}. Anal. Cald. for $C_{39}H_{26}N_2OCl_6.C_3H_6O$(acetone) Found: C, 62.32; H, 3.98. Found: C, ; H,

21. N,N'-Bis(9-phenyl-9-fluorenyl)urea **68**

In a procedure similar to that used for **29**, reaction of **48** (2.5 g, 8.83 mmol) with 9-amino-9-phenyl fluorene[86] (1.95 g, 7.58 mmol) in 100 mL of t-butanol was refluxed for 8 h to give crude product. Column chromatography of this crude product over silica gel, eluting with 7:3 methylene chloride/hexane gave a 2.47 g (60.3%) of **68**; m.p. 253-254°C; ^{1}H NMR ($CDCl_3$) : δ 5.14 (s, 2 H), 6.91-6.94 (m, 4 H), 7.08-7.33 (m, 18 H), 7.54-7.57 (d, 2 H); ^{13}C NMR ($CDCl_3$) : δ 69.53, 120.05, 125.08, 125.17, 127.22, 128.14, 128.37, 128.54, 139.46, 142.57, 148.49, 156.51; mass spectrum, m/e (relative intensity) 540 (M^+, 5), 299 (50), 283 (18), 257

(10), 256 (13), 241 (54), 239 (29), 180 (100), 119 (17), 91 (18); IR (KBr) 3346, 1666 cm^{-1}. Anal. Calcd. for $C_{39}H_{28}N_2O$: C, 86.64; H, 5.22. Found: C, 86.56; H, 5.30

22. N-Tri(p-methoxyphenyl)methyl- N'-triphenylmethyl urea 69

In a procedure similar to that used for 29, reaction of trityl isocyanate[58] (2 g, 7.02 mmol) with 37 (1.5 g, 4.29 mmol) in 60 mL of t-butanol was refluxed for 10 h to give 2.3 g (84.5%) of 69 which was recrystallized from ethyl acetate; m.p. 215-216.5°C; ^1H NMR ($CDCl_3$) : δ 3.76 (s, 9 H), 5.37 (s, 1 H), 5.46 (s, 1 H), 6.72 (d, 6 H), 6.96-7.23 (m, 21 H); ^{13}C NMR ($CDCl_3$) : δ 55.15, 68.68, 69.91, 113.17, 126.81, 127.78, 128.66, 129.75, 137.13, 144.66, 155.71, 158.27; mass spectrum, m/e (relative intensity) 634 (M^+, 2), 392 (21), 391 (83), 334 (27), 333 (100), 302 (13), 243 (19), 242 (39), 208 (12), 182 (30); IR (KBr) 3417, 3346, 1661 cm^{-1}. Anal. Calcd. for $C_{42}H_{38}N_2O_4$: C,79.47; H, 6.03. Found: C, 79.55; H, 6.23

23. N-9-phenyl-9-fluorenyl- N'-triphenylmethyl urea 70

In a procedure similar to that used for 29, reaction of 9-amino-9-phenylflourene[86] (0.45 g, 1.76 mmol) with 0.5 g (1.75 mmol) of trityl isocyanate[58] in 100 mL of t-butanol was refluxed for 12 h to give 0.542 g (57.2%) of 70 which was recrystallized from acetone; m.p. 235-237°C; ^1H NMR ($CDCl_3$) : δ 5.34 (s, 2 H), 6.87 (m, 6 H), 7.12-7.55 (m,

22H); ^{13}C NMR ($CDCL_3$) : δ 69.60, 126.68, 127.53, 127.74, 128.41, 128.50, 128.59, 128.83, 139.50, 142.97, 144.62, 148.47, 155.97 (one peak overlaps with other peaks); mass spectrum, m/e (relative intensity) 542 (M^+, 3), 302 (20), 301 (100), 299 (19), 243 (14), 241 (35), 182 (54), 180 (19), 104 (44); IR (KBr) 3411, 3204, 1668 cm^{-1}. Anal. Calcd. for $C_{39}H_{30}N_2O$: C, 86.32; H, 5.57. Found: C, 86.44; H, 5.54

24. N-[2,7-Dihydrodinaphtho(2,1-c:1',2'-e) azepenyl]- N'-triphenylmethyl urea 71

In a procedure similar to that used for 29, reaction of 39 (2.4 g, 8.14 mmol) with trityl isocyanate (3 g, 10.5 mmol) in 150 mL of t-butanol was refluxed for 4 days to give a solid. Column chromatography of this solid over silica gel, eluting with 7:3 methylene chloride/hexane gave 2.45 g (52.5%) of 71 which was recrystallized from chloroform/ethanol; m.p. 263-265^oC (dec); ^1H NMR ($CDCl_3$) : δ 3.72 (d, 2 H), 4.83 (d, 2 H), 5.71 (s, 1 H), 7.23-7.28 (m, 17 H), 7.44-7.52 (m, 4 H), 7.58-7.61 (d, 2 H), 7.95-8.00 (m, 4 H); ^{13}C NMR ($CDCl_3$) : δ 48.36, 70.18, 125.84, 126.08, 126.75, 127.40, 127.84, 128.34, 128.66, 129.19, 131.40, 133.34 (overlap), 134.87, 145.54, 155.89 (one peak overlaps with other peaks); mass spectrum, m/e (relative intensity) 337 (M^+-243, trace), 295 (13), 285 (27), 267 (17), 266 (22), 265 (20), 243 (29), 208 (100), 165 (34), 105 (15), 77 (50) ; IR (KBr) 3418, 1668 cm^{-1}. Anal. Calcd. for $C_{42}H_{32}N_2O$: C, 86.87; H, 5.55. Found: C, 86.79; H, 5.52

25. N,N'-Bis(diphenylmethyl)urea **74**

To a suspension of 1.5 g (5.9 mmol) of diphenylmethylamine hydochloride in 100 mL of methylene chloride under argon atmosphere, was added 0.6 g (5.91 mmol) of triethylamine. The solution was stirred for 10 min. To this solution, was added 1.33 g (5.46 mmol) of diphenylmethyl isocyanate in 100 mL of methylene cholride dropwise. After being stirred for 10 h, the solution was washed twice with 50 mL of 10% dilute hydrochloric acid, water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Vacuum removal of the solvent gave 2.05 g (95.7%) of **74** which was recrystallized from acetone; m.p. 272-273°C (dec). (lit[92] 272-273°C); ^1H NMR ($CDCl_3$) : δ 4.98 (d, 2 H), 5.92 (d, 2 H), 7.15-7.32 (m, 18 H); ^{13}C NMR (DMSO-d_6) : δ 56.90, 126.72 (overlap), 128.33, 143.53, 156.27; mass spectrum, m/e (relative intensity) 392 (M^+, 29.2), 225 (34), 183 (14), 182 (100), 167 (26), 152 (14), 106 (16), 104 (33), 77 (20); IR (KBr) 3317, 1630 cm^{-1}.

26. N,N'-Bis[(phenyl-p-tolyl)methyl]urea **75**

In a procedure similar to that used for **74**, reaction of (phenyl-p-tolyl)methylamine hydrochloride[87] (2.3 g, 9.85 mmol) with triethylamine (1.0 g, 9.85 mmol) in 100 mL of anhydrous methylene chloride and 2 g (8.96 mmol) of **50** in 25 mL of anhydrous methylene chloride gave 3.45 g (91.7%) of **75** which was recrystallized from acetone; m.p. 261-262°C; ^1H NMR ($CDCl_3$): δ 2.31 (s, 6 H), 4.98 (d, 2 H), 5.86 (d, 2 H),

7.01-7.29 (m, 18H); ^{13}C NMR (DMSO-d_6) : δ 20.50, 56.58, 126.66 (overlap), 128.27, 128.86, 135.80, 140.56, 143.77, 156.27; mass spectrum, m/e (relative intensity) 420 (M^+, 19), 239 (47), 197 (18), 196 (100), 181 (21), 166 (18), 165 (24), 120 (17), 118 (12), 106 (12), 104 (29), 91 (17), 77 (13); IR (KBr) 3307, 1631 cm^{-1}. Anal. Calcd. for $C_{29}H_{28}N_2O$: C, 82.82; H, 6.71. Found: C, 82.95; H, 6.75

27. N,N'-Bis[(phenyl-m-tolyl)methyl]urea 76

In a procedure similar that used for 74, reaction of (phenyl-m-tolyl)methylamine hydrochloride[87] (1.6 g, 6.85 mmol) with triethylamine (0.69 g, 6.85 mmol) in 25 mL of dry methylene chloride and 1.6 g (7.17 mmol) of 52 gave 2.2 g (76.4%) of 76 which was recrystallized from methanol; m.p. 251-252°C; ^1H NMR ($CDCl_3$) : δ 2.28 (s, 6 H), 5.00 (d, 2 H), 5.86 (d, 2 H), 6.93-7.28 (m,18H); ^{13}C NMR (DMSO-d_6) : δ 21.00, 56.88, 123.89, 126.72, 127.30, 127.36, 128.25 (overlap), 128.30, 137.42, 143.45, 143.65, 156.27; mass spectrum, m/e (relative intensity) 420 (M^+, 22), 239 (36), 197 (15), 196 (100), 181 (16), 166 (19), 165 (17), 104 (19), 91 (15), 77 (12); IR (KBr) 3330, 1630 cm^{-1}. Anal. Calcd. for $C_{29}H_{28}N_2O$: C, 82.82; H, 6.71. Found: C, 82.67; H, 6.69

28. N,N'-Bis[(phenyl-o-tolyl)methyl]urea 77

In a procedure similar to that used for 74, reaction of (phenyl-o-tolyl)methylamine hydrochloride[87] (2.0 g, 8.56 mmol) with triethylamine (0.87 g, 8.58 mmol) in 100 mL of

anhydrous methylene chloride and 1.27 g (5.7 mmol) of **54** in 25 mL of dry methylene chloride gave 2.62 g (72.8%) of **77** which was recrystallized from acetone; m.p. 266-267°C (dec); ^{1}H NMR ($CDCl_3$) : δ 2.25 (s, 6 H), 4.83 (d, 2 H), 6.13 (d, 2 H), 7.03-7.31 (m, 18 H); ^{13}C NMR (DMSO-d_6) : δ 18.92, 53.61, 125.92, 126.48, 126.78, 126.98, 128.27, 130.27, 135.19, 141.45, 142.65, 156.21; mass spectrum, m/e (relative intensity) 420 (M^+, 24), 239 (21), 197 (15), 196 (100), 181 (26), 180 (28), 179 (21), 166 (20), 165 (25), 120 (19), 106 (27), 104 (33), 91 (22); IR (KBr) 3332, 1637 cm^{-1}. Anal. Calcd. for $C_{29}H_{28}N_2O$: C, 82.82; C, 6.71. Found: C, 82.72; H, 6.79

29. N-2,2,2-Triphenylethyl-N'-triphenylmethyl urea **78**

In a procedure similar to that used for **74**, reaction of 2,2,2-triphenylethylamine hydrochloride[93] (1.5 g, 4.84 mmol) with triethylamine (1.45 g, 1.42 mmol) in 100 mL of dry methylene chloride and 1.38 g (4.84 mmol) of trityl isocyanate in 100 mL of dry methylene chloride gave 2.03 g (75.2%) of **78** which was recrystallized from ethyl acetate; m.p. 225-226.5°C; ^{1}H NMR ($CDCl_3$) : δ 3.89 (t, 1 H), 4.18 (d, 2 H), 5.74 (s, 1 H), 6.95-71.4 (m, 30 H); ^{13}C NMR ($CDCl_3$) : δ 48.96, 56.66, 69.07, 126.15, 127.06, 128.03, 128.18, 128.44, 129.09, 143.94, 145.23, 156.97; mass spectrum, m/e (relative intensity) 558 (M^+, 1), 315 (16), 285 (1), 243 (100), 165 (41); IR (KBr) 3415, 3203, 1644 cm^{-1}. Anal. Calcd. for $C_{40}H_{34}N_2O.C_3H_6O$: C, 85.82; H, 6.53. Found: C, 85.79; H, 6.68

30. N,N'-Bis(2,2,2-triphenylethyl)urea 79[64b]

In a procedure similar to that used for 74, reaction of β-triphenylethylamine hydrochloride (0.412 g, 1.33 mmol) with triethylamine (0.135 g 1.34 mmol) in 100 mL of dry methylene chloride and 0.3 g (1.00 mmol) of β-triphenylethyl isocyanate in 25 mL dry methylene chloride gave 0.45 g (78.6%) of 79 which was recrystallized from methanol; m.p. 240-241°C (lit.[93] 218.5-219°C) ^{1}H NMR ($CDCl_3$) : δ 3.75 (t, 2 H), 4.21 (d, 4 H), 7.13-7.29 (m, 30 H); ^{13}C NMR ($CDCl_3$) : δ 49.11, 56.99, 126.56, 128.24, 129.15, 145.23, 156.85; mass spectrum, m/e (relative intensity) 572 (M^+, 26), 329 (8), 300 (1), 272 (1), 256 (13), 244 (20), 243 (100), 179 (13), 178 (12), 165 (61); IR (KBr) 3314, 1640 cm^{-1}. Anal. Calcd. for $C_{41}H_{36}N_2O$: C, 85.98; H, 6.34. Found : C, ; H,

31. N-Triphenylmethyl-N'-9-triptycylmethyl urea 80

In a procedure similar to that used for 74, reaction of 9-triptycene-methylamine hydrochloride[93] (0.62 g, 1.94 mmol) with triethylamine (0.363 g, 3.58 mmol) in 100 mL of dry methylene chloride and 0.5 g (1.75 mmol) of trityl isocyanate in 25 mL of anhydrous methylene cholride gave 0.8 g (80.3%) of 80 which was recrystallized from ethyl acetate; m.p. 264-266°C (dec); ^{1}H NMR ($CDCl_3$) : δ 4.71 (s, 3 H), 5.24 (s, 1 H), 5.89 (broad s, 1 H), 6.77-7.30 (m, 27 H); ^{13}C NMR ($CDCl_3$) : δ 38.61, 52.66, 54.22, 69.66, 122.10, 123.29, 124.94, 125.09, 127.26, 128.12, 128.56, 143.99, 146.33

157.49 (one peak overlaps with other peaks); mass spectrum, m/e (relative intensity) 568 (M^+, 23), 265 (13), 252 (22), 243 (29), 182 (100), 165 (61); IR (KBr) 3437, 3320, 1656 cm^{-1}. Anal. Calcd. for $C_{41}H_{32}N_2O$: C, 86.59; H, 5.67. Found: C, 86.77; H, 5.62

32. N,N'-Bis(dehydroabietyl)urea **81**

To a stirred solution of 1.8 g (5.79 mmol) of **58** in 50 mL of dry methylene chloride under argon atmosphere, was added dropwise of 2.0 g (7.02 mmol) of dehydroabietylamine in 50 mL of dry methylene chloride. The solution was stirred at room temperature for 8 h. Vacuum removal of the solvent gave an oily liquid which was triturated with ether to give 2.23 g (64.7%) of **81**. Recrystallization of **81** from acetone gave needles ; m.p. 169-171^{o}C; ^{1}H NMR ($CDCl_3$) : δ 0.85 (s, 6 H), 1.18-1.41 (m, 26 H), 1.54-1.85 (m, 8 H), 2.21-2.26 (m, 8 H), 2.72-2.91 (m, 6 H), 3.01-3.04 (d, 4 H), 4.36 (t, 2 H), 6.87 (m, 2 H), 6.94-6.97 (m, 2 H), 7.13-7.36 (m, 2 H); ^{13}C NMR ($CDCl_3$) : δ 18.60, 18.78, 23.95, 25.18, 30.07, 33.42, 36.01, 37.42, 38.36, 44.89, 50.65, 123.75, 124.10, 126.81, 134.81, 145.51, 147.33, 158.45 (3 peaks overlap with other peaks); mass spectrum, m/e (relative intensity) 596 (M^+, 3), 239 (11), 173 (37), 131 (11), 88 (100); IR (KBr) 3460, 1633 cm^{-1}. Anal. Calcd. for $C_{41}H_{60}N_2O$: C, 82.50; H, 10.13. Found : C, 82.55; H, 9,98

33. N-Diphenylmethyl- N'-triphenylmethyl urea 82

In a procedure similar to that used 74, reaction of 1 g (4.56 mmol) of diphenylmethylamine hydrochloride in 50 mL of methylene chloride with 0.47 g (4.58 mmol) of triethylamine and 1.1 g (3.86 mmol) of trityl isocyanate in 25 mL of dry methylene chloride gave 1.45 g (69.7%) of 82 which was recrystallized from ethyl acetate; m.p. 240-241°C (lit.[94] 226-227°C); ^{1}H NMR ($CDCl_3$) : δ 4.73 (d, 1 H), 5.79 (s, 1 H), 5.95 (d, 1 H), 6.79-7.33 (m, 25 H); ^{13}C NMR ($CDCl_3$) : δ 57.83, 69.65, 126.93, 127.16, 127.37, 128.25, 128.72, 142.07, 144.43, 156.54; mass spectrum, m/e (relative intensity) 468 (M^+, 2), 301 (18), 225 (49), 182 (100), 106 (29), 105 (22), 77 (66). Anal. Calcd. for $C_{33}H_{28}N_2O$: C, 84.58; H, 6.02

34. N,N'-Bis[tri(p-t-butylphenyl)methyl]urea 83

To a stirred solution of 33 in 25 mL of dry THF at -78°C under argon atmosphere, was added n-butyllithium (0.84 mmol) in 20 mL of THF. The solution was stirred at -78°C for additional 10 min. To this solution, was added 45 (0.4 g, 0.88 mmol) in 10 mL dry THF over 10 min. After being stirred for 1 h, the solution was allowed to warm to room temperature and stirred for an additional 2 h. Vacuum removal of the solvent gave a residue which was tritruated with ether to yield 0.42 g (58.2%) of 83. Recrystallization of 83 from $CH_3OH/CHCl_3$ mixture gave white crystals; m.p. 272-273°C; ^{1}H NMR ($CDCl_3$) : δ 1.28 (s, 27H), 5.44 (s, 2 H),

6.85-7.07 (m, 12 H), 7.15 (m, 12 H); ^{13}C NMR ($CDCl_3$) : δ 31.31, 34.30, 69.23, 124.52, 128.40, 141.93, 149.28, 155.92; mass spectrum, m/e (relative intensity) 880 (M^+, trace), 469 (71), 411 (26), 294 (49), 57 (100); IR (KBr) 3407, 1702 cm^{-1}. Anal. Calcd. for $C_{63}H_{80}N_2O$: C, 85.94; H, 9.16. Found : C, ; H,

35. N,N'-Bis(5-phenyl-dibenzo[a,d]-5-cycloheptenyl)urea 84

In a procedure similar to that used for 83, reaction of 35 (1.83 g, 6.46 mmol) with n-butyllithium (6.75 mmol) in 50 mL of dry THF and 46 (1.42 g, 4.59 mmol) in 50 mL of dry THF gave a crude product mixture. Column chromatography of this crude mixture over silica gel, eluting with methylene chloride gave 1.15 g (42.2%) of 84 which was recrystallized from toluene; m.p. 266-268^oC; ^1H NMR ($CDCl_3$) : δ 5.96 (broad s, 2 H), 6.61 (m, 8 H), 6.95 (m, 6 H), 7.26 (m, 16 H); ^{13}C NMR ($CDCl_3$) : δ 67.83, 124.55, 126.56, 126.70, 127.97, 128.50, 129.26, 129.38, 131.56, 134.11, 139.50, 142.47 (overlap), 156.35; mass spectrum, m/e (relative intensity) 592 (M^+, 1), 325 (16), 310 (14), 309 (59), 284 (22), 283 (100), 282 (18), 268 (22), 267 (94), 254 (21), 232 (16), 206 (41), 179 (13), 178 (46), 105 (38), 104 (41); IR (KBr) 3419, 1667 cm^{-1}. Anal. Calcd. for $C_{43}H_{32}N_2O.2(C_3H_7NO)$: C, 79.65; H, 6.27. Found: C, 79.79; H, 6.34

36. N-5-Phenyl-dibenzo[a,d]-5-cycloheptenyl- N'-triphenylmethyl urea 85

In a procedure similar to that used for 83, reaction of 35 (0.98 g, 3.46 mmol) with n-butyllithium (3.64 mmol) in 50 mL of dry THF and trityl isocyanate (1.1 g, 3.86 mmol) in 20 mL of dry THF gave a crude product. Column chromatography of this crude product over silica gel, eluting with 9:1 hexane/ethyl acetate gave 1.06 g (53.7%) of 85; m.p. 238-240°C; ^{1}H NMR ($CDCl_3$) : δ 5.46 (broad s, 1 H), 5.58 (broad s, 1 H), 6.44-6.66 (m, 4 H), 6.87-7.36 (m, 26 H); ^{13}C NMR ($CDCl_3$) : δ 69.94, 70.18, 123.87, 126.28, 126.99, 127.19, 127.93, 128.11, 128.76 (overlap), 129.05 (overlap), 131.40, 133.78, 139.22, 144.43, 155.96; mass spectrum, (CI) m/e (relative intensity) 569 (M^++1, 18), 267 (99), 243 (100); IR (KBr) 3416 (overlap NH), 1671 cm^{-1} . Anal. Calcd. for $C_{41}H_{32}N_2O.C_4H_{10}O$: C, 84.08; H, 6.59. Found: C, 83.86; H, 6.75

37. N-(5-Phenyl-dibenzo[a,d][1,4]-5-cycloheptanyl)-N'-triphenyl methylurea 86

In a procedure similar to that used for 83, reaction of 41 (0.2 g, 0.70 mmol) with n-butyllithium (0.75 mmol) in 25 mL of dry THF and triphenylmethyl isocyanate (0.3 g, 1.05 mmol) in 10 mL of dry THF gave a crude mixture. Column chromatography of this crude mixture over silica gel, eluting with 8.5:1.5 hexane/ethyl acetate gave 0.12 g (30%) of 86; m.p. 225-227°C; ^{1}H NMR ($CDCl_3$) : δ 2.65-2.75 (m, 2

H), 2.92-3.02 (m, 2 H), 5.29 (s, 1 H), 5.36 (s, 1 H), 6.85 (m, 8 H), 7.02-7.31 (m, 18 H), 7.88 (m, 2 H); ^{13}C NMR (CDCl3) : δ 34.77, 69.79, 70.85, 126.37, 126.52, 127.25, 127.55, 127.99, 128.08, 128.52, 130.55, 130.59, 140.46, 142.10, 144.78, 147.25, 155.13 (one peak overlaps with other peaks) ; mass spectrum, m/e (relative intensity) 570 (M^+, 1), 327 (40), 302 (23), 301 (100), 243 (12), 182 (48), 165 (23); IR (KBr) 3429, 3227, 1668 cm^{-1}. Anal. Calcd. for $C_{41}H_{34}N_2O$: C, 84.04; H, 6.41. Found: C, 84.15; H, 6.42

38. N-Triphenylmethylurea **87**[58]

Into a stirred solution of 4 g (14.0 mmol) of trityl isocyanate in 100 mL of dry methylene chloride, was bubbled anhydrous ammonia gas for 3 h. Vacuum removal of the solvent gave 3.85 g (91.2%) of **87**. Recrystallization of the crude product from ethyl acetate gave white crystals; m.p. 251-252°C. (lit.[58] 242°C)

39. N-Tri(p-tolyl)methylurea **88**

In a procedure similar to that used for **87**, treatment of **43** (0.36 g, 1.1 mmol) in 50 mL of dry methylene chloride with anhydrous ammonia gas for 3 h gave 0.37 g (97.8%) of **88**, which was recrystallized from acetonitrile; m.p. 235-236°C; ^1H NMR ($CDCl_3$) : δ 2.33 (s, 9 H), 4.16 (s, 2 H), 5.78 (s, 1 H), 7.09-7.18 (m, 12 H); ^{13}C NMR (DMSO-d_6) : δ 20.42, 67.76, 127.80, 128.30, 134.98, 143.42, 157.56; mass spectrum, m/e (relative intensity) 344 (M^+, 23), 285 (23),

210 (72), 118 (100); IR (KBr) 3423, 3398, 1654 cm^{-1}. Anal. Calcd. for $3(C_{23}H_{24}N_2O).C_3H_6O$(acetone) : C, 79.23; H, 7.20. Found : C, 79.14; H, 7.28

40. N-Tri(p-t-butylphenyl)methylurea 89

In a procedure similar to that used for 87, treatment of 45 (0.92 g, 2.03 mmol) with ammonia gas in 50 mL of dry methylene chloride gave 0.82 g (85.9%) of 89 which was recrystallized from acetone; m.p. 252-254°C; ^1H NMR ($CDCl_3$) : δ 1.29 (s, 27 H), 4.19 (s, 2 H), 5.85 (s, 1 H), 7.25 (dd, 12 H); ^{13}C NMR ($CDCl_3$) : δ 31.25, 34.42, 69.12, 124.99, 128.34, 141.57, 149.98, 158.57; mass spectrum, m/e (relative intensity) 470 (M^+, 4), 453 (2), 411 (27), 294 (100), 104 (100); IR (KBr) 3477, 3350, 1655 cm^{-1}. Anal. Calcd. for $C_{32}H_{42}N_2O$: C, 81.65; H, 8.99. Found: C, 81.70; H, 8.99

41. N-Dehydroabietylurea 90

In a procedure similar to that used for 87, treatment of 58 with anhydrous ammonia gas in 100 mL of dry methylene chloride gave 4.1 g (97.2%) of 90 which was recrystallized from acetone; m.p. 190-191°C; ^1H NMR ($CDCl_3$) : δ 0.91 (s, 3 H), 1.20-1.46 (m, 13 H), 1.59-1.88 (m, 4 H), 2.24-2.29 (m, 1 H), 2.76-3.13 (m, 5 H), 4.40 (s, 2 H), 4.78 (t, 1 H), 6.88 (s, 1 H), 6.96-6.99 (m, 1 H), 7.14-7.18 (m, 1 H); ^{13}C NMR ($CDCl_3$) : δ 18.60, 18.83, 23.95, 25.18, 30.07, 33.36, 35.95, 37.36, 38.36, 45.01, 50.77, 123.75, 124.16, 126.81, 134.80, 145.51, 147.21, 159.50 (3 peaks overlap with other

peaks); mass spectrum, m/e (relative intensity) 328 (M^+, 4), 173 (36), 74 (100); IR (KBr) 3472, 3337, 1632 cm^{-1}. Anal. Calcd. for $C_{21}H_{32}N_2O$: C, 76.78; H, 9.82. Found : C, 76.87; H, 9.62

42. N-9-Triptycyl urea 91

Into a solution of 9-triptycyl isocyanate[65] (0.65 g, 2.20 mmol) in 50 mL of dry methylene chloride, was bubbled anhydrous ammonia gas for 1.5 h. The white precipitate 0.65 g (94.5%) of 91 was filtered and recrystallized from ethanol; m.p.314-315^oC. ^1H NMR (DMSO-d_6) : δ 5.59 (s, 1 H), 6.24 (s, 3 H), 6.98-7.02 (m, 6 H), 7.36-7.48 (m, 6 H); ^{13}C NMR (DMSO-d_6) : δ 52.06, 65.73, 121.86, 123.13, 124.13, 124.86, 144.33, 144.45, 157.92; mass spectrum, m/e (relative intensity) 312 (M^+, 21), 295 (7), 268 (29), 267 (31), 252 (100), 165 (14); IR (KBr) 3601, 3333, 1649 cm^{-1}. Anal. Calcd. for $C_{21}H_{16}N_2O$: C, 80.75, H, 5.16. Found: C, 80.60, H, 5.25

43. N,N'-Ditrityl malonamide 93

To a stirred solution of 2.59 g (10 mmol) of triphenylmethylamine[91] in 10 mL of dry toluene under argon, was added dropwise 0.26 g (1.85 mmol) of malonyl chloride in 20 mL of dry toluene. The solution was stirred for 10 min. To this solution was added 1.01 g (10 mmol) of triethylamine. The solution was allowed to reflux for an additional 10 h. The precipitate of the reaction mixtures

was filtered, and the solvent was removed under reduced pressure to give a solid residue which was extracted three times with methylene chloride. The combined organic solvents were washed twice with 100 mL of 10% dilute hydrochloric acid, water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Vacuum removal of the solvent gave 0.42 g of **93**. Recrystallization of crude **93** from acetone gave 0.35 g (32%) of white needles; m.p. 293-294°C (lit.[95], 302°C); ^1H NMR ($CDCl_3$) : δ 3.28 (s, 2 H), 7.11-7.35 (m, 30 H), 7.74 (s, 2 H); ^{13}C NMR ($CDCl_3$) : δ 46.43, 70.72, 127.06, 127.97, 128.58, 144.23, 166.05; mass spectrum, m/e (relative intensity) 586 (M^+, 21), 343 (88), 243 (88), 182 (47), 165 (100), 104 (53), 77 (60), 50 (42), 40 (82); IR (KBr) 3365, 3300, 1665 cm^{-1}.

44. N,N'-Ditrityl-2-methylmalonamide **95**

In a procedure similar to that used for **93**, reaction of 1.847 g (7.13 mmol) of triphenylmethylamine[91] in 100 mL of toluene with 0.05 g (3.5 mmol) of 2-methylmalonyl chloride[96] in 10 mL of dry toluene and 1.44 g (14.26 mmol) of triethylamine gave crude **95**. Recrystallization of the crude product from acetonitrile gave 1.06 g (48.8%) of white needles, m.p. 299-300°C (dec); ^1H NMR ($CDCl_3$) : δ 1.49 (d, 3 H), 3.10 (q, 1 H), 7.14-7.28 (m, 30 H), 7.63 (s, 2 H); ^{13}C NMR ($CDCl_3$) : δ 17.03, 51.02, 70.42, 127.03, 127.97, 128.53, 144.32, 169.99; mass spectrum, m/e (relative intensity) 600 (M^+, 16), 357 (63), 243 (75), 182 (21), 165

(100), 104 (37), 85 (56), 77 (39), 40 (54). IR (KBr) 3492, 3298, 1660 cm^{-1}. Anal. Calcd. for $C_{42}H_{36}N_2O_2$: C, 83.97; H, 6.04. Found : C, 84.01; H,6.15

45. N,N'-Ditrityl succinamide 97

In a procedure similar to that used for 91, reaction of 5.2 g (20 mmol) of triphenylmethylamine[89] in 150 mL of dry toluene, with 1.55 g (10 mmol) of succinyl cholride in 25 mL of dry toluene ,and 4.06 g (40.2 mmol) of triethylamine gave crude 97. Recrystallization of the crude product from acetonitrile gave 0.7 g (11.6%) of crystals; m.p. 302-303°C (dec); ^{1}NMR ($CDCl_3$) : δ 2.62 (s, 4 H), 6.97 (s, 2 H), 7.16-7.20 (m, 30 H); (^{13}C NMR is not available due to poor solubility of the compound) mass spectrum, m/e (relative intensity) 600 (M^+, 4), 357 (15), 263 (25), 244 (16), 243 (58), 182 (39), 166 (19), 165 (83), 104 (23), 85 (100); IR (KBr) 3300, 1651 cm^{-1}. Anal. Calcd. for $C_{42}H_{36}N_2O_2$: C, 83.97; H, 6.04. Found : C, 83.85; H, 6.19

46. N,N'-ditrityl fumaramide 99

In a procedure similar to that used for 91, reaction of 2.59 g (100 mmol) of triphenylmethylamine[89] in 250 mL of dry toluene , with 5.37 g (35.1 mmol) of fumaryl chloride in 50 mL of dry toluene, and 7.09 g (70.2 mmol) of triethylamine gave 97. Recrystallization of the product from acetonitrile gave 13.6 g (64.8%) of needles, m.p. 307-308°C; ^{1}H NMR ($CDCl_3$) : δ 6.89 (s, 2 H), 6.93 (s, 2 H), 7.23 (m, 30 H);

^{13}C NMR ($CDCl_3$) : δ 71.04, 127.26, 128.09, 128.62, 134.23, 144.11, 163.02; mass spectrum, m/e (relative intensity) 598 (M^+, 8), 417 (3), 355 (54), 261 (48), 243 (100), 182 (64), 165 (78), 104 (32), 77 (36), 40 (50); IR (KBr) 3422, 3390, 1667 cm^{-1}. Anal. Calcd. for $C_{42}H_{34}N_2O_2$: C, 84.25; H, 5.72. Found : C, 84.38; H, 5.82

47. N-Triphenylmethyl-3,3',3''-propanamide **101**

To a stirred solution of 3,3'3''-triphenylpropanoyl chloride[64b] (1 g, 3.12 mmol) in 30 mL of anhydrous THF under argon atmosphere, was added dropwise 0.9 g (3.47 mmol) of tritylamine in 20 mL of dry THF. The solution was stirred for 5 min. To this solution, was added 0.363 g 3.58 mmol) of triethylamine. After being stirring for 10 h, the solution was washed twice with 50 mL of 10% dilute hydrochloric acid, water, saturated NaCl and dried over anhydrous $MgSO_4$. Vacuum removal of the solvent gave oily material which was triturated with ether to give 1.3 g (76.7%) of **101**. Recrystallization of **101** from ethanol gave white needles, m.p. 169-170°C; ^1H NMR ($CDCl_3$) : δ 3.71 (s, 2 H), 6.21 (s, 1 H), 6.82-6.86 (m, 6 H), 7.13-7.24 (m, 24 H) ; ^{13}C NMR ($CDCl_3$) : δ 50.27, 56.00, 70.59, 126.52, 126.64, 127.64, 128.22, 128.64, 129.37, 144.34, 146.22, 169.04; mass spectrum , m/e (relative intensity) 543 (M^+, 2), 301 (23), 300 (100), 244 (12), 243 (54), 182 (23), 85 (18); IR (KBr) 3403, 1667 cm^{-1}. Anal. Calcd. for $C_{40}H_{33}NO$: C, 85.99; H, 5.01. Found: C, 86.06; H, 5.03

48. N-Triphenylmethyl-4,4'4''-butanamide **102**

In a procedure similar to that used for **101**, reaction of **60** (0.6 g, 1.78 mmol) in 30 mL of anhydrous THF with 0.55 g (2.12 mmol) of tritylamine in 20 mL of anhydrous THF and 0.29 g (2.86 mmol) of triethylamine gave 0.47 g (47.3%) of **102** which was recrystallized from acetone; m.p. 263-265^{o}C (dec); ^{1}H NMR ($CDCl_3$) : δ 2.04 (m, 2 H), 2.94 (m, 2 H), 6.29 (s, 1 H), 7.11-7.29 (m, 30 H); ^{13}C NMR ($CDCl_3$) : δ 34.31, 35.26, 56.19, 70.51, 126.00, 127.03, 127.94, 128.00, 128.71, 129.15, 144.76, 146.85, 171.61; mass spectrum, m/e (relative intensity) 557 (M^+, 6), 244 (21), 243 (100), 182 (20), 167 (15), 165 (29); IR (KBr) 3359, 1661 cm^{-1}. Anal. Calcd. for $C_{41}H_{35}NO$: C, 88.29; H, 6.33. Found : C, 88.37; H, 6.32

49. N,N'-Ditrityl tartaramide **103**

To a stirred solution of 2.5 g (4.18 mmol) of **99** in 225 mL of dry pyridine at 0^{o} C, was added 2.26 g (6.19 mmol) of tetrabutylammonium permanganate[68] in 100 mL of dry pyridine dropwise over 30 min. After being warmed up to room temperature and stirred for 8 h, the solution was poured into 100 mL of 10% of dilute hydrochloric acid and 100 mL of 20 % aqueous sodium bisulfate mixture. The solid was filtered and dissolved in 150 mL of methylene chloride. The organic solvent was washed twice with 50 mL of 10% dilute hydrochloric acid, water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Vacuum removal of the solvent gave 2.6

g of crude **103**. Recrystallization of the crude product from methylene chloride gave 2.3 g (87%) of white needles, m.p. 278-279°C; ^{1}H NMR ($CDCl_3$) : δ 4.31 (dd, 2 H), 5.00 (dd, 2 H), 7.14-7.26 (m, 30 H), 8.35 (s, 2 H); (^{13}C NMR is not available due to the poor solubilty of the compound); mass spectrum, m/e (relative intensity) 632 (M^+, 2), 389 (2), 346 (3), 243 (100), 165 (13). IR (KBr) 3374, 3357, 1679, 1660 cm^{-1}. Anal. Calcd. for $3(C_{42}H_{36}N_2O_4).C_3H_6O$: C, 79.20; H, 5.87; N, 4.30. Found: C, 79.05; H, 5.87; N, 4.47

50. O-2-Naphthyl- N-trityl carbamate **104**

To a suspension of 0.84 g (35 mmol) of sodium hydride in 125 mL of dry THF under argon atmosphere, was added dropwise of 5.05 g (35 mmol) of β-naphthol in 125 mL of dry THF. The solution was stirred for 30 min. To this solution, was added dropwise trityl isocyanate (5 g, 17.5 mmol) in 50 mL of dry THF. The solution was allowed to stir for 48 h. The reaction was quenched with water and extracted three times with ether. The combined organic solvents were washed with saturated NaCl solution, and dried over anhydrous $MgSO_4$. Vacuum removal of the solvent gave an oily material. Chromatograpy of the oil over silica gel, eluting with 7:3 chloroform/hexane gave 2.0 g (26.5%) of **104** ,which was recrystallized from ethyl acetate; m.p. 196-198°C. ^{1}H NMR ($CDCl_3$) : δ 6.39 (s, 1 H), 7.32 (m, 19 H), 7.75 (m, 3 H); ^{13}C NMR ($CDCl_3$) : δ 70.25, 118.09, 121.20, 125.29, 126.26, 127.23, 127.56, 128.06, 128.64, 129.03, 131.08, 133.67,

144.46, 148.55, 152.90; mass spectrum, m/e (relative intensity) 286 (M^+-143, 8), 285 (39), 244 (12), 243 (49), 208 (100), 165 (39), 144 (82); IR (KBr) 3292, 1704 cm^{-1}. Anal. Calcd. for $C_{30}H_{32}NO_2$: C, 83.89; H, 5.39. Found: C, 83.86; H, 5.41

51. N,N'-Ditrityl-1,3-diaminopropane **106**

To a stirred solution of trityl chloride (4 g, 14.4 mmol) in 100 mL of dry methylene chloride under argon atmosphere, was added dropwise 1,3-diaminopropane (0.53 g, 7.18 mmol) in 20 mL of dry methylene chloride. After being stirred for 10 min, triethylamine (1.45 g, 14.4 mmol) was added. The solution was allowed to stir for an additional 10 h. The precipitate was fitered and the organic solvent was washed twice with 100 mL of 10% of dilute hydrochloric acid, water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Vacuum removal of the solvent gave a residue which was triturated with ether to give **106**. Recrystallization of **106** from chloroform/petroleum ether (30-60^oC) gave 2.38 g (59.4%) of white crystals; m.p. 179-181^oC; ^1H NMR ($CDCl_3$) : δ 1.66 (t, 2 H), 1.89 (broad s, 2 H), 2.21 (t, 4 H), 7.13-7.28 (m, 18 H), 7.41-7.45 (m, 12 H); ^{13}C NMR ($CDCl_3$) : δ 31.42, 42.53, 71.00, 126.16, 127.75, 128.89, 146.21; mass spectrum, m/e (relative intensity) 243 (M^+-315, 100), 165 (46), 73 (22), 44 (41), 43 (14); IR (KBr) 3400 cm^{-1}. Anal. Calcd. for $C_{41}H_{38}N_2$: C, 88.13; H, 6.85. Found : C, 88.26; H, 6.85

52. N,N'-dityrityl-1,4-diaminobutane **108**

In a procedure similar to that used for **106**, reaction of trityl chloride (4 g, 14.4 mmol) in 100 mL of dry methylene chloride, with 1,4-diaminobutane (0.625 g, 7.09 mmol) in 20 mL of methylene chloride and triethylamine (1.45 g, 14.4 mmol) gave **108**. Recrystallization from acetone gave 2.1 g (51.8%) of white needles; m.p. 154-155°C; ^{1}H NMR ($CDCl_3$) : δ 1.49 (m, 6 H), 2.07 (m, 4 H), 7.12-7.27 (m, 18 H), 7.42-7.46 (m, 12 H); ^{13}C NMR ($CDCl_3$) : δ 28.57, 43.51, 70.83, 126.11, 127.69, 128.60, 146.28; mass spectrum, m/e (relative intensity) 315 (M^+-257, 1), 244 (23), 243 (100), 165 (26); IR (KBr) 3316 cm^{-1}. Anal. Calcd. for $C_{42}H_{40}N_2$: C, 88.07; H, 7.04. Found : C, 87.81; H, 7.28

53. N,N'-Dityrityl-1,5-diaminopentane **110**

In a procedure similar to that used for **106**, reaction of trityl chloride (6.5 g, 23.3 mmol) in 100 mL of dry methylene chloride, with 1,5-diaminopentane (1.02 g, 10 mmol) in 25 mL of dry methylene chloride and triethylamine (2.22 g, 22 mmol) gave 4.5 g of crude **110**. Recrystallization of the crude product from acetone gave 4.01 g (68.4%) of white crystals; m.p. 148-149°C; ^{1}H NMR ($CDCl_3$) : δ 1.32 (m, 8 H), 2.08 (t, 4 H), 7.13-7.28 (m, 18 H), 7.44-7.47 (m, 12 H); ^{13}C NMR ($CDCl_3$) : δ 25.13, 30.83, 43.48, 70.88, 126.16, 127.75, 128.69, 146.37; mass spectrum, m/e (relative intensity) 343(M^+-243, 1), 258 (1), 244 (22), 243 (100); IR (KBr) 3329 cm^{-1}. Anal. Calcd. for $C_{43}H_{42}N_2$: C, 88.01; H, 7.21. Found : C, 88.07; H, 7.29

54. N,N'-Dityrityl-1,6-diaminohexane **112**

In a procedure similar to that used for **106**, reaction of trityl chloride (4.1 g, 14.7 mmol) in 100 mL of dry methylene chloride, with 1,6-diaminohexane (0.854 g, 7.36 mmol) in 25 mL of dry methylene chloride and triethylamine (1.49 g, 14.7 mmol) gave 2.64 g (59.8%) of **112** which was recrystallized from acetone; m.p. 188-189°C; ^{1}H NMR ($CDCl_3$) : δ 1.23 (m, 4 H), 1.46 (m, 6 H), 2.08 (t, 4 H), 7.13-7.28 (m, 18 H), 7.45-7.47 (m, 12 H); ^{13}C NMR ($CDCl_3$) : δ 27.25, 30.78, 43.42, 70.83, 126.11, 127.69, 128.63, 146.34; mass spectrum, m/e (relative intensity) 600 (M^+, trace), 357 (2), 258 (6), 244 (25), 243 (100), 165 (16); IR (KBr) 3320 cm^{-1}. Anal. Calcd. for $C_{44}H_{44}N_2$: C, 87.96; H, 7.38. Found: C, 87.94; H, 7.42

55. Ethylene bistriphenyl methyl ether **114**[70]

A stirred solution of ethylene glycol (1.08 g, 17.5 mmol), and 9.75 g (35 mmol) of triphenylmethyl chloride in 80 mL of dry pyridine was refluxed for 30 min. The solution was cooled and poured into 1000 mL of 10% dilute hydrochloric acid. Suction filtration of the solution gave 5.2 g of crude **114**. Recrystallization of the crude product in toluene gave 4.68 g (49.3%) crystals; m.p. 188-189°C. (lit.[70] 188°C)

56. Diethylene bistriphenyl methyl ether **116**[97]

In a procedure similar to that used in **114**, reaction of 1.69 g (15.9 mmol) of diethylene glycol and 8.9 g (31.9

mmol) of triphenylmethyl chloride in 80 mL of dry pyridine gave 5.8 g of crude **116**. Recrystallization of the crude product in toluene gave 5.28 g (56%) of white crystals; m.p. 157-158°C. (lit.[97] 158°C)

57. Prodcedure for Inclusion Studies

DTU (0.2 g) was dissolved in 3 mL of hot ethyl acetate in a 25 mL erlenmeyer flask. The flask was sealed with a rubber septum. The guest (20 mole equivalents) was added to the warm host solution via syringe. The host-guest mixture was allowed to cool to room temperature. If no crystals formed, the solution was further cooled to 5°C. The precipitated crystals were filtered. The resulting crystalline complexes were dried at room temperature under 0.5 to 1.5 torr of reduced pressure for 10 h. The stoichiometric ratio of the complexes were identified by NMR integrations of the hosts and the guests.

Inclusion studies and guest discrimination experiments of the other hosts were carried out similarly except 0.05 g to 0.1g of hosts were used. In the inclusion studies of the solid guests, two mole equivalents instead of 20 mole equivalents of guests were used. The procedure used to study solid guest was similar to the study of the liquid guest. The procedure for the selectivity study of the mixture of 2,2-dimethylpropanamide and acetamide guests was as follows. DTU (0.2 g) was dissolved in 3 mL of hot ethyl acetate. The flask was sealed with a rubber septum. Guest mixtuer (0.2 mole

equivalents of 2,2-dimethylpropanamide and 0.2 mole equivalents of acetamide in 3 mL of ethyl acetate solutioin) was added to the warm host solution via syringe. The ratio of the guest components in the mixture was determined by the solution NMR technique.

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Appendix

Data Collection of the Crystal Complexes

Data collection of DTU : acetone, DTU : acetaldehyde, DTU : methylene chloride, DTU : ethyl acetate, DTU : acetonitrile, N-triphenylmethyl-3,3,3-triphenylpropanamide : acetone, N-triphenyl-N'-9-trityclmethyl urea : diethyl ether and N-triphenyl-N'-9-trityclmethyl urea complex were performed with Mo $K_\alpha$radiation (λ=0.71073 Å) on a Nicolet P3F computer controlled 4-circle diffractometer equipped with a graphite crystal incident beam monochromator. The data were reduced; the structures were solved by direct methods; and the refinement was by full-matrix least-squares techniques. All calculations were performed on a VAX-11/750 computer using SDP-PLUS.[98]

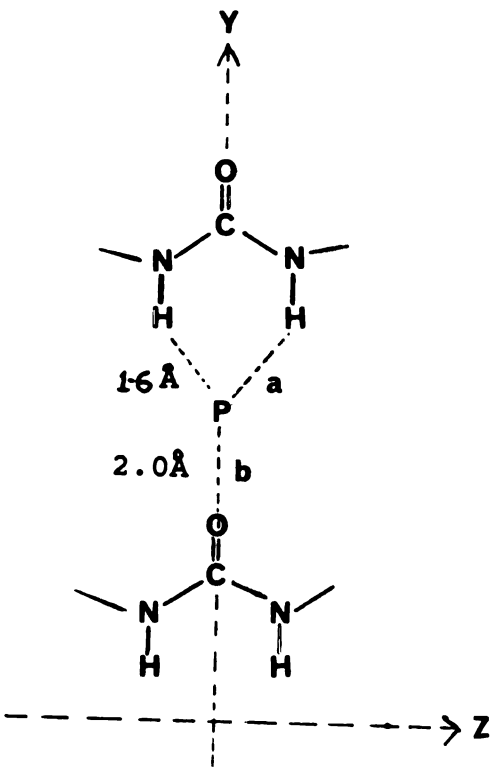
Data collection of ethylene glycol-di-trityl-toluene complex was determined using a Picker FACS-I diffractometer and Mo $K_{\alpha 1}$ (λ=0.70926Å) radiation. The data were reduced; the structure was solved by direct methods; and the refinement was by full-matrix least-squares techniques. All calculations were performed on a CDC-750 computer using Allan Zalkin's programs.[99]

All the computer-generated figures were drawn by the Program ''ORTEP''.[100]

DETERMINATION OF THE DIMENSIONS OF THE VOID

There is no simple way to measure the exact size of the void. The void dimension which are determinated by the method described below are roughly estimated.

The position of the point P was determined by solving the equation assuming that the distance (a) from P to the amide hydrogen atom was equal to the distance (b) from P to the oxygen atom of the carbonyl group (see Figure below). From this point P, the distances from P to all the surrounding atoms were measured by using the ''ORTEP''program.[100]



The estimated cavity space of the host was then derived from the following way. The arbitarily distances between P and the closest surrounding atoms were chosen along the x, y and z axes. The van der Waals' radii of these surrounding atoms were then subtracted from these distance to give the approximate space available between P and these atoms. Summation of the distances between P and particular atoms in a specific direction, for example 1.4Å and 2.0Å in y-axis, gives approximate dimension of the void 3.4Å in the y-axis. The dimensions of the void in the x and the z axes were derived similarly. This technique was used to determine the void dimension of DTU-acetone, DTU-acetaldehyde and DTU-acetonitrile complexes.

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