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**Linear, dendritic and hyperbranched polyimides; The tetrahydro[5]helicene unit as
a novel building block for an exercise in macromolecular architecture.**

by

Timothy P. Bender

B.Sc. (Carleton)

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of

Doctor of Philosophy

Department of Chemistry

Carleton University

Ottawa, Ontario, Canada.

July 8 1999.

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of the thesis,

Linear, dendritic and hyperbranched polyimides; The tetrahydro[5]helicene unit as a
novel building block for an exercise in macromolecular architecture.

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Oct 26/99

Chair, Department of Chemistry, Prof. Gerald Buchanan

Date

Oct. 26, 1999

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Date

July 8, 1999

External supervisor, Dr. Allan S. Hay, McGill University

Date

For my parents...

Paul R. Bender

February 1 1946 – August 9 1999

Everything he was is forever a part of me.

None the less, he is and will be deeply missed.

Abstract.

A number of chemical derivatives of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride have been made. Each derivative can be made by simple and selective chemical transformations using readily available reagents. Each derivative has a unique spatial arrangement of its functionality and as a result, this single core molecule has been incorporated into a variety of macromolecules. Although all the macromolecules share the same root functionality, they differ in their molecular architecture.

Specifically, an AB-type monomer 3-amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**3-1**) has been shown to undergo polymerization in the solid state. This is possible because this monomer is stable at ambient and moderate temperatures yet becomes activated to polymerization at elevated temperatures. Furthermore, the polymerization is facilitated by its tendency to self assemble in the solid state through the formation of hydrogen bonds between its amino and anhydride functionalities. It is the thermally induced collapse of this hydrogen bond that results in the polyimide formation. The facile nature of the solid state polymerization process has been shown to be compatible with inorganic dopants and as a result has been used to form hybrid polyimide-inorganic materials. Furthermore, the method of solid-state polymerization has been extended to the solid-state polymerization of an A₂B-monomer (**3-3**), which produces hyperbranched polyimides (**3-4**).

A model has been proposed to explain the stability observed for AB-monomer **3-1** and several other AB-monomers have been proposed that fit the model and in theory should behave similarly to monomer **3-1**.

It has been demonstrated that the use of the transimidization reaction is a feasible route to a polyimide when a target AB-monomer is not stable. The synthesis and polymerization of an AX-type amino imide monomer containing the tetrahydro[5]helicene unit was accomplished. It underwent a self-transimidization reaction and produced polyimide **4-3**. Polyimide **4-3** could be incorporated into a series of block copolymers by copolymerization with a suitable diamine and dianhydride. A model is proposed which would allow for the control of the molecular weight of polyimides made from AX-type monomers by the use of different X-groups. The methodology presented has been extended to the synthesis of an A₂X-type monomer **4-9**.

Dendritic aryl imides from generation one to three, containing the tetrahydro[5]helicene unit have been synthesized. Each of the dendrons underwent either one or two electrochemical reductions. When a dendritic aryl imide was compared with its linear analog, differences were found in the hydrodynamic volumes, glass transition temperatures, and fluorescence and electrochemical behaviour.

Several AA-type diamine monomers containing the tetrahydro[5]helicene core have been made. In one case polyimides derived from AA-type diamine monomers **6-2a** and **6-2b** were used as precursors to [5]helicene containing polyimides, which were otherwise unobtainable. Diamines **6-2a** and **6-2b** have also been shown to impart improved solubility characteristics to the polyimides for which they are a part. The enhanced solubility observed for these polyimides can be directly attributed to the presence of diads in the polymer backbone, alternating repeat units, the large spatial volume occupied by the tetrahydro[5]helicene unit and its structural mobility.

Another AA-type diamine monomer containing a helically locked *o*-terphenyl unit (**6-13**) has been synthesized and copolymerized to form a series of copoly(ether imide)s. The tendency of the copolymers to be of lower molecular weight and form macrocyclic materials at higher molar percentage of monomer **6-14** has been demonstrated. It has also been shown that the glass transition of the copoly(ether imide) can be controlled and varied depending on the amount of monomer **6.13** present.

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Hey there everyone,

On the conclusion of my Ph.D. degree I would like to thank a number of people. Some, of who without, this thesis would not have been possible, some helped out along the way.

My sincere thanks to Prof. Wayne Zhi Yuan Wang for his guidance and support along the way. His knowledge of the scientific process and the human condition has made him the type of supervisor everyone hopes for.

Many thanks to my labmates both former and current (grad students, post-docs & research associates, there are too many of you to name) for your patience and understanding. Special thanks to Sean MacKinnon, your friendship has meant a lot.

To Tony O'Niell and Kieth Bourque, thanks for the help with experiments and stuff and your patience both in my thesis and my TA assignments.

As this thesis was selected as one of two awarded the MSED/Bayer Inc. Award for the best Ph.D. thesis in Canada in Macromolecular Science and Engineering for 1999, I would like to thank both the MSED of the CSC and Bayer Inc. for the award.

Finally, and certainly not least, I would like to thank my parents Pat and Paul Bender, for their unwavering support throughout this long, and sometimes trying, journey. It seems like a lifetime ago when I left for Ottawa to study and in some ways it was. This thesis represents the last 3 ½ years of it.

It likely was not easy explaining why their son was still in school when he was 28 years old.

As I finish writing this thesis, there are some 206 days left until the turn of the millennium and Ottawa is experiencing its first heat wave of the summer of 1999. When I set out to do this I said I would finish before the turn of the millennium (just in case the world or at least all the computers in the world crash) and I made it with time to spare.

Take care, everyone...

c-ya later...

I am outta here...

--

Tim :-)

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To know chemistry, is to know a little piece of nature -- Tim

"FEAR: the general public has long been divided into two parts: those who think science can do anything, and those who are afraid that it will." -- Dixy Lee Ray

"If we knew what it was we were doing, it would not be called research, would it?" -- Albert Einstein

"Millions saw the apple fall, but Newton was the one who asked why." --Bernard M. Baruch

"The principle goal of education is to create (wo)men who are capable of doing new things, not simply of repeating what other generations have done - (wo)men who are creative, inventive and discoverers." --Jean Piaget

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And now a song:

Sung to the tune "Here We Go 'Round the Mulberry Bush"

What's inside a polymer, polymer, polymer?
What's inside a polymer?
Let's find out.

The atom is the smallest thing, smallest thing, smallest thing.
The atom is the smallest thing
In a polymer.

They're joined together as molecules, molecules, molecules.
They're joined together as molecules
In a polymer.

The molecules will make a chain, make a chain, make a chain.
The molecules will make a chain
In a polymer.

The chain is very, very long, very long, very long.
The chain is very, very long
In a polymer.

That's what's in a polymer, polymer, polymer.
Atoms joined as molecules
In a long, long chain.

Take care. Will talk at you soon. 'c'ya.

: -) Mom

--

"when life gives you lemons, make lemonade..."

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List of abbreviations.

6FDA	2,2-hexafluoroisopropylidene diphthalic anhydride
BAPB	bis-4,4'-(4-aminophenoxy)biphenyl
BAPP	2,2-bis[4-(4-aminophenoxy)phenyl]propane
BAPS	bis[4-(4-aminophenoxy)phenyl]sulfone
BTDA	3,3',4,4'-Benzophenonetetracarboxylic dianhydride
DMA	dynamic mechanical analysis
DMAc	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DMSO	Dimethylsulfoxide
DSC	differential scanning calorimetry
DSDA	3,3,4,4'-diphenylsulfone tetracarboxylic dianhydride
FT-IR	Fourier transform infrared
GPC	gel permeation chromatography
HRMS	high resolution mass spectroscopy
MALDI-TOF MS	matrix assisted laser desorption ionization time of flight mass spectrometry
Mn	number average molecular weight
MS	mass spectrum
Mw	weight average molecular weight
NCP	N-cyclohexyl-2-pyrrolidinone
NMP	N-methyl-2-pyrrolidinone

NMR	nuclear magnetic resonance
ODPA	4,4'-oxydiphthalic anhydride
PMDA	pyromellitic dianhydride
s-BPDA	3,4,3',4'-biphenyltetracarboxylic dianhydride
SEC	size exclusion chromatography
TCE	1,1,2,2-tetrachloroethane
Td	5 wt% decomposition temperature
Tg	glass transition temperature
TGA	thermal gravimetric analysis
THF	Tetrahydrofuran
TMA	thermal mechanical analysis
TPE-Q	bis-1,4-(4-aminophenoxy)benzene
UV	Ultraviolet
Vis	Visible
WAXD	wide angle x-ray diffraction

Chapter 1. Polyimides.

1.1. History.

Polyimides belong to a general class of polymeric materials commonly called high-temperature plastics. They are described as organic polymeric materials which retain their useful properties after exposure to high temperatures for prolonged periods of time under static air conditions. Admittedly this definition is vague since what is a high temperature for one, may be considered moderate to another, depending on one's perspective. However, under this definition polyimides share common reference with such polymer classes as poly(phenylene oxide)s, poly(phenylene sulfide)s, polybenzimidazoles, polyquinoxalines, poly(aryl ether ketone)s and poly(aryl ether sulphone)s.¹

The first reported synthesis of wholly aromatic polyimides was made by Sroog *et al* in 1965 from the Film and Plastics Department of I.E. DuPont de Nemours and Company Inc. (now DuPont).² They described the synthesis of what they termed polypyromellitimides, which were polyimides derived from the polycondensation of pyromellitic dianhydride (PMDA) with a variety of aromatic diamines. The synthetic approach to these highly insoluble polyimides (some were only soluble in conc. H₂SO₄) was to make a precursor poly(amic acid) solution in either N,N-dimethylformamide (DMF) or N,N-dimethylacetamide (DMAc). The precursor solution was then cast into a film and thermally imidized to give the corresponding polyimide. Although this report is over 30 years old, their reported method for polyimide synthesis is still commonly used today both in research and production facilities. This early work led to the

commercialization of the polyimide derived from PMDA and ODA (oxydianiline) by DuPont, which is sold as a thin film known as Kapton™ and is illustrated in Figure 1-1 along with some other examples of commercial polyimides.

Figure 1-1. Commercially available polyimides.

1.2. Polyimides.

The original polyimides of Sroog *et al*² suffered from one particular and enormous drawback. Namely, the polyimides could not be directly synthesized from their components because they were neither soluble nor meltable. Rather they had to be made from precursor poly(amic acid)s and therefore could not be directly cast into films or other forms. This extremely low solubility and nonexistent melt is thought to be a result of the extreme rigidity of the polyimide backbone which leads to strong π -acid/ π -

base interactions occurring between the electron deficient pyromellitimide moieties and the electron rich phenyl rings within the polyimide backbone (Figure 1-2). This electronic interaction causes the polymer chains to pack extremely well in the solid state. The π - π interaction is at a maximum for polyimides derived from PMDA and planar aromatic diamines, similar to the one shown in Figure 1-2 (derived from PMDA and *p*-phenylene diamine (PPD)) and is responsible for the characteristic yellow/orange colour commonly associated with aromatic polyimides.

Figure 1-2. Polyimide from PMDA and PPD and its interactions in the solid state.

Much of the early research after the 1960's focused on the structural modification of aromatic polyimides in order to improve their solubility (and hence their processability) without sacrificing their characteristically good thermal and mechanical properties. Very few of these polyimides were made from monomers having exclusively imide and phenyl moieties within their polymeric structure. Most are made from monomers that contain either two phthalic or aniline moieties that are chemically joined through another functionality. The introduction of "kinking" units within the backbone

of a polyimide was done in order to perturb the polyimide within the solid state by decreasing the chain-chain interactions (therefore the π - π interactions) and thereby improving either the solution or melt processability of the resulting polyimide. Kinking groups are defined as moieties that join either the phthalic or aniline functions within a dianhydride or a diamine monomer, respectively. They are generally tetrahedral (sp^3 hybridized) which serves to break the conjugation between the aromatic units of the monomers. For example, commonly used kinking groups are oxygen, methylene, isopropylidene, hexafluoroisopropylidene and sulphone. One exception is 3,4,3',4'-benzophenone tetracarboxylic dianhydride (BTDA) which links two phthalic anhydride groups with a carbonyl (an sp^2 hybridized species). A wide variety of bisphthalic anhydrides (Figure 1-3) and bisanilines (Figure 1-4) containing kinked linking units have now become commercially available.

Figure 1-3. Dianhydride monomers used for polyimide synthesis.

Figure 1-4. Diamine monomers used for polyimide synthesis.

Recently, Colquhoun *et al* were able to obtain direct evidence for the role that these kinking units play in the arrangement of oligoimide segments within the backbone of a polyimide.³ They obtained x-ray determined structures for bis-(4-phenoxyaniline) derivatives of 2,2'-hexafluoroisopropylidene diphthalic anhydride (6FDA) and 3,4,3',4'-diphenylsulphone tetracarboxylic dianhydride (DSDA). These two compounds serve as model compounds for polyimides made from 6FDA and DSDA with ODA and their x-ray structures can be used to speculate on the nature of the chain-chain interaction within these polyimides. As an example, the ORTEP plot of the x-ray determined structure for the 6FDA derivative is shown in Figure 1-5. Within the single crystal of this derivative

there was a perturbation of the π - π interaction between the π -acid phthalimide units and the π -base phenyl units as indicated by the measured distances between the moieties. The distance was large enough to rule out strong electronic interaction between these moieties and this increased distance can be attributed to the presence of the sp^3 hybridized hexafluoroisopropylidene (6F) unit within the model compound by contrast with a similar model compound made from PMDA. This later model compound showed measured distances between the π -acid and π -base moieties that indicated electronic interaction takes place.⁴

Figure 1-6. Polyimides derived from isomeric dianhydrides (left) and isomeric diamines (right).

Another approach to the structural modification of polyimides is the synthesis of isomeric monomers that will change the polymer morphology (mechanical properties) without sacrificing the thermal properties of the polyimide (thought to be derived from the chemical composition of the polyimide). Two examples of this approach are illustrated in Figure 1-6. However, the variation in observed thermal properties and solubilities (mechanical properties) for the series of polymers illustrated was small.

The addition of pendent groups to the polyimide backbone is also known to decrease the amount of chain-chain interaction through an increase in the amount of steric repulsions present. For example, polyimides of 3,6-diphenyl and 3,6-ditrifluoromethyl-PMDA are known to have increased solubility over the equivalent polyimide made using simple PMDA.

The above mentioned examples of early design and synthesis of new polyimides were limited to the study of factors effecting the use of a polyimide as a structural material (solubility, processability). Recently polyimides have been investigated for use as functional materials (redox active polymers, optical waveguides). A survey of the patent literature over the past 10 years shows that patents issued pertaining to polyimides have stayed steady at 700/year from the period 1992 to 1997 (Figure 1-7).⁵ In 1998 there was a marked increase in the number of patents issued pertaining to polyimides to nearly 1000. This increase is an indication that the use of polyimides as functional materials is on the increase.

Figure 1-7. Patents issues pertaining to polyimides over the past 10 years.

1.3. Methods for polyimide synthesis.

There are predominately two different synthetically facile methods for the synthesis of polyimides on a laboratory scale. Although many others are known (for

example phosphorylation⁶, condensation of a dianhydride with a diisocyanate⁷ and palladium catalyzed carbonylation⁸) the discussion of such methods other than the most common is beyond the scope of this introduction.

Figure 1-8. Methods for polyimide synthesis: (a) polycondensation and (b) nucleophilic displacement polymerization.

The two most common methods used for polyimide synthesis are the polycondensation of a dianhydride with a diamine and the displacement of a phthalic nitro group by a bisphenoxide salt (a and b respectively in Figure 1-8).

The polycondensation method can either be a direct 1-step polycondensation, either in a high boiling solvent (*m*-cresol, NMP) or in the melt to give the corresponding

polyimide or it can involve a 2-step polymerization by the formation of a precursor poly(amic acid) followed by dehydration to give the polyimide (Figure 1-8 a). The use of direct polycondensation in solution may appear to be the more facile on both laboratory and production scale. For example, the commercial poly(ether imide) known as Ultem (Figure 1.1) is made by one step condensation of its component dianhydride and diamine in the melt. More often polyimides have limited solubility or high melt temperatures and therefore can not be made by direct polycondensation. Therefore, in these cases, a precursor poly(amic acid) solution is made and films of it are cast, which are then thermally cured effecting imidization giving the final polyimide as a thin film. Poly(amic acid)s can also be chemically imidized in solution using pyridine and acetic anhydride. Recently, polyimide films have been formed from thermal treatment of poly(amic acid) films cast from volatile solvents such as THF/methanol mixtures.⁹

Alternatively, polyimides can be made by nucleophilic displacement polymerization of a bis-(nitrophthalimide) with a phenoxide salt (Figure 1-8 b). The procedure involves the synthesis of a bis-(nitrophthalimide) derivative of suitably functionalized diamine. Subsequent polymerization of this bis-nitro derivative with a suitably functionalized bisphenol in the presence of base gives the polyimide.¹⁰ This synthetic procedure is limited to the synthesis of poly(ether imide)s since the polymerization itself results in the formation of an ether bond. This method however has several drawbacks, one of which is that the sodium or potassium nitrite produced in this reaction is known to decompose imide functionalities at high temperatures. However, since high temperature is often necessary for the formation of the bisphenoxide salt needed for polymerization, careful temperature control must be maintained during the

polymerization to ensure formation of the desired product. As a result, this method has never been practically applied to the synthesis of commercial polyimides.

1.4. Rational design of new monomers for polyimide synthesis.

The synthesis of isomeric or new dipthalic anhydrides or dianilines as a method for the modification of existing or synthesis of new polyimides has been done extensively over the past 30 years. However, as the focus of polyimide research moves away from their use as structural materials and toward their use as functional materials the need to custom synthesize new monomers with specific function, molecular structure and/or molecular conformation becomes increasingly important.

Therefore, the author has set out to design a novel monomer system to study two distinctly different areas of concern to current research in polyimides.

- 1. The testing of new concepts in polymer-forming reactions and synthetic pathways specific to polyimide synthesis and chemistry.*
- 2. The incorporation of a new and unique molecular structure into the framework of a polyimide.*

Ideally, in order to test both of these concepts within the framework of a polyimide, one would choose polycondensation instead of nitro-displacement as the polymer forming reaction, for a variety of reasons, not the least of which is the facile nature in which polycondensation reactions tend to occur. Secondly, nitro-displacement

polymerization is limited in application to nitrophthalimide and nitronaphthalimide derivatives of diamino compounds. Since this approach would require the synthesis of a new diamine anyway, polycondensation seems a more sensible approach. Finally, polycondensation is less sensitive than nitro-displacement polymerization to factors such as temperature, nature of the base used, cyclodepolymerization/ether cleavage and it minimizes other chemical species present in the polymerization reaction mixture and ultimately the polymer such as inorganic salts.

Additionally, the synthetic chemist would want a versatile core molecule from which a variety of functionalized monomers can be made, thus limiting the number of synthetic steps necessary to make a new monomer. This approach is similar to the parallel synthesis approach used extensively in the synthesis of complex natural products. An example of a versatile unit used extensively in polymer synthesis is the hexafluoroisopropylidene (6F) unit, which is derived from hexafluoroacetone. It has been utilized in a variety of polymer systems by its incorporation into a number of monomers including bisphenols, diamines, a dicarboxylic acid and a dianhydride. The 6F core has been shown to increase solubility, thermal stability and produce materials with low dielectric constants.¹¹

One such versatile core molecule that the author has discovered is 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride. From this core molecule several key derivatives can be made by use of readily available reagents. The facile and selective way in which this core can be functionalized with these reagents makes it ideally suited for use in polymeric systems. Furthermore, it is uniquely suited, because of its molecular

conformation, for studying a variety of macromolecules all of which share the same core functionality yet differ in their macromolecular architecture.

1.5. References.

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Chapter 2. The structure, conformation, chemistry and chirality of tetrahydro[5]helicene.

2.1. Helical molecules.

The term “helical” is derived from the word helix, which comes from the Greek word for spiral. According to the Concise Oxford English Dictionary:

Helix: **1.** A spiral curve (like a corkscrew) or a coiled curve. **2. Geom.** A curve that cuts a line on a solid cone or cylinder, at a constant angle within the axis.

Helical: *adj.* Having the form of a helix.

Many types of helical molecules are known in chemistry and biology. DNA, the molecule that carry every living species' genetic information is a helical molecule.

Within the realm of organic chemistry there are also many examples of helical molecules, some of which are illustrated in Figure 2-1. All of the compounds illustrated are chiral and form a pair of enantiomers, but their chirality is not due to a configuration around a chiral carbon, as with more traditional enantiomers. Rather, the illustrated compounds all form a pair of helical enantiomers, which because of a conformation they are forced into due to the presence of steric repulsions within the molecule, they are so called conformational enantiomers.¹ Representatives of this class of chiral compounds include arylalkenes, triphenylenicenes, tetraphenylenicenes, pentaphenylenicenes, helicenes, heterohelicenes and bihelicenes. All the molecules illustrated in Figure 2-1 have been synthesized, resolved, their optical rotations determined and in some cases their absolute

conformations determined by x-ray crystallography. Unlike the case where the relationship between the configuration of a traditional enantiomer and the direction in which it rotates plane polarized light is not known, the same is not true for helical enantiomers. If a molecule forms a helix in the right handed sense then it is designated the P (plus) enantiomer and rotates plane polarized light in the positive direction. Conversely, if the molecule forms a helix in the left handed sense then it is designated as the M (minus) isomer and rotates plane polarized light in the negative direction.²

Figure 2-1. Some examples of helical molecules (**A**) arylalkenes (**B**) triphenylenicenes, tetraphenylenicenes, pentaphenylenicenes and (**C**) helicenes, heterohelicenes and bihelicenes.

2.2. Helicenes.

Helicenes, the first of which was synthesized by Newman in 1956,³ are polycyclic aromatic compounds that, due to an overlapping of their terminal aromatic rings, possess a helical conformation. As a result of the helical conformation they form a pair of conformational enantiomers, which upon resolution (into their P and M enantiomers) exhibit extremely large optical rotations ($[\alpha]_D^{25}$) of the order of 1000° to 10000° . The magnitude of a helicene's optical rotation is known to increase nonlinearly with an increase in the number of fused aromatic rings within the helicene structure. Furthermore, helicenes are known to racemize thermally and the half-life ($t_{1/2}$) for racemization is known to increase with increasing helicene size. A common nomenclature is used when naming helicenes of the form $[n]$ helicene, where n is the number of fused aromatic rings. Hence, a helicene with 6 fused aromatic rings (originally called hexahelicene by Newman) is referred to as $[6]$ helicene. Using this naming method phenanthrene is $[3]$ helicene, although it is well known to be a planar polycyclic aromatic compound and not helical. $[5]$ Helicene is the smallest helicene to possess a stable helical conformation and can therefore be resolved into its constituent enantiomers.⁴ Helicenes are also photoluminescent and the luminescence changes depending on both the length of the conjugation and the electronic environment of the helicene.⁵

Traditionally, helicenes were synthesized by photocyclization of an appropriately structured stilbene derivative. There are two inherent problems associated with this approach. Firstly, photocyclization reactions need to be done under high dilution conditions, which makes synthesis of large quantities of materials experimentally

difficult. Secondly, for a non-substituted stilbene the photocyclization reaction provides the possibility of two isomers being formed for every cyclization site. For example the synthesis of [5]helicene requires a precursor with two cyclization sites, leading to the formation of four possible isomers upon photocyclization. Again this makes large-scale preparation and isolation of the target compound problematic.

The desire to study helicenes (a structurally unique molecule) within the framework of a macromolecule is two fold. Firstly and perhaps more academic, the unique conjugated structure and helical conformation should impart novel properties into a polymeric or macromolecular system not otherwise obtainable with “traditional” aromatic systems. For example, polymers containing helicene units are likely to possess some interesting photochemical and/or electrochemical properties derived directly from the unique extended π -system. Secondly, from a practical point of view the unique extended nonplanar aromatic helicene unit should maintain the usual thermal stability and polymer chain rigidity found when “traditional” aromatic units such as 1,4-phenylene, 2,6-naphthylene, 1,4-naphthylene and 4,4'-biphenylene are incorporated into a polymeric system. However, unlike these more traditional planar aromatic systems, the helicene unit occupies more free volume and should therefore increase the inter-chain distances within a polymer: a phenomenon known to increase the solubility of polymers. However, clearly for incorporation of a helicene unit into a macromolecule or polymer one needs a large-scale non-photochemical route to the preparation of functionalized helicenes.

2.3. Synthesis of compound 1.

We have selected 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**1**, Scheme 2-1) as a helical compound for incorporation into a variety of macromolecules, for a number of reasons. First, it is a known precursor to a [5]helicene derivative, [5]helicene-7,8-dicarboxylic anhydride, and is therefore a helicene analogue.⁶ Secondly, compound **1** can be prepared via a non-photochemical synthetic route that we have modified from the literature procedure, so that large quantities can be readily made in a laboratory setting. Additionally, compound **1** already contains functionality at the 7 and 8 positions (see numbering Scheme 2-1) and therefore requires less subsequent derivatization to produce a monomer suitable for incorporation into either a macromolecule or a polymer, than a non-functionalized building block.

Pinacol coupling of up to 1 kg of α -tetralone in the presence of aluminum and catalytic amounts of mercury(II) chloride results in the formation of the desired pinacol mixture in excellent yield (Scheme 2-1). Subsequent dehydration using acetic anhydride and acetic acid gives the diene, 3,4,3',4'-tetrahydro-1,1'-binaphthyl. Reaction with maleic anhydride in a neat melt gives the desired Diels-Alder adduct which can be partially aromatized to give compound **1** with elemental bromine in acetic acid and chloroform. Starting with 1 kg of α -tetralone one can obtain up to 350 g of compound **1** with purity >98%. Compound **1** can be recrystallized from acetic anhydride, acetic acid and high boiling hydrocarbons such as decane and dodecane. The ¹H NMR of compound **1** (400 MHz, CDCl₃, Figure 2-2) exhibits the expected aromatic resonances with the anticipated splitting patterns. However the protons from the ethylene bridge (at positions 5,6 and 9,10) exhibits 3 distinct resonances at 2.58, 2.95 and 3.96 ppm with integration

ratio 1:2:1, respectively. This resonance pattern is due to the magnetic non-equivalence of these protons, brought on by their fixed conformation of the tetrahydro[5]helicene unit. This pattern of resonances for the ethylene protons is also seen in all derivatives of compound 1.

Scheme 2-1. Synthesis of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (Compound 1).

Figure 2-2. ¹H NMR of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (Compound 1, 400 MHz, CDCl₃).

2.4. Derivatives of compound 1.

We have found that compound **1** displays a rich and diverse chemistry. It reacts specifically and selectively with a variety of simple reagents, to produce a number of functionalized tetrahydro[5]helicenes and [5]helicenes. Compound **1** can be divided into 3 different reactive and chemically unique sites (Figure 2-3). The author and his research group have found the terminal aromatic rings can react with electrophiles (positions 1, 3, 12 and 14), the anhydride group (positions 7 and 8) can react with certain nucleophiles and the ethylene units (positions 5,6 and 9,10) are labile to free radicals and oxidation. This level of control is necessary if one is to design new polymeric materials at the molecular level and serves not to limit the types of macromolecular systems that the tetrahydro[5]helicene unit can be incorporated into.

Figure 2-3. Reactive sites of compound 1.

The anhydride functionality of compound **1** is unusually stable to nucleophiles. It is stable in water and it is nearly impossible to isolate ester-acid derivatives on reaction with a primary or secondary alcohol. During isolation, the products have a tendency to revert back to **1** and the free alcohol. Similarly, amide-acid (a.k.a. amic acid) derivatives of **1** are also unstable. The anhydride group also remains intact in the presence of a Lewis acid (AlCl_3) and fluorobenzene. However, imide derivatives (**2-5a-m**, Scheme 2-

2) of compound **1** are easily made by reaction of the appropriate primary amine (aliphatic or aromatic) with **1** at moderate to high temperatures in the presence of a polar aprotic solvent (DMF or DMAc) or in *o*-dichlorobenzene with isoquinoline catalyst. Examples include reaction with ethanolamine (**2-5b**), both *m*- and *p*-nitroaniline (**2-5c-d**), hydrazine (**2-5f**), enantiomerically pure amines (**2-5e**, **2-5g-i**) and electron deficient aminopyridines (**2-5j-m**) all giving the corresponding imide derivatives of compound **1**. Furthermore, compound **1** will form its benzimidazole derivative (**2-10**, Scheme 2-2) on condensation with *o*-phenylene diamine in the presence of *p*-toluenesulphonic acid at high temperatures. This compound is highly fluorescent and has a measured quantum yield >90%.⁷ Finally, in the presence of hydroxide base (Na, K, Rb or Cs) in ethanol compound **1** readily forms its biscarboxylate salt (**2-6**, Scheme 2-2) which on isolation is soluble in water and DMSO.

Reactions of compound **1** with a number of electrophiles of inorganic acids (ClSO₃H, HNO₃, H₂SO₄) under a variety of conditions, leads to compounds substituted primarily in the 3 and 12 positions, with minor products having substitution at the 1 position (see numbering Scheme 2-1). In all cases the substitution pattern is governed by the ortho/para directing ability of the *o*-terphenyl moiety present within **1**.

Compound **1** can be selectively nitrated using different nitrating conditions to give mono-nitrated compounds **2-2a** and **2-2b**, a di-nitrated compound **2-3** and tri-nitrated compound **2-4** in high to moderate yields (Scheme 2-2). Mono-nitration of compound **1** was achieved by use of a mild two-phase reaction system consisting of a mixture of sulfuric acid, nitric acid and acetic acid droplets suspended in a chloroform solution. These mild nitration conditions allow for the selective introduction of a single

nitro group into compound **1**, which as a result of its C_2 symmetry contains two equally reactive sites. This selectivity could not be achieved using more standard nitration conditions. Isolation of **2-2a** from **2-2b** could be accomplished by two successive precipitations of a chloroform solution of **2-2a** and **2-2b** into methanol. Placement of **2-2a** once isolated back into the same nitration conditions gave the di-nitrated product **2-3** and a structural isomer, of which **2-3** could be isolated in moderate yield (43%) after recrystallization from dichloromethane. Direct dinitration of **1** gave a mixture of nitrated compounds, which were difficult to separate by recrystallization and other common means, presumably due to the presence of polynitrated species. Under much harsher nitration conditions compound **1** could be selectively tri-nitrated to give compound **2-4**.

The dinitro derivative **2-3** (Figure 2-4) is the only compound found where the resonances from the ethylene bridge are distinct enough in the ^1H NMR spectrum such that the assignment of the individual resonances can be made. By the use of both NOSEY and COSEY NMR spectroscopy the assignment of the proton resonance from left to right starting at ~ 4 ppm are H_{6b} , H_{5b} , H_{5a} and H_{6a} (see labeling Figure 2-4).

Figure 2-4. ¹H NMR of 3,12-dinitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (2-3).

Another worker in the author's laboratory has studied the action of both chlorosulphonic acid and sulphuric acid on compound **1**. Briefly, chlorosulfonation of **1** produces the desired disulfonyl chloride compound **2-9** (Scheme 2-2). This compound can then react with fluorene under standard Friedel-Crafts conditions to give a difluorenyl sulphone derivative. Direct reaction of compound **1** with sulfuric acid yields the corresponding sulphonate derivative (**2-7**) which is water soluble and fluorescent. Reaction of **2-7** with acetic acid and acetic anhydride gives the anhydride **2-**

8 which is also water soluble and fluorescent.⁸ Surprisingly, the anhydride functionality remains intact in water solution. As of yet, we have not fully explored the potential uses of these sulphonate derivatives.⁹

Figure 2-5. ¹H NMR of compound **1** and its fully aromatic analogue **2-11**.

Top: Compound **1**. *Bottom:* Compound **2-11** from a crude reaction mixture after aromatization with atmospheric oxygen.

The fully aromatic [5]helicene-7,8-dicarboxylic anhydride (compound **2-11**, Scheme 2-2) can be made by reaction of **1** with a variety of reagents, including atmospheric oxygen, elemental bromine, *N*-bromosuccinimide, *N*-chlorosuccinimide and palladium on charcoal. All of the above reagents abstract hydrogen atoms (radicals) from the ethylene units of **1**. It will be shown later that the aromatization of compound **1** to its fully aromatic analogue is synthetically versatile and can be done either *pre-* or *post-*

polymerization. The transformation can be easily detected by ^1H NMR as there is a marked shift in the resonance of the aromatic protons (Figure 2-5) as well as loss of the resonances from the ethylene bridge at positions 5,6 and 9,10.

The ease to which the nitro group (which on reduction is easily converted to an amino group) can be introduced into the tetrahydro[5]helicene unit, makes it perfectly suited for incorporation into polyimides. Furthermore, the nature and the arrangements of chemically distinct functionalities on the tetrahydro[5]helicene unit makes it suitable for an exploration in both the testing of new concepts in polyimide-forming reactions (from its 3-nitro derivative (**2-3**, Scheme 2-2) and 3,12-nitro derivative (**2-4**)) and the incorporation of new and unique molecular structures into the framework of a polyimide.

However, this is not the first attempt at the incorporation of a helicene into a polyimide. Frimer *et al* has reported the synthesis and polymerization of a dianhydride containing a [5]helicene moiety, [5]helicene-5,6,9,10-tetracarboxylic dianhydride. The polyimides made exhibited excellent thermal stability, rivaling that of PMR-15 polyimide composite, but were very insoluble.¹⁰

Whereas Frimer's dianhydride was limited in scope (one dianhydride from which a series of polyimides could be made) the tetrahydro[5]helicene unit is significantly different both chemically and conformationally. It is a polycyclic aromatic compound with rigid aromatic rings which should possess a higher level of flexibility within the overall molecular free volume of the tetrahydro[5]helicene. This type of arrangement should allow for the retention of the characteristically high thermal stability of traditional polyimides and yet allow for an increase in the polyimides solubility and hence processability.

Scheme 2-2. Derivatization of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**1**).

However, if one needs to confirm any experimentally determined property differences and to test this hypothesis one needs to examine the structure, conformation and molecular motion of the tetrahydro[5]helicene unit on a molecular level. In order to do this there are two techniques available: x-ray crystallography and molecular modeling.

2.5. Structure, conformation and molecular motion of compound 1.

A single crystal of compound **1** could be formed by slow diffusion of diethyl ether into a saturated solution of **1** in toluene. An ORTEP plot of its molecular structure within a single crystal as determined by x-ray diffraction is illustrated in Figure 2-6 (x-ray determined coordinates as well as distance and angles tables are given in Appendix B). From this illustration the expected helical conformation of compound **1** can be seen and several geometric details can be measured. For example the C1-C14 atom-to-atom distance (by numbering given in Scheme 1-1) is measured to be 3.22 Å and the twist angle between the terminal phenyl moieties and the core fully substituted phenyl group was found to be 32.4°.

Figure 2-6. ORTEP plot of compound **1** (atomic coordinates determined by x-ray diffraction).

Since it is unlikely that single crystals of all derivatives of compound **1** can be obtained it would be of interest to compare geometric parameters of compound **1** obtained by x-ray diffraction to those obtained using two commercially available molecular modeling software packages. Furthermore, x-ray crystallography can not provide any details about the molecular motion that occurs within the tetrahydro[5]helicene unit. Therefore, compound **1** was investigated with a variety of computational methods on two different computer platforms, the results of which are tabulated in Table 2-1.

In a typical experiment to determine the energy minimized molecular structures, the input structures are first minimized using a molecular mechanics force field then finally refined using the appropriate method to an energy gradient of less than 0.01 kcal mol⁻¹. The results obtained using the Merck molecular mechanics force field as

implemented in the SGI version of Spartan 5 proved to give geometric parameters for compound **1** that were closest to those obtained by x-ray diffraction. As compared to semi-empirical methods (AM1, PM3), DFT method and AB initio method, molecular mechanics calculations take the least amount of computational time. For example, obtaining an energy minimum for compound **1** using the Merck molecular mechanics force field took less than 1 min, whereas using an AB initio method (STO-3G, the smallest basis set) took 270 min 30 sec. When each software package is compared, there is only a slight difference seen in the geometries predicted using their only common computational method, AM1.¹¹

Table 2-1. Geometric parameters of compound **1** obtained by computer aided molecular modeling and their comparison with equivalent parameters obtained by x-ray diffraction.

Method	X-ray	MM+ ^a	AM1 ^a	Merck MM ^b	AM1 ^b	PM3 ^b	DFT ^b	STO-3G ^b
C1-C14 distance. (Å)	3.22	2.87	2.89	3.14	2.88	2.99	2.94	3.03
Twist angle. (°)	32.4	24.9	30.7	31.5	30.6	32.5	29.6	33.2

^a – As implemented in Hyperchem ver 5.01 (Hypercube Inc.) for PC computers.

^b – As implemented in Spartan ver 5.0 (Wavefunction Inc.) for SGI computers.

It would therefore seem that computer aided molecular modeling provides a versatile way of predicting and studying the conformation of compound **1** and therefore should be adequate to study its derivatives. One would ideally use the Merck molecular

mechanics method as implemented in Spartan 5. However, molecular mechanics methods are limited to the prediction of molecular conformations and are not useful for prediction of thermodynamic parameters such as heat of formation (ΔH_f).

Given that the tetrahydro[5]helicene unit is helical and therefore chiral, the question remains whether or not it can be resolved into its enantiomeric forms. Whether it can or can not can provide information on its motion on a molecular level. In order to examine this and the basic chiral properties of the tetrahydro[5]helicene, several imide derivatives of compound **1** with enantiomerically pure amines were made. The results of this should be the formation of a pair of diastereomers, the presence of which can be confirmed by NMR spectroscopy. For example, compound **1** was imidized with (S)-methylbenzylamine, (R)-2-aminobutanol and (R)-3-phenyl-2-amino-1-butanol to give compounds **2-5e** and **2-5h-i** respectively. Taking compound **2-5e** as an example, there was no evidence by ^1H or ^{13}C NMR that compound **2-5e** exists as a pair of diastereomers, at least at room temperature and on the time scale of the NMR experiment. This implies that the tetrahydro[5]helicene unit has a lower energy barrier for racemization than [5]helicene. This is in contrast to [5]helicene itself which can be resolved at room temperature into its enantiomeric forms, although the measured half-life for [5]helicene is only 62 minutes.¹² It would therefore be of interest to determine the racemization barrier of the tetrahydro[5]helicene unit as the energy required to overcome this barrier will give an idea of the amount of free motion that this unit has within its molecular free volume.

It is generally agreed that the racemization of a helicene is strictly a thermally induced process and the magnitude of the energy required is related only to the steric bulk of the helicene itself. Since the thermal twisting of large aromatic structures seems

unlikely, the racemization of helicenes was initially thought to involve a Diels-Alder Retro-Diels-Alder path. However, this pathway has since been disproven using deuterium labeling experiments. The thermal racemization starts with the helicene in its C_2 symmetric P form, which then undergoes a thermally induced rearrangement to a C_s transition state, which thermally relaxes to the other enantiomer, the C_2 symmetric M form. Several research groups have used molecular modeling to study the racemization barrier of several $[n]$ helicenes and substituted $[n]$ helicenes using semi-empirical methods.¹³ One can assume with a great degree of certainty that the tetrahydro[5]helicene unit undergoes the same thermal racemization pathway (illustrated in Figure 2-7). Therefore, we set out to calculate the energy barrier to thermal racemization of the tetrahydro[5]helicene unit using the AM1 semi empirical method.¹¹

Figure 2-7. Mechanism for racemization of [5]helicene and tetrahydro[5]helicene.

Since the anhydride group is not directly involved in the thermal racemization process and does not provide any steric hindrance to the process one can assume it does not effect the energy required to racemize the tetrahydro[5]helicene unit. As a result, in order to reduce the amount of computation time required, the anhydride group of compound **1** was omitted and only the transition state for the unfunctionalized tetrahydro[5]helicene unit was calculated.

Figure 2-8. Calculated racemization barriers of [5]helicene and tetrahydro[5]helicene.

P-tetrahydro[5]helicene (C_2 symmetry)

transition state (C_3 symmetry)

M-tetrahydro[5]helicene (C_2 symmetry)

Figure 2-9. Calculated molecular conformations of P-tetrahydro[5]helicene, transition state and M-tetrahydro[5]helicene.

The results of these calculations are illustrated in Figure 2-8 and Figure 2-9. The molecular models shown in Figure 2-9 are rendered from energy minimized structures obtained for both the C_2 symmetric P and M enantiomers and the C_s symmetric transition state. By looking at the difference between the heat of formation (H_f) calculated for the P and M states with the transition state, the energy for racemization can be estimated to be $13.88 \text{ kcal mol}^{-1}$. Furthermore, the energy of racemization between the P and M forms and the transition state can be thought to have a Gaussian distribution of energies as shown in Figure 2-8. When the same method was used to calculate the energy of racemization of [5]helicene it was estimated to be $23.91 \text{ kcal mol}^{-1}$, which is nearly twice that obtained for tetrahydro[5]helicene.

In order to gain perspective on the calculated racemization energies, let us consider the amount of thermal energy available at room temperature. The amount of thermal energy available at any given temperature (E_T) is given by:

$$E_T = k \cdot N \cdot T$$

where k is the Boltzmann constant ($1.38066 \times 10^{-23} \text{ J K}^{-1}$), N is the number of molecules per mole ($6.02214 \times 10^{23} \text{ mol}^{-1}$) and T is the temperature in Kelvins. Using this equation the amount of energy available at room temperature can be calculated to be $9.5 \text{ kcal mol}^{-1}$ ($1 \text{ cal} = 4.184 \text{ J}$). On comparison with the calculated racemization barriers of tetrahydro[5]helicene and [5]helicene one can see that the racemization barrier of tetrahydro[5]helicene is on the order of the available energy at room temperature whereas the same from [5]helicene is ~ 2.5 times the energy available at room temperature.

This supports the observation that the tetrahydro[5]helicene unit does not exist as two distinct enantiomeric forms at room temperature. Furthermore, the low racemization

barrier is an indication that the tetrahydro[5]helicene unit has significantly more motion within its molecular free volume than [5]helicene. As a result, the tetrahydro[5]helicene unit should possess a higher mobility within its molecular free volume once incorporated into a polymeric system as compared to [5]helicene. If this is true there will be an observable difference in the physical properties (e.g. T_g , solubility) of a polymer containing a tetrahydro[5]helicene unit compared to the same containing a [5]helicene unit.

2.6. Conclusion.

In conclusion, due to the number of functional derivatives of the tetrahydro[5]helicene unit that can be made and the specific arrangements of those chemical functionalities in space, the tetrahydro[5]helicene unit fits the criteria set out for a versatile core molecule. For example, from this core molecule several key derivatives can be selectively made by use of readily available reagents. It can therefore be used to test new polyimide-forming reactions and synthetic pathways specific to polyimide synthesis and chemistry. Furthermore, one can study the effect that the incorporation of this new and unique molecular structures has on the physical properties of the polyimide for which it is a part. Additionally, one can attribute any observed differences in the physical properties of the polyimide directly to the presence of the tetrahydro[5]helicene unit because of its known and predicted molecular conformation and motion.

2.7. Experimental.

For general experimental methods see Appendix A.

5,6,9,10-Tetrahydro-[5]helicene-7,8-dicarboxylic anhydride (1).

The reported procedure¹⁴ was modified for large-scale preparation as follows: (a) In a 10 L reaction vessel α -tetralone (1200 g, 8.20 mol) was dissolved in 3.5 L of toluene and 2.0 L of absolute ethanol. To this solution aluminum foil (227 g, 8.40 mol, approx. 2 x 2 cm) and HgCl_2 (7.00 g, 25.0 mmol) were added and the solution was vigorously stirred with gentle heating. The reaction was sufficiently exothermic to the solvent to reflux. After 4 h, an aqueous HCl solution (800 mL of conc. HCl diluted to 4 L) was added in one portion and the resulting heterogeneous mixture was allowed to stir overnight. The organic phase was decanted, dried over MgSO_4 and removed to yield the pinacol product as a slightly yellow solid. The remaining aqueous phase was extracted with diethyl ether (3 x 3 L). The ethereal extract was dried and removed to yield more product. The yield was 867 g (71%). This product (498 g, 1.70 mol) was mixed with 600 mL of acetic anhydride and 400 mL of acetic acid and refluxed overnight. The reaction was allowed to cool to room temperature and the precipitate was filtered to give the corresponding diene (329 g, 74%). (b) The diene (329 g, 1.30 mol) and maleic anhydride (950 g, 9.70 mol) were placed in an Erlenmeyer flask and heated at 155 °C for 3 h. While still hot and homogeneous, the reaction mixture was dumped into 2.0 L of hot water with vigorous

stirring. The resulting slurry was stirred for 2 h. The solid was filtered and divided into two portions which were then stirred in water (2 L each) overnight. The solid was filtered and washed with 450 mL of glacial acetic acid. The solid was once again filtered and dried. The corresponding Diels-Alder adducts of endo and exo isomers was obtained (387 g, 85%). (c) The Diels-Alder products (385 g, 1.10 mol) were dissolved in chloroform (2.1 L) and stirred at room temperature in a 4 L, 3-necked, round-bottomed flask fitted with a gas outlet routed to an aqueous KOH solution. To this chloroform solution, Br₂ (440 g, 2.80 mol) in acetic acid (200 mL) was added dropwise over 1.5 h. The reaction mixture was allowed to stir at room temperature overnight. The precipitate was filtered, washed with methanol (2 x 1.0 L) and dried (60-80 °C, 5 mmHg) to give anhydride **1**: 317 g (82% or 37% yield based on α -tetralone); mp 286-287 °C (lit^{12a} 282 °C, lit^{12b} 275 °C).

3-Nitro-5,6,9,10-tetrahydro-[5]helicene-7,8-dicarboxylic anhydride (2-2a).

Anhydride **1** (30.0 g) was dissolved in 1.1 L of chloroform, to which was added 300 mL of acetic acid. The nitrating agent (390 g of 70% nitric acid and 450 g of concentrated sulfuric acid in 450 mL of acetic acid) was added dropwise to the above solution with vigorous stirring at room temperature (22 °C). The reaction continued for 4 h until TLC showed no more starting material. After the stirring was stopped the organic phase (top)

was separated from the acid phase (bottom). Extraction of the acid phase with chloroform gave no product. The organic phase was washed with water until the washings were pH 7 to litmus. The chloroform layer was dried with MgSO_4 to give a mixture of compound **2-3a** and **2-3b** (90/10 ratio by ^1H NMR). Two successive precipitations of a dichloromethane solution into methanol, filtering and drying in a vacuum oven ($60\text{ }^\circ\text{C}$, 5 mmHg) gave pure compound **3a** (26.0 g, 76%). Evaporation the filtrate afforded 6.6 g (20%) of a mixture of the isomers **3a** and **3b** in about a 1:1 ratio. Compound **3a** could be recrystallized from a mixture of acetonitrile and dichloromethane as a yellow crystalline solid. mp $267.3\text{ }^\circ\text{C}$ (DSC); IR (KBr, C=O) $1763, 1830\text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3) δ 8.23 (1 H, d, $J = 2.36\text{ Hz}$), 7.80 (1 H, q, $J = 2.36\text{ Hz}$, $J = 4.36\text{ Hz}$), 7.34 (3 H, m), 7.01 (2 H, m), 4.02 (2 H, t, $J = 19.3\text{ Hz}$), 3.07 (4 H, m), 2.64 (2 H, m); ^{13}C NMR (50 MHz, CDCl_3) δ 162.78, 162.74, 147.31, 142.21, 140.95, 140.60, 140.42, 139.34, 138.37, 132.07, 130.92, 130.41, 129.90, 128.46, 126.91, 126.52, 125.65, 123.29, 123.13, 121.13, 28.26, 28.10, 24.18, 24.11; MS (EI, m/e, relative intensity %) 397 (M^+ , 100).

3,12-Dinitro-5,6,9,10-tetrahydro-[5]helicene-7,8-dicarboxylic anhydride (2-3).

Compound **2-2a** (30.0 g) was dissolved in 1.0 L of chloroform, to which was added 300 mL of acetic acid. The nitrating agent (275 mL of 70% nitric acid and 250 mL of

concentrated sulfuric acid in 450 mL of acetic acid) was added dropwise to the above solution with vigorous stirring at room temperature (22 °C) over a 0.5 hr period. The reaction continued for 3 days until TLC showed no more starting material. After the stirring was stopped the organic phase (top) was separated from the acid phase (bottom). Extraction of the acid phase with chloroform gave no product. The organic phase was washed with water (6 x 250 mL, until the washings were pH 5 to litmus), 10% KHCO_3 (2 x 250 mL) dried with MgSO_4 and removed. The solid was dissolved in a minimum of hot CH_2Cl_2 (450 mL), which on slow evaporation gave 3 crops of yellow crystals, compound **2-3** (14.0 g, 43% yield). mp >300 °C; IR (KBr, C=O) 1762, 1835 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, 1H, $^4J=2.3$ Hz), 7.75 (dd, 1H, $^3J=8.6$ Hz, $^4J=2.3$ Hz), 7.13 (d, 1H, $^3J=8.6$ Hz), 4.0 (d, 1H, $^2J=15.5$ Hz), 3.1 (d, 1H, $^2J=12.1$ Hz), 2.9 (td, 1H, $^2J=12.1$ Hz, $^3J=3.3$ Hz), 2.6 (t, 1H, $^2J=15.5$ Hz) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 163.2, 148.6, 141.9, 141.7, 140.5, 139.2, 132.0, 128.1, 124.5, 122.4, 29.1, 24.8 ppm; MS (EI, m/e, relative intensity %) 442 (M^+ , 100). HRMS calcd. for $\text{C}_{24}\text{H}_{14}\text{N}_2\text{O}_7$ 442.0801, found 442.0808 .

1,3,12-Trinitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (2-4).

Anhydride **1** (20.0 g, 56.8 mmol) was dissolved in conc. sulfuric acid (300 mL) at -5 to -10 °C. To this solution a mixture of 70% HNO_3 (18.4 g) and conc. sulfuric acid (50 mL)

was added of a period of 30 min. 30 minutes after addition was complete, the reaction mixture was dumped over 2000 mL of crushed ice. The crude yellow precipitate was collected by filtration, washed with water (2 x 1 L) and dried under vacuum overnight (5 mmHg, 50 °C). The dried product could be recrystallized from dichloromethane to give orange crystals, compound **4** (23.2 g, 83.3% yield). mp >300 °C; IR (KBr, C=O) 1760, 1837 cm⁻¹; ¹H NMR (200 MHz, DMSO-d₆) δ 8.42 (s, 1H), 8.31 (d, 1H), 7.86 (d, 1H), 7.67 (s, 1H) 7.28 (d, 1H), 3.12 (m, 4H), 2.95 (m, 2H), 2.55 (m, 2H); ¹³C NMR (50 MHz, DMSO-d₆) δ 168.9, 168.8, 146.7, 146.2, 141.8, 140.3, 140.2, 139.2, 138.9, 137.6, 137.4, 133.9, 133.3, 132.4, 131.8, 131.2, 126.4, 125.1, 122.9, 121.1, 28.1, 27.9, 26.7, 26.6; MS (EI, m/e, relative intensity %) 487 (M⁺, 100). HRMS calcd. for C₂₄H₁₃N₃O₉ 487.0651, found 487.0640.

Imide derivatives of **1** (2-5a-i)

Imides 2-5a, 2-5b, 2-5e and 2-5f. General procedure: To a heterogeneous mixture of the tetrahydro[5]helicene anhydride (1 equivalent) in DMF (20% w/v, dried over molecular sieves) was added the amine (2-3 equiv.). After stirring at room temperature for 1 hr, the solution was clear and homogeneous (except for **2-5f** which formed a white

precipitate which dissolved on heating) at which point it was set to reflux overnight. The yellow homogeneous solution was cooled to room temperature and added dropwise with vigorous stirring to a 10% HCl aqueous solution (6 x DMF volume). The resulting yellow precipitate was filtered, washed with water (until the washings were neutral to litmus) and dried in vacuo overnight (80 °C, 5mmHg).

5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic-N-(n-butyl) imide (2-5a). A yellow amorphous powder: yield 71.0 %: m.p. 166 - 168 °C: IR (KBr, C=O) 1754, 1702 cm^{-1} : ^1H NMR (400 MHz, CDCl_3) δ 7.28 (t, 1H), 7.17 (d, 1H), 7.13 (d, 1H), 6.90 (t, 1H), 4.07 (s, 1H), 3.65 (t, 1H), 2.9 (d, 2H), 2.5 (s, 2H), 1.65 δ (m, 1H), 1.37 (m, 1H), 0.92 (t, 1.5H): MS (EI, m/e, rel. %) 407 (M^+ , 100).

5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic-N-(2-hydroxyethyl) imide (2-5b). A yellow amorphous powder: yield 94 %: m.p. >290 °C: IR (KBr) 3536 (OH), 1757, 1706 (C=O) cm^{-1} : ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, 2H), 7.15-7.25 (m, 4H), 6.95 (t, 2H), 4.1 (b, 2H), 3.9 (m, 2H), 2.9 (m, 4H), 2.5 (b, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 176.6, 170.1, 139.8, 139.51, 134.18, 130.9, 129.09, 128.44, 126.5, 119.3, 62.2, 41.3, 29.2, 24.9 ppm. MS (EI, m/e, rel. %) 395 (M^+ , 100): HRMS calcd. for $\text{C}_{26}\text{H}_{21}\text{NO}_3$ 395.1521, found 395.1512.

5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic-N-((S)-2-ethylbenzene) imide (2-5e). A pale yellow amorphous powder; yield 74 %: IR (KBr) (C=O) 1756, 1704 cm^{-1} : ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, 2H), 7.22-7.40 (m, 5H), 7.18 (t, 2H), 7.14 (d, 2H), 6.92 (t, 2H), 5.59 (q, 1H), 4.10 (d, 2H), 2.89 (d, 2H), 2.49 (b, 2H), 1.93 (d, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 140.5, 139.2, 138.8, 138.5, 133.5, 130.2, 128.7, 128.4,

127.7, 127.5, 127.4, 125.8, 125.7, 49.4, 28.6, 24.1, 17.3 ppm. MS (EI, m/e, rel. %) 455 (M^+ , 100); $[\alpha]_D^{25}(\text{CHCl}_3) = -57.4^\circ$ (25 °C, 1 mg mL⁻¹ CHCl₃).

5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic-N-amino imide (2-5f).

A pale yellow amorphous powder; yield 94 %; m.p. > 300 °C; IR (KBr) 1709, 1760 (C=O); 3280, 3347 (-NH₂) cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 6.3 (bm, 6H), 5.9 (bm, 2H), 2.9 (bm, 2H), 1.9 (bm, 4H), 1.5 (bm, 2H) ppm; ¹³C NMR (50 MHz, CDCl₃) δ 167.6, 139.7, 139.4, 139.3, 133.9, 130.7, 128.9, 128.3, 126.3, 124.5 ppm; MS (EI, m/e, rel. %) 366 (M^+ , 100).

Imides 2-5c and 2-5d. General procedure: Anhydride **1** (20.0 g, 56.8 mmol) and *m*- or *p*-nitroaniline (11.8 g, 85.2 mmol) was placed in a mixture of 100 mL of DMF and 50 mL of acetic acid. The heterogeneous reaction mixture was heated at reflux overnight. The homogenous reaction mixture was dumped into 300 mL of vigorously stirred dilute HCl solution. The resulting precipitate was filtered and washed with dilute HCl (200 mL), water until the washings were neutral to litmus and finally methanol (2 x 100 mL). After drying in air and then at 50 °C under vacuum (5 mmHg), the corresponding imide was obtained.

5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic-N-(3-nitrophenyl) imide (2-5c):

55% yield; m.p. 215-219 °C; IR (KBr) 1763 cm⁻¹, 1712 cm⁻¹ (C=O, imide); ¹H NMR (400 MHz, CDCl₃) δ 2.58 (m, 1H), 2.94 (m, 1H), 4.14 (m, 1H), 6.95 (t, 2H), 7.1-7.3 (m, 6H), 7.67 (t, 1H), 7.86 (d, 1H), 8.24 (d, 1H), 8.43 (s, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 24.37, 28.56, 121.68, 122.34, 125.29, 125.97, 127.86, 128.70, 129.71, 130.33,

132.27, 133.26, 133.40, 139.19, 139.64, 139.88, 148.55, 167.07 ppm; MS (EI, m/e, relative intensity %) 472 (M^{+} , 100.0).

5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic-N-(4-nitrophenyl) imide (2-5d):

78% yield; m.p. 244 - 248 °C; IR (KBr) 1764 cm^{-1} , 1713 cm^{-1} (C=O, imide); ^1H NMR (400 MHz, CDCl_3) δ 2.58 (m, 1H), 2.96 (m, 2H), 4.16 (m, 1H), 6.95 (t, 1H), 7.19 (m, 2H), 7.33 (d, 1H), 7.75 (d, 1H), 8.35 (d, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 24.35, 28.54, 124.32, 125.28, 125.99, 126.62, 127.87, 128.73, 130.32, 133.38, 137.92, 139.16, 139.68, 139.97, 146.31, 166.65 ppm; MS (EI, m/e, relative intensity %) 472 (M^{+} , 36.7).

Imides 2-5g, 2-5h and 2-5i. General procedure:

To a solution of compound **1** (3.00 mmol) in *o*-dichlorobenzene (10 mL) in a round-bottomed flask fitted with a Dean-Stark trap and argon inlet was added the amine (3.06 mmol) and isoquinoline (0.1 mL). The solution was stirred at room temperature for 1 h, and then set to reflux overnight. The *o*-dichlorobenzene solution could be directly precipitated into methanol and the yellow powder removed by filtration. Alternatively, the *o*-dichlorobenzene solution could be concentrated. The concentrate was then dissolved in chloroform and precipitated into *n*-pentane and the resulting yellow solid was filtered.

5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic(N-(R/S)-1-ethyl-2-hydroxyethyl) imide (2-5g).

2.98 g (83% yield); m.p. 185- 190 °C; IR (KBr) 1754, 1698 (C=O), 3438 (OH) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.1-7.4 (m, 6H), 6.91 (t, 2H), 3.7-4.4 (m, 5H), 2.89 (m, 4H), 2.51 (m, 2H), 1.90 (m, 2H), 0.95 (t, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3)

δ 170.08, 139.43, 139.35, 139.04, 133.76, 130.55, 128.64, 128.01, 126.09, 125.87, 63.67, 55.35, 28.84, 24.41, 22.01, 11.21 ppm; MS (EI, m/e, relative intensity %) 423 (46.5).

5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic(N-(R)-1-ethyl-2-hydroxyethyl) imide (2-5h). 15.5 g (81% yield); m.p. 180- 183 °C; IR (KBr) 1755, 1698 (C=O), 3438 (OH) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, 2H), 7.21 (t, 2H), 7.17 (d, 2H), 6.95 (t, 2H) 4.31 (m, 1H), 4.08 (m, 3H) 3.91 (d, 1H), 2.93 (m, 4H), 2.53 (m, 2H), 1.93 (m, 2H), 1.75 (s, 1H, OH), 0.98 (t, 3H) ppm: ^{13}C NMR (100 MHz, CDCl_3) δ 169.83, 139.18, 139.11, 138.79, 133.50, 130.30, 128.39, 127.75, 125.83, 125.60, 63.43, 55.08, 28.59, 24.14, 21.74, 10.93 ppm; MS (EI, m/e, relative intensity %) 423 (43.2); HRMS calcd. for $\text{C}_{28}\text{H}_{25}\text{NO}_3$ 423.1834, found 423.1823; $[\alpha]_{\text{D}} = +10^\circ$ (25 °C, 1mg mL^{-1} , CHCl_3).

5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic(N-1-phenyl-2-hydroxyethyl) imide (2-5i). 800 mg (58% yield); m.p. 103-105 °C; IR (KBr) 1754, 1698 (C=O), 3385 (OH) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.15-7.35 (m, 11H), 6.92 (t, 2H), 4.7 (d, 1H, OH), 4.2-3.9 (m, 3H), 3.2-3.4 (m, 3H), 2.85 (m, 4H), 2.5 (m, 2H) ppm: ^{13}C NMR (100 MHz, CDCl_3) δ 169.57, 139.15, 139.10, 138.76, 138.14, 133.48, 130.28, 129.15, 128.57, 128.40, 127.76, 126.40, 125.83, 125.52, 62.85, 54.84, 34.92, 28.54, 24.09 ppm; MS (EI, m/e, relative intensity %) 485 (43.8); HRMS calcd. for $\text{C}_{33}\text{H}_{27}\text{NO}_3$ 485.1991, found 485.2016; $[\alpha]_{\text{D}} = +72^\circ$ (25 °C, 1 mg mL^{-1} CHCl_3).

[5]Helicene-7,8-dicarboxylic anhydride (2-11). **Oxidation with bromine.**

To a refluxing solution of anhydride **1** (1.00 g, 2.84 mmol) in TCE (10 mL), was added Br₂ (1.13 g, 7.10 mmol) dropwise over 10 min. After 1 h the reaction solution was cooled to room temperature and poured into 50 mL of hexane. The resulting yellow precipitate was collected by filtration, washed twice with hot hexane, and dried in a vacuum oven (5 mmHg) at 130 °C. The pure anhydride **2-11** was obtained as a yellow solid and could be further recrystallized from DMAc: 0.96 g (97%);

Oxidation with atmospheric oxygen.

A finely divided powder of anhydride **1** (20 mg) was placed in a sealed glass tube (10 cm long, 0.5 cm I.D.) with an atmosphere of air. The tube was then placed in a preheated oven at 300 °C. After 2.5 h the tube was removed and cooled to room temperature. The contents were dissolved in chloroform and some insoluble material was filtered. The filtrate was dried over MgSO₄ and the solvent was removed under reduced pressure to give [5]helicene-7,8-dicarboxylic anhydride (**2-11**, 17-18 mg, 86-91%).

mp 276-277 °C, 275.7 °C (DSC) (lit >360 °C); IR (KBr, C=O) 1839, 1756 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.91 (1 H, d, J = 8.76 Hz), 8.39 (1 H, d, J = 8.56 Hz), 8.15 (1 H, d, J = 8.76 Hz), 8.02 (1 H, d, J = 8.04 Hz), 7.64 (1 H, t d, J₁ = 1.00 Hz, J₂ = 8.04 Hz), 7.31 (1 H, t d, J₁ = 1.00 Hz, J₂ = 8.56 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 163.52,

133.77, 132.90, 131.00, 130.43, 129.54, 128.80, 128.33, 126.53, 126.38, 125.68, 120.96;

MS (EI, m/e, relative intensity %) 348 (M^+ , 64.1), 276 (100); HRMS calcd. for $C_{24}H_{12}O_3$

348.0786, found 348.0798.

2.8. References.

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Chapter 3. Polyimide formation in the solid state.

3.1. An AB-type amino anhydride monomer.

Unlike polyesters and polyamides, which can be made by polycondensation of either two difunctional monomers (AA + BB) or a bifunctional monomer (AB), conventional polyimides are made exclusively by polycondensation of an aromatic dianhydride with an aromatic diamine (AA + BB). Few attempts have been undertaken to synthesize polyimides from AB-type amino-anhydride monomers presumably because common wisdom dictates that such a monomer should self-polymerize and form a poly(amic acid) at ambient temperatures.

Figure 3-1. Synthesis and solution polymerization of 3-Amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**3-1**). Conditions: (i) H₂ (60 psi), PtO₂, AcOH (cat.), THF. (ii) *m*-Cresol, isoquinoline, 200 °C.

However, our lab has reported the first case of a stable AB-type amino-anhydride monomer. 3-Amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**3-1**,

Figure 3-1) is indefinitely stable in the solid state and does not form the expected poly(amic acid) at ambient temperatures nor in solution in certain non-polar or non-hydrogen bonding solvents. It will however, form a poly(amic acid) if placed in strong polar solvents such as DMSO and DMAc. At elevated temperatures it becomes activated to polymerization and can be readily polymerized at 200 °C in *m*-cresol to give a high molecular weight polyimide **3-2** (Figure 3-1).¹ A single crystal of AB-monomer **3-1** was grown from chloroform solution and the molecular structure was determined by x-ray diffraction. The results of which are included in Appendix E.

During the course of the investigation into monomer **3-1** it was observed that it formed coherent yet brittle films on evaporation of its solutions from certain organic solvents (Figure 3-2). These films are red in colour, transparent and were shown to be completely devoid of crystalline regions as indicated in their WAXD spectrum (Figure 3-3).

Figure 3-2. Films of AB-monomer **3-1** from CHCl₃ solution as viewed under plane polarized light.

Figure 3-3. WAXD spectrum of a film of AB-monomer **3-1**.

On closer examination of the arrangement of AB-monomer **3-1** within its single crystal it can be seen that compound **3-1** is arranged such that there is a hydrogen bonding interaction between the amino and anhydride groups of adjacent molecules. The amino and anhydride functions form a six-membered hydrogen bonded moiety having hydrogen-oxygen distances of 2.48 Å and 2.50 Å. In other words the assembly of the AB-monomer within its single crystal is governed not only by crystal packing interactions but also by the formation of an array of hydrogen bonded molecules. The anhydride carbonyl involved in the hydrogen-bonding entity is the one that is *para* to the amino group. In order to determine whether this hydrogen-bonding association is unique to the single crystal or happens under other conditions, monomer **3-1** was examined using STM.

Figure 3-4. STM image of monomer **3-1** as deposited on the surface of graphite from CHCl_3 solution.

An STM image of monomer **3-1** as deposited on the surface of graphite from chloroform solution is shown in Figure 3-4. It clearly shows the graphite surface (upper left) and two intersecting monolayers of monomer **3-1** (bottom and right). The thickness of the layer can be measured using STM, and its identification as such can be confirmed by verifying that the thickness of the layer falls between the expected range for monomer **3-1** (4 – 7 Å). Furthermore, the period of the monolayer (11.3 Å x 6.9 Å) corresponds well to the length and width of **3-1** (Figure 3-5).² Such a regularity and breadth (over 20 nm) in the molecular arrangement suggests that there is method to the assembly of this molecule.

Therefore based on the arrangement of monomer **3-1** within its single crystal and on the surface of graphite, one can conclude that monomer **3-1** has a tendency to self-assemble in the solid-state (Figure 3-5). Furthermore, the assembly is governed by the tendency to form hydrogen-bonding entities between adjacent amino and anhydride groups.

Figure 3-5. Self-assembly of AB-type amino anhydride monomer **3-1**.

Given the tendency of monomer **3-1** to self-assemble in the solid-state through formation of a hydrogen-bonding moiety between its amino and anhydride groups and given that this monomer can be activated to polymerization at elevated temperatures in solution, the following question arises:

Will simple heating in the solid state result in a collapse of the hydrogen-bonding entity and formation of an imide bond?

In order to test the presented hypothesis, monomer **3-1** was spin cast from THF solution (0.20 g mL^{-1}) onto either silicon wafer or Pyrex[®] glass. The deposited film of monomer

3-1 was then thermally treated under argon atmosphere using a specific temperature profile.

Scheme 3-1. Solid-state polymerization of AB-type amino anhydride monomer **3-1**.

Thin polyimide films of the type shown could be made by thermal treatment under inert atmosphere in the solid state (**3-2**, Scheme 1). Thermal treatment induces the monomer to first form oligoimides at 350 °C and final thermal treatment at 450 °C (above the glass transition temperature of the oligoimides³) is necessary to effect complete transformation to high molecular weight polyimide **3-2**. The stepwise transformation from monomer **3-1** to polyimide **3-2** can be confirmed on silicon wafer using FT-IR spectroscopy, by monitoring the disappearance of the C=O anhydride stretching absorptions (1827 cm⁻¹ and 1761 cm⁻¹) and the appearance of the C=O imide stretching absorptions (1764 cm⁻¹ and 1713 cm⁻¹). After treatment at 350 °C the presence of both anhydride and imide functionality can be clearly seen (Figure 3-6). Furthermore GPC analysis indicated that only oligomers were formed (n=1-5) at 350 °C (Figure 3-7). Heating to 450 °C resulted in the complete disappearance of the anhydride absorptions. The film of AB-monomer **3-1** and oligoimides of **3-2** are completely soluble in many solvents and can easily be scratched off of the silicon surface. However the final polyimide film of **3-2** is remarkably scratch resistant and is completely insoluble to

common organic solvents (chloroform, THF, NMP, TCE) even after being exposed to boiling solvents for days.

Figure 3-6. IR spectra of powdered sample of monomer **3-1** in KBr (top), monomer **3-1** as spin-cast on silicon wafer, thin film after treatment at 350 °C and polyimide **3-2** thin film after thermal treatment at 450 °C (bottom).

Figure 3-7. GPC of oligoimide film after treatment at 350 °C.

Heating to this temperature may seem extreme, nonetheless polyimide **3-2** is stable up to temperatures of 490 °C under inert atmosphere. Furthermore, aging experiments of specifically synthesized oligoimides of type **3-2**⁴ have shown them to be stable for prolonged periods of time (18 hours at 350 °C by TGA, Figure 3-8).

There is no indication that this process is a melt process since the appearance of oligoimides of **3-2** can be verified with no visible signs of melting. Using DSC one can observe a melting point only for powdered samples of monomer **3-1** and not a spin-cast film of the same.

Figure 3-8. Mass vs. time for thermal aging of oligoimide of type **3-2**.

The final polyimide films are optically transparent (Figure 3-9), are nearly defect free and show no signs of stress fracturing from the curing process. Examination of the surface topology of both the monomer **3-1** and polyimide **3-2** using SEM shows that the spin-cast film of **3-1** on the surface of the silicon wafer (Figure 3-10a) is coherent, shows

no sign of powdering, has several topographical features and is not of uniform thickness. Whereas the polyimide film 3-2 (Figure 3-10b) is free of defects on its surface and does not show any signs of stress fractures, and is of nearly uniform thickness.

Figure 3-9. Monomer 3-1 film as deposited on glass (left) and polyimide 3-2 film on glass after thermal treatment (right).

Figure 3-10. SEM images of (a) a film of monomer 3-1 as deposited on silicon wafer and (b) a film of polyimide 3-2 on silicon wafer after thermal treatment at 450 °C.

Figure 3-11 illustrates the results obtained using TGA for analysis of both a powdered sample and a film of monomer **3-1**. The use of TGA can provide information as to the mass changes associated with its solid-state polymerization and hence give some insight into the mechanism of the process. When TGA analysis was carried out on dried powdered samples of monomer **3-1** there was a mass loss on heating to 350 °C of ~8% which agrees well with the expected loss of a single molecule of water per repeat unit. The mass of the sample remained constant on continued heating at 350 °C. Similar behaviour was observed for a cast film of monomer **3-1** except that the initial mass loss was ~28% indicating that the spin-cast film contains up to 20% residual solvent. On heating to 450 °C there was a significant weight loss for both samples of ~20%. As the amount of residual water present in these samples can not be nearly that high, the mass loss must be from another source, the loss of residual monomer **3-1**.

In order to account for this observation a model must be proposed which takes into account the possibility for the loss of a quantity of the monomer during the solid-state polymerization process. Hence, the spin-cast films of monomer **3-1** must contain up to 20% monomer that is not self-assembled. This is illustrated in Figure 3-12. Heating to 350 °C is sufficient to form oligoimides from the monomers that are self-assembled (coloured black in Figure 3-12). However, as heating above the glass transition is necessary to effect complete imidization of the oligoimides, this temperature must also allow the monomer units that are not self-assembled (coloured grey in Figure 3-12) to sublime from the polymer film before they can become polymerized and hence incorporated into the polyimide. GPC analysis supports this model as the peak

corresponding to the monomer makes up ~20% of the total sample after heating to 350 °C (Figure 3-7).

Figure 3-11. TGA analysis of dried powder and spin-cast film of monomer **3-1** (the T_g of oligoimides of **3-2** is marked for reference).

Figure 3-12. Proposed model for self-assembly within a spin-cast film of monomer **3-1** (self-assembled molecules are coloured black, non-self-assembled molecules are coloured grey).

Other cases of solid-state polymerization are known. For example, Epple *et al* has shown that salts of α -halo-acetic acids could be thermally polymerized in the solid state (also within a single crystal) to produce the corresponding polyester.⁵ Imai *et al* were able to produce both aromatic and aromatic/aliphatic polyimides by thermal treatment of nylon-salt-type monomers in the solid state.⁶ Furthermore, vapour deposition techniques have been used extensively to form thin and ultra-thin polyimide (e.g., Kapton) films.⁷ This process requires the use of a specialized apparatus and is limited in general utility because only a few diamine and dianhydride monomers can be used.⁸

The unique ability of monomer **3-1** to undergo a solid-state polymerization differentiates it from the mentioned examples in two ways. Firstly, it is stable to self-polymerization at room temperature, making isolation and manipulation possible. Yet the monomer becomes activated to polycondensation at elevated temperatures. Secondly, the solid-state polymerization is brought about by the collapse of a hydrogen-bonding entity between an amino and an anhydride group which is possible because monomer **3-1** has a tendency to self-assemble through the formation of this hydrogen-bonding entity.

This method for polyimide thin film formation has several advantages over traditional methods. Polyimide films, produced by vapour deposition polymerization of the respective monomers, are highly ordered ultra-thin films and the polymer chains are perpendicular to the substrate surface, frequently making them brittle and noncoherent.⁹ Although monomer **3-1** is orientated parallel to the surface of graphite within a monolayer (as shown by STM, Figure 3-4) the deposited films are enormously thick by comparison. Therefore the orientation of the molecules within these films (both pre- and

post-cured films) can be considered to be random and as a result amorphous (in contrast to polyimide films made by vapour deposition). The result is a polyimide film that is structurally coherent and highly scratch resistant.

Spin coating proved to be an effective way to deposit thin films of **3-1** onto the surface of silicon wafers and Pyrex glass plates. Deposited films of monomer **3-1** from 1 to 10 drops of a THF solution drops successfully underwent the solid state polymerization process and produced coherent non-fractured films. As a result, although this system is limited in the number of solvents that can be used,¹⁰ it allows for the control of the polyimide film thickness simply based on the amount of monomer deposited on the substrate. The use of volatile organic solvent such as THF leaves the spin cast monomer films nearly free of solvent, making the presented approach to polyimide thin-film formation a nearly dry process. Removal of any residual THF from the final polyimide film is simple because of its high volatility. In contrast, common polyimides are practically applied as precursor poly(amic acid) solutions in an amide solvent such as NMP (1-methyl-2-pyrrolidinone), with a thermal cure to effect polyimide film formation and solvent removal. Poly(amic acid) solutions when cast are typically 80 wt% solvent and these solutions are extremely viscous (as they are polymer solutions). Furthermore, NMP has low volatility, making its removal from the final polyimide film difficult.

3.2. Polyimide-inorganic hybrid materials.

Given the relative ease, to which the solid-state polymerization of AB-monomer **3-1** can be achieved, it would be of interest to see if the process is compatible with inorganic dopants.

Therefore, two different methods of doping the inorganic species into the polyimide film were investigated. The first, a homogeneous doping, can be accomplished by simply dissolving a soluble inorganic species into a THF solution of monomer **3-1**. For example addition of $\text{Fe}_2(\text{CO})_9$ (20 mg mL^{-1}) to a THF solution of monomer **3-1** (200 mg mL^{-1}) creates a homogeneous solution which can be spin-cast onto either silicon wafer or glass. X-ray analysis of the deposited monomer/iron film showed the presence of iron throughout the monomer film, with only minor local concentrations (Figure 3-13a). Thermal treatment of this spin-cast film resulted in both the solid-state polymerization of monomer **3-1** and the thermal decomposition of $\text{Fe}_2(\text{CO})_9$ to Fe^0 with release of carbon monoxide, forming a polyimide-inorganic hybrid. However this process did not produce a polyimide with iron doped homogeneously throughout the polymer film. In fact, it produced a film with localized iron clusters throughout its structure, measuring up to $10 \text{ }\mu\text{m}$ in diameter (Figure 3-13b). Furthermore, the iron clusters seem to have formed within the polymer structure and then pushed out from the inside, causing a blister on the surface of the polyimide film (shown as dark areas). It therefore seems futile to attempt homogeneous doping if the result is clustering of the inorganic species during the thermal treatment process.

Figure 3-13. Films of (a) monomer **3-1** doped with $\text{Fe}_2(\text{CO})_9$ and (b) polyimide **3-2** doped with Fe^0 .

The second method for doping inorganic species into a polyimide matrix, heterogeneous doping, can be done by mechanically dispersing an insoluble inorganic species into a solution of monomer **3-1**. For example, CdS and elemental Au can be mechanically dispersed in a THF solution of monomer **3-1** (200 mg mL^{-1}) at levels of 100 mg mL^{-1} and 200 mg mL^{-1} respectively and again, spin-cast onto either silicon wafer or glass. Thermal treatment of the cast monomer film produced polyimide thin film doped with the inorganic species described. Figure 3-16 illustrates polyimide thin films containing CdS (Figure 3-14a) and Au (Figure 3-14b) as seen under an electron microscope. Each shows the overall distribution of the inorganic species (lightly coloured) throughout the polyimide film and no significant amounts of clustering can be seen. Furthermore, unlike when these films were homogeneously doped, examination of the films before (not shown) and after thermal treatment shows that there is no change in the distribution or density of the inorganic species within the films (i.e. no clustering occurs during the thermal treatment).

Figure 3-14. Thin film of polyimide 3-2 doped with (a) CdS and (b) Au.

In addition, when the polyimide films are examined at an incline of 60° to the surface (using gold as an example, Figure 3-15) the inorganic particles are clearly coated in a layer of both monomer (before thermal curing, Figure 3-15a) and a polymer film (after thermal curing, Figure 3-15b). This behaviour suggests that this monomer system or one similar could be used as a microencapsulating agent.

Figure 3-15. Thin films of (a) monomer 3-1 and (b) polyimide 3-2 doped with Au sub-micron powder.

Other examples of hybrid polyimide-inorganic thin film formation are known. For example, St. Claire *et al* doped poly(amic acid) solutions of ODA and BTDA with Ag(I) salts (silver(I)perfluorocarboxylates). Thermal treatment of these films resulted not only in the thermal imidization of the poly(amic acid) to the corresponding polyimide, but also the thermal reduction of Ag(I) to Ag⁰. Additionally, during the curing process the Ag⁰ migrated to, and formed clusters on, the surface of the polyimide film. The result was a reflective layer of silver on the surface of the polyimide film.¹¹

However, all attempts to dope polyimide **3-2** with Ag⁰ by dissolving a silver(I)perfluorocarboxylate into the monomer solution of **3-1**, spin coating and thermally curing the monomer film were unsuccessful. The reason for this is two-fold. Firstly, the ability of the presented monomer (**3-1**) to undergo a solid state polymerization is brought about by its tendency to self-assemble in the solid-state and the self-assembly itself is a result of the formation of a hydrogen-bonding entity between the amino and anhydride functions present in monomer **3-1**. Therefore any inorganic species present in the monomer solution or deposited film of **3-1** that will interfere with the self-assembly will, as a consequence, impede the solid-state polymerization. Silver(I)trifluoroacetate is a known Lewis acid and likely complexes with the amino group and hinders the self-assembly of **3-1**. Secondly, any species that can undergo a thermal reduction, will act as an oxidant and induce the tetrahydro[5]helicene unit to aromatize to its [5]helicene analogue, as the aromatization of the tetrahydro[5]helicene unit with molecular oxygen is known.¹² The thermal reduction of Ag(I) to Ag⁰ was desirable in the study presented by St Clair *et al*, but is highly undesirable in the process presented in this paper as it is likely to induced the aromatization of the tetrahydro[5]helicene unit in **3-1** to its [5]helicene

analogue. The self-assembly, and hence solid-state polymerization, of the fully aromatic analogue to monomer **3-1** is not presently known.

3.3. An A₂B-type diamino anhydride monomer.

In an effort to extend this concept of solid-state polymerization, compound **3-3** was made by reduction of its dinitro precursor **2-3** with iron and hydrochloric acid (Scheme 3-2). Compound **3-3** is an A₂B-type diamino anhydride as such should form hyperbranched polyimides on polymerization. However, unlike its AB-analogue compound **3-3** is not stable to self-polymerization at room temperature in solution and as a result can only be isolated in low yield. However, it is stable at room temperature in the solid-state and for short periods of time in solution. As a result it can be spin-cast onto a silicon wafer from THF solution. As with compound **3-1** thermal treatment as before results in the formation of hyperbranched polyimides within the solid-state (**3-4**).

Scheme 3-2. Synthesis and solid-state polymerization of 3,12-diamino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**3-3**). Conditions: (i) Fe, HCl, EtOH, THF, 50 °C. (ii) Δ .

The step-wise transformation of A₂B-monomer **3-3** to hyperbranched polyimide **3-4** can again be confirmed using FT-IR spectroscopy by monitoring the disappearance of the

anhydride stretching frequencies and the appearance of the imide stretching frequencies (Figure 3-16). As is the case with AB-monomer **3-1**, the IR spectrum of the spin-cast film of A₂B-monomer **3-3** is identical to its spectrum obtained as a KBr pellet. On heating to 350 °C there is an appearance of an imide stretching absorption although significant amounts of anhydride are left. The hyperbranched oligoimides produced are not soluble in chloroform and therefore GPC analysis is not possible. Heating to 450 °C again resulted in the complete imidization of the sample producing hyperbranched polyimide **3-4** by solid-state polymerization (Figure 3-16).

Figure 3-16. IR spectra of powdered sample of monomer **3-3** in KBr (top), monomer **3-3** as spin-cast on silicon wafer, thin film after treatment at 350 °C and polyimide **3-4** thin film after thermal treatment at 450 °C (bottom).

The IR spectrum of polyimide **3-4** also confirms the presence of residual amino groups as would be expected given the hyperbranched structure. Attempts to

functionalize the amino groups present on the surface with reagents such as perfluorooctanoyl chloride and 3-(isocyanate)propyltriethoxysilane were likely successful however not confirmed due to the inability to detect the chemical change on the surface by the means available.

3.4. AB-monomer stability.

AB-monomer **3-1** is stable at room temperature whereas A₂B-monomer **3-3** is not. Therefore the stability of monomer **3-1** is not due to the tetrahydro[5]helicene moiety specifically. *So why is it stable?* In order to attempt to explain this observation molecular modeling was conducted on AB-monomer **3-1** and several analogous compounds illustrated in Figure 3-17 using the AM1 semi-empirical method as implemented in HyperChem version 5.01. The compounds were chosen since all contain an amino group and a carbonyl group in conjugation across a biphenyl moiety. In some cases the biphenyl moiety is bridged with an ethylene group (**3-5**, **3-7**) and in others it is not (**3-6**, **3-8**).

Figure 3-17. Analogous AB-type monomers.

Several geometric and electronic parameters can be considered:

- The C-N bond length in the amino group
- The sum of the bond angles within the amino group[†]
- The global charge of the amino group[‡]
- The C-C bond length of the carbonyl group para to the amino group across the biphenyl moiety
- The electron density on both the nitrogen and the carbonyl groups.

What was found by calculation for the compounds illustrated in Figure 3-17 was a shortening of the C-N bond distance and the amino group having more sp^2 character as compared to other aromatic amino compounds.[§] Furthermore, the global charge of the amino group (Q_g) was more positive indicating a decrease in the electron density present on the amino group. Furthermore, for the carbonyl para across the biphenyl moiety there was a calculated increase in the electron density and a lengthening of the C-C bond distance as compared to other aromatic anhydrides.^{**} Therefore based on these

[†] The closer the sum of the bond angles is to 360° the more sp^2 character is present within the amino group.

[‡] The global charge is defined as $Q_g = Q_N + Q_H + Q_H$ where Q is the AM1 calculated charge density.

[§] Diamines used for comparison: PPD, MPD, ODA, MDA and 2,2-isopropylidene dianiline, 2,2-hexafluoroisopropylidene dianiline (see Figure 1-3).

^{**} Dianhydrides used for comparison: PMDA, s-BPDA, BTDA and 6FDA (see Figure 1-2)

calculated trends, one can therefore propose the following mechanism for stabilization of AB-monomer **3-1**:

Figure 3-18. Proposed mechanism of stabilization of AB-monomer **3-1**.

The amino and carbonyl groups, through conjugation across the biphenyl moiety form an electronic “push-pull” system that allows for the delocalization of electron density away from the amino group and toward the carbonyl group. Chemically, the result is a decrease in the basicity of the amino group and hence a decrease in its reactivity. Conversely there is an increase in the electron density of the carbonyl group and hence also a decrease in its reactivity to acylation.

3.5. Conclusion.

In conclusion it has been shown that an AB-type amino anhydride monomer **3-1** is stable at room temperature yet can be activated to polymerization at elevated temperatures. The polymerization of this monomer can also be done in the solid-state as well as the previously demonstrated solution polymerization. The polymer forming reaction that occurs within the solid-state is the formation of an imide bond that occurs by the thermally induced collapse of a hydrogen bonding moiety that exists between the amino and anhydride groups.

A new method for the formation of hybrid polyimide-inorganic thin films has been presented and has been used to prepare polyimide-inorganic hybrid thin films containing Fe^0 , CdS and elemental Au. Two different methods for doping the inorganic species into the polyimide film have been explored. Heterogeneous doping proved to be better than homogeneous doping.

The method of solid-state polymerization has been extended to the solid-state polymerization of an A_2B -monomer (**3-3**), which produces hyperbranched polyimides (**3-4**). Although the A_2B -monomer is not stable in solution, it is stable in the solid-state and can be isolated from reaction in low yield.

A model has been proposed to explain the stability observed for AB-monomer **3-1** and several other AB-monomers have been proposed that fit the model and in theory should behave similarly to monomer **3-1**.

3.6. Experimental.

Materials. Tetrahydrofuran (THF) was 99.9% anhydrous HPLC grade inhibitor free and was purchased from Aldrich Chemicals. Cadmium sulphide was obtained as a 1 – 3 μm powder and gold was obtained as a sub-micron powder, both from Aldrich Chemical Co.

Characterization. For general experimental methods see Appendix A.

Apparatus.

Typical method for spin-casting of monomer 3-1 onto substrate.

Two drops of a solution (100 ± 2 mg of 3-1 in 0.50 mL of THF) were deposited onto the surface of a silicon wafer or Pyrex[®] glass plates by spin-casting. Spinning was continued for 30 sec – 1 min in order to ensure maximum evaporation of the solvent.

Typical procedure for the thermal polymerization of monomer 3-1.

A film of monomer **3-1** was heated to 350 °C over 1 h, held for 4 to 18 h then heated to 450 °C, held for 15 min then cooled to room temperature.

3,12-Diamino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (3-3).

Compound **3-2** (0.5919 g) was dissolved in THF (50 mL). To this solution H₂O (10 mL), HCl (1 mL) and Fe powder (6 g) was added. The mixture was sonicated at 50 °C for 2 h. The solution was concentrated to 25 mL then EtOAc (50 mL) was added and the solution was washed with KHCO₃ (20%, 2 x 15 mL), dried over MgSO₄ and removed to yield a red solid. 40% yield; mp >195 °C (dec); IR (KBr) 3457, 3370 (NH₂) 1825, 1760 (C=O) cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 7.08 (d, 2H), 6.61 (s, 2H), 6.31 (d, 2H), 3.8 (m, 2H), 2.5 (m, 4H), 2.1 (m, 2H) ppm.

3.7. References.

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- ² The length and width of **1** shown in Figure 3-5 are the atom to atom distances and not the distances as would be projected onto the graphite surface.
- ³ The glass transition temperature (T_g) for an oligoimide of type **3-2** is ~ 435 °C. See Chapter 5.
- ⁴ Oligoimides of **3-2** are produced after treatment of monomer **3-1** at 350 °C in the solid state. Oligoimides of **3-2** were specifically prepared. The details of which are given in Appendix F.
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- ⁷ (a) Review: Kubono, A.; Okui, N.: *Prog. Polym. Sci.*, **1994**, 19, 389. Specific examples: (b) Kubono, A.; Higuchi, H.; Umemoto, S.; Okui, N.: *Thin Solid Films*, **1993**, 232, 256. (c) Yanagishita, H.; Nakane, T.; Nozoye, H.; Yoshitome, H.: *J. Appl. Polym. Sci.*, **1993**, 49, 565. (d) Liberman, V.; Malba, V.; Bernhardt, A.F.: *Thin Solid Films*, **1997**, 305, 26.
- ⁸ Hutchings, C.W.; Grunze, M.: *Rev. Sci. Instrum.*, **1995**, 66, 3943.
- ⁹ Bitzer, T.; Richardson, N. V.: *Appl. Phys. Lett.*, **1997**, 71(5), 662.
- ¹⁰ Monomer **1** is only soluble in THF at concentrations of 0.20 g mL⁻¹. Other solvents also tried unsuccessfully: acetone, methylethylketone, dichloromethane, chloroform.
- ¹¹ (a) Southward, R.E.; Boggs, C.M.; Thompson, D.W.; St Clair, A.K.: *Chem. Mater.*, **1998**, 10, 1408. (b) Southward, R.E.; Thompson, D.S.; Thompson, D.W.; St Clair, A.K.;

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¹² See Chapter 2 and Chapter 6.

Chapter 4. The transimidization reaction and its application to the synthesis of polyimides, segmented block copolyimides and hyperbranched polyimides.

4.1. Introduction.

Although we have demonstrated that AB-monomer **3-1** and its fully aromatic analogue are stable, common thought would dictate that such monomers should form poly(amic acid)s at ambient temperatures. Furthermore, it must be acknowledged that these monomers may be the only cases of stable AB-type amino anhydride monomers. Indeed the simplest AB-type amino anhydride, 4-aminophthalic anhydride readily forms a poly(amic acid) at ambient temperatures in solution.¹ We therefore wish to develop methodology that can be used when the target AB-monomer is not stable at ambient temperatures. Furthermore, similar to the case with AB-monomer **3-1**, this methodology should allow for the facile purification of the monomer at ambient and moderate temperatures (25 – 100 °C) and activation of the monomer to polymerization at elevated temperatures (150 – 200 °C).

Other methods exist for the synthesis of polyimides from other AB-type monomers. For example, Feld *et al* have synthesized polyimides from AB-type monomers where the anhydride group is masked as a diester moiety. However, only low molecular weight materials were obtained.² The use of such an approach relies on the *in situ* transamidization of the ester groups as the polymer forming reaction. Furthermore, formation of the imide bond involves the removal of another molecule of alcohol from

the amide-ester intermediate, which thought not to be as facile as the removal of a molecule of water.

Polyimides can also be made from AB-type amino (ester-acid) monomers (where the anhydride group has been masked as an ester-acid function). However, monomers of this type are hard to purify, as they tend to revert to the anhydride moiety at moderate to elevated temperatures.

Consider, if the anhydride functionality of a target AB-monomer can be directly masked by the formation of an imide moiety with an electron deficient heterocyclic amine (e.g., 2-aminopyridine or 2-aminopyrimidine) then this has the effect of rendering the anhydride functionality inert. The "AX-type monomer" (X being a masking imide group) can then be activated by either heat or catalyst or both at which time it would undergo a transimidization reaction with itself and form a polyimide.

The transimidization reaction as a method for polyimide synthesis has been known since the 1970s. It was originally used by researchers at GE Company to overcome difficulties in the synthesis and handling of ultra-high purity dianhydrides by blocking the anhydride functionality with an aryl amine.³ The use of electron deficient aryl amines, such as aminopyridines and aminopyrimidines, to block the anhydride group allowed for an exchange reaction to take place with an electron-rich (i.e. more basic) aryl amine (such as aniline). When this aryl amine was a high purity diamine the result was a polymer forming reaction which produced a high molecular weight polyimide. Since that time, except for one case,⁴ this reaction has been largely ignored.

Therefore, an AX-type amino imide monomer has been constructed containing the tetrahydro[5]helicene unit in order to explore this methodology. The

tetrahydro[5]helicene core has been chosen as a model because our lab is familiar with its preparation and the properties of the polyimides which it produces. In addition, given that the A₂B-type diamino anhydride monomer based on the tetrahydro[5]helicene core is not stable to self polymerization, this methodology has been extended to the synthesis of an A₂X-type diamino imide monomer.

4.2. Discussion.

4.2.1. Monomer synthesis.

In order to explore the above concept, compound **4-2** has been synthesized and fully characterized. It was made from mononitro precursor **2-2a** (Scheme 4-1) by imidization with 2-aminopyridine in *o*-dichlorobenzene giving **4-1** in high yield. Compound **4-1** could be reduced with H₂ by use of PtO₂ catalyst to give **4-2** high yield. Both steps were quantitative and did not require purification.

Scheme 4-1. Synthesis of AX-type amino imide monomer **4-2**.

Conditions: (i) 2-aminopyridine, *o*-dichlorobenzene, reflux. (ii) H₂, PtO₂, AcOH, THF.

The spectra obtained for compound **4-2** were consistent with the proposed structure. Furthermore, compound **4-2** had a decomposition temperature of 175 °C. This temperature is considerably lower than the melting points observed for other tetrahydro[5]helicene imide derivatives. This is an indication that the decomposition is a result of polymerization and further indicates that monomer **4-2** meets the requirements stated above. That is, monomer **4-2** is stable at low to moderate temperatures yet polymerizes at elevated temperatures.

4.2.2. Polymer Synthesis.

AX-monomer **4-1** undergoes a transimidization reaction when heated in *m*-cresol at 200 °C and forms a polyimide **4-3** (Scheme 4-2) with release of 2-aminopyridine. No attempt was made to remove the produced 2-aminopyridine from the reaction so that equilibrium conditions could be established. Polyimide **4-3** has been illustrated specifically to emphasize the presence of reactive endgroups. The presence of such groups can be confirmed using ^1H NMR spectroscopy as the resonances from the pyridyl group are distinct. For example, the ^1H within polyimide **4-3** indicated in Scheme 4-2 resonates at 8.74 ppm as shown in the expanded ^1H NMR of polyimide **4-3** (Figure 4-1).

Scheme 4-2. Synthesis of polyimide **4-3** by transimidization reaction of AX-type monomer **4-2**. Conditions: (i) Δ .

Figure 4-1. ^1H NMR spectrum of polyimide **4-3** expanded in the aromatic region.

Both the rate of reaction and obtained molecular weight of polyimide **4-3** are affected by the presence of catalyst and the concentration of the polymerization solution. In order to quantify the effects, experiments were conducted where the molecular weight of polyimide **4-3** was monitored over time using GPC. In order to obtain an accurate determination of the absolute molecular weight using GPC, the instrument was calibrated relative to oligoimides of type **3-2** which were of known molecular weight (absolute molecular weights were determined using MALDI-TOF MS, see Appendix F). Furthermore, as the monomer, dimer, trimer and tetramer of **4-2** were distinguishable in the GPC chromatogram, their molecular weights could also be used for calibration. The instrument had a molecular weight vs. retention time relationship as follows:

$$\text{Retention time} = -0.8752 \ln(\text{mw}) + 15.476$$

for oligoimides of type **3-2** and **4-3**. The best-fit line had an R^2 value of 0.9819.

Figure 4-2. Molecular weight vs. function of time for the formation of polyimide **4-2** via transimidization. Conditions are noted on the figure.

Several experiments were conducted to examine the effect of catalyst and solvent concentration on the formation of polyimide **4-3** via transimidization of monomer **4-2**. The results are illustrated in Figure 4-2. Polyimide **4-3** was formed with highest molecular weight when $\text{Zn}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (a Lewis acid) was used as a catalyst at a monomer concentration of 5 wt% in *m*-cresol. The transimidization reaction was also catalyzed by the presence of isoquinoline. Furthermore, reasonable molecular weight was even obtained when the transimidization was carried out in the absence of catalyst

present. For reference, monomer **3-1** when placed in m-cresol without any catalyst formed only dimers and trimers over a period the same period. When the transimidization reaction was carried out in NCP, monomer **4-2** did not polymerize to any great extent. Therefore it would appear that the use of a phenolic solvent is also necessary in order for the reaction to proceed.

4.2.3. Segmented block copolymer synthesis.

Given that ^1H NMR can confirm the presence of reactive endgroups in polyimide **4-3**, this means that the AX-monomer produces "AX-oligoimides". This leads to the question of whether these oligomers can be used to form block copolyimides by reaction with a dianhydride and a diamine in equal molar amounts. Indeed they can be used in such a way. In these cases the transimidization reaction has been carried out in the absence of catalyst.

In order to facilitate the proof of formation of block copolyimides one needs to choose each block or segment carefully. Given that the glass transition temperature of polyimides of type **4-3** is known to be above 400 °C, this segment can be considered "hard" and "rigid". Therefore the other segment (hereby referred to as the parent polymer) in a block copolymer should be chosen to have a considerably lower glass transition and hence be "soft" and "flexible". This difference in glass transition temperatures should allow for the detection of each by DSC analysis. Indeed this is the case. Additionally, both segments should be soluble in chloroform to make GPC analysis possible. Polyimides of type **4-3** are known to be chloroform soluble in the powdered form. Therefore one needs a parent polymer that has a substantially lower glass

transition than 400 °C and is chloroform soluble. Likely candidates are poly(ether imide)s which generally have glass transition temperatures around 250 °C.

Several poly(ether imide)s were first examined as potential parent poly(ether imide)s for incorporation into block copolyimides with **4-3**. Poly(ether imide)s of BAPP/ODPA (**4-4**), BAPB/ODPA (**4-5**) and TPE-Q/ODPA (**4-6**) were all made by polycondensation in m-cresol at 200 °C with isoquinoline catalyst (Scheme 4-3). All were endcapped with phthalic anhydride and their physical properties examined. All the glass transitions for **4-4**, **4-5** and **4-6** were distinct and easily detectable in the range 246 – 275 °C using DSC in normal mode. However, only the poly(ether imide) of BAPP and ODPA (**4-4**) was soluble in chloroform (Table 4-1). For this reason, this monomer pair was chosen for use as the parent polymer for copolymerization with **4-3**.

Scheme 4-3. Synthesis of poly(ether imide)s (**4-4**, **4-5** and **4-6**). Conditions: (i) m-cresol, isoquinoline, 200 °C.

Table 4-1. Physical properties of poly(ether imide)s **4-4**, **4-5** and **4-6**.

	soluble		Td (°C)		Tg	[η] (dL g ⁻¹)	E'
	CHCl ₃	NMP	N ₂	air			(GPa)
4-4	+	+	499	475	258	1.62 ^a	2.25
4-5	–	–	539	510	275		
4-6	–	–	528	513	246		

^a – measured in NMP

Segmented block copolyimides were synthesized by reaction of **4-3** with equal molar amounts of ODPA and BAPP. These monomers could be added directly to a solution of **4-3** in *m*-cresol immediately after transimidization to the desired molecular weight was complete (see Table 4-2). The polymerization solution was maintained at 5% solids throughout by addition of *m*-cresol with the additional monomers. Isoquinoline was also added to effect imidization of the ODPA and BAPP. Block copolyimides **4-7a-d** formed tough flexible films cast from the polymerization solution, were readily soluble in chloroform, and were obtained as yellow fibrous solids after isolation. Alternatively, polyimide block **4-3** could be first isolated as a powder and then used in copolymerization (**4-7e**). In order to show the versatility of the process, copolymer **4-7a-e** was made having a poly(ether sulfone imide) as one of the blocks, derived from DSDA and BAPS. Polyimide **4-3** was fed into the copolymerization reaction at 20 wt% and its incorporation ratio could be determined using UV-Vis spectroscopy.

Scheme 4-4. Synthesis of segmented block copolyimides **4-7a-e**.

In all cases GPC analysis showed there was an increase in the molecular weight of the block copolyimide from the molecular weight of the block. The homogeneous incorporation of block **4-3** into the copolymer could be confirmed using GPC with detection at two different wavelengths. Polyimide **4-3** has a distinct absorption at 375 nm whereas the parent poly(ether imide) from ODPa and BAPP does not. Figure 4-3 illustrates two GPC traces of block copolymer **4-7d**, one detected at 254 nm and one detected at 375 nm. It can be seen that in each trace the block copolymer has identical retention time and molecular weight distribution, indicating the homogeneous incorporation of the block **4-3** into copolymer **4-7d**.

Figure 4-3. GPC trace of block copolyimide **4-7d** detected at both 254 nm and 375 nm.

DSC measurements of copolymers **4-7c** and **4-7d** showed that the copolymer underwent two distinct glass transitions. The first occurred in the expected temperature range for the parent poly(ether imide) (~ 250 °C) and the second above 400 °C (432 - 433 °C) as expected for the tetrahydro[5]helicene containing block (Table 4-2). As the second glass transition was only detectable in these block copolymers, which contain the longest block of **4-3**, the presence or absence of such a transition must be governed by the length of block **4-3** within the copolymer. The second glass transition for copolymer **4-7e** was not detected, as the 5% decomposition temperature for the parent polymer was 454 °C and as a result the DSC experiment was only run to 400 °C (Table 4-2).

Table 4-2. Physical properties of segmented block copolyimides **4-7a-e**.

	Formation Time of 4-3 (h)	Average m.w. of 4-3 (amu) ^a	Feed weight % of 4-3 in 4-7	Incorporated weight % of 4-3 in 4-7 ^b	M _w ^c	M _w /M _n ^c	[η] _{inh} ^d (dL g ⁻¹)	T _d (°C, N ₂)	T _g (°C)
4-7a	4	540	20.0	19.3	12,750	2.3	0.38	497	240
4-7b	8	1290	20.0	18.4	22,250	2.6	0.42	497	240
4-7c	24	2650	20.0	18.3	20,550	2.3	0.43	492	240, 433
4-7d	24 ^e	2650	20.0	18.2	26,400	2.8	0.49	490	246, 432
4-7e	24	2650	20.0	19.3	13,900	2.3	0.27	432	274 ^f
ODPA/BAPP	---	---	---	---	---	---	1.62	499	258
DSDA/BAPS	---	---	---	---	---	---	0.32	454	273 ^f

^a – determined from GPC calibration relative to a series of oligomers, see Appendix F.^b – determine via UV spectroscopy by calibration against **4-3** ($\lambda_{\text{max}} = 375 \text{ nm}$)^c – relative to polystyrene standards.^d – measured in NMP solution (0.5 g dL⁻¹)^e – isolated powder of **4-3** was used to form copolymer.^f – weak glass transition

Figure 4-4. Transamidization reaction mechanism illustrated using compound **4-2**.

The mechanism for transamidization reaction presumably takes place by initial nucleophilic attack of the reactant amine on the masked pyridyl imide group forming a bis-amide intermediate. Collapse of the bis-amide to form an imide with the more basic amine results in a polymer forming reaction in the case of monomer **4-2** (Figure 4-4). In order for the reaction to take place, with a preference for the desired imide formation, the amino group of the reactant molecule must be more basic than the amino group of the molecule, in this case 2-aminopyridine, used to mask the anhydride group. The difference in basicity will give rise to an equilibrium reaction in which the imide of the more basic amine is preferentially formed (Figure 4-5).

Figure 4-5. Transamidization equilibrium.

Furthermore, if one considers for this process, in a qualitative fashion, an equilibrium constant k and if the polymer forming reaction is in equilibrium, the obtained molecular weight n for the oligoimide is related to k as follows:

$$k \propto \text{pKa}(\text{L-NH}_2)$$

$$k \propto n$$

where, in the case of monomer **4-2**, L is 2-pyridyl. Then if equilibrium is established, the pKa of the leaving group governs the molecular weight of the polymer formed when using the transimidization reaction as a polymer forming reaction. As a result, by simply changing the leaving group the molecular weight of the polyimide formed by transimidization of an AX-type monomer can be controlled by the formation of an equilibrium instead of by a time-controlled process.

In order to determine the pKa of an amine one can use NMR spectroscopy by comparison to compounds with known pKa.⁵ The basicity (as measured by its pKa) of an amino group can be related to the NMR chemical shifts of both the nitrogen atom (as measured using ¹⁵N NMR) and the hydrogen atoms of the amino group (as measured using ¹H NMR) when measured in DMSO-d₆ solution.⁶ The lower the measured chemical shift (in ppm) of the amino protons the greater the basicity. It follows then, in order to determine whether or not a transimidization reaction will take place, one only needs to measure the amino hydrogen atom's chemical shift in DMSO and compare it to the chemical shift of the amino group that is masking the anhydride moiety. Similarly, ¹H NMR could be used to determine the relative equilibrium constants of different transimidization processes. Table 4-3 shows the measured chemical shifts of the amino protons for 2-aminopyridine, compound **4-2**, BAPP and BAPS as measured in DMSO.

From this one can see that compound **4-2**, BAPP and BAPS all possess amino groups which are more basic than 2-aminopyridine. Confirming the observation that all these compounds undergo a transimidization reaction with **4-2** (and as a consequence **4-3**) by displacing the 2-aminopyridine masking group.

Table 4-3. Amino group ^1H chemical shifts of selected compounds.

Compound	$\delta_{\text{NH}_2}(\text{DMSO})^{\text{a}}$
2-aminopyridine	5.93
4-3	5.49
BAPS	5.12
BAPP	4.95

^a – corrected to tetramethylsilane internal standard

4.2.4. Synthesis of A₂X-type diamine imide monomer.

Given the instability of AB-type diamino anhydride monomer **3-3** in solution it is of interest to extend the use of the transimidization reaction to the synthesis and polymerization of A₂X-type diamino imide of similar structure.

Scheme 4-5. Synthesis of A₂X-type diamino imide monomer **4-9**.

Conditions: (i) 2-aminopyridine, o-dichlorobenzene, reflux. (ii) H₂, PtO₂, AcOH, THF or cyclohexene, Pd/C.

Imidization of dinitro derivative of tetrahydro[5]helicene **2-3** with 2-aminopyridine gave compound **4-8** in high yield. Initially reduction of dinitro derivative **4-8** was performed using H₂ with PtO₂ catalyst in THF. However, the isolated red powder required purification by flash chromatography (SiO₂, 1:1 CH₂Cl₂:acetone). The isolated yield of monomer **4-9** was very low and significant amounts of material remained adhered to the silica. Therefore another reduction method was tried. Reduction of compound **4-8** using cyclohexene and palladium on charcoal again gave compound **4-9** which also needed purification. The isolated yield of monomer **4-9** was again very low. None the less, the identity of the compound could be confirmed using IR and ¹H NMR spectroscopy. All attempts to obtain a mass spectrum failed. Furthermore, unlike AX-monomer **4-2**, A₂X-monomer **4-9** is not stable in polar solvents (DMSO) making characterization by ¹³C NMR impossible.

Monomer **4-9** decomposed on heating to 145 °C and presumably undergoes a self-polymerization reaction. Indicating that if a suitable synthesis could be found to provide this material in high yield, this monomer would again meet the criteria of being stable at ambient temperatures yet activated to polymerization at elevated temperatures.

A₂X-monomer **4-9** was heated in *m*-cresol at 200 °C without catalyst to produce a hyperbranched polyimide. However, in all cases the polymer formed an insoluble gel after a short reaction time. Due to the gelation, purification and characterization of this material was not possible.

However, if the gelation problem could be overcome, A₂X-monomer **4-9** could produce an “A_nX-oligoimide” which contains *n* reactive A-groups and only one reactive

X-group. These materials could be incorporated into hyperbranched block copolymers as with AX-oligoimide **4-3**.

In order to test the viability of producing hyperbranched block copolyimides, several copolymers were made from compound **5-2** (a second generation dendrimer containing terminal amino groups), BAPP and ODPA (Scheme 4-6). Several copolymerization conditions were used:

- Sequential reaction of **5-2** with ODPA with addition of BAPP after a length of time (equal molar amounts of ODPA and BAPP).
- Sequential reaction of **5-2** with ODPA with addition of BAPP after a length of time (excess amounts of ODPA to compensate for amino groups of **5-2**).
- One-pot copolymerization of **5-2** with BAPP and ODPA (excess amounts of ODPA to compensate for amino groups of **5-2**).

In each case the result was a dendritic initiated block copolyimide. Furthermore, the block copolymer obtained remained soluble in the reaction medium (*m*-cresol) and was chloroform soluble. GPC analysis showed the copolymers to be of reasonable molecular weight and the polydispersity of the obtained polymers was relatively narrow.

Comparison with polystyrene standards provided no useful information on the true molecular weight. The presence of **5-2** within the obtained copolymers could again be confirmed by GPC with the detector set at 375 nm.

Obtaining soluble copolymer using this approach indicates that if a soluble A_nX -oligoimide could be obtained from polymerization of an A_2X -monomer, the incorporation of such species into hyperbranched block copolymers would be very likely.

Scheme 4-6. Synthesis of dendritic initiated hyperbranched polyimide copolymers 4-10.

4.3. Conclusion.

It has been demonstrated that the use of the transimidization reaction is a feasible route to a polyimide when the target AB-monomer is not stable. The synthesis and polymerization of an AX-type amino imide monomer containing the

tetrahydro[5]helicene unit was accomplished. It underwent a self-transimidization reaction and produced polyimide **4-3** which was confirmed to contain reactive chain ends by ^1H NMR spectroscopy. Polyimide **4-3** could be incorporated into a series of block copolymers by reaction with BAPP and ODPA or BAPS and DSDA.

A model is proposed which allows for the molecular weight of polyimides made from AX-type monomers to be controlled by the use of different X-groups.

The methodology presented has been extended to the synthesis of an A_2X -type monomer **4-9**. Although it produced an insoluble gel on polymerization evidence suggests that its incorporation into hyperbranched block copolyimides is at least feasible.

4.4. Experimental.

Characterization. For general experimental methods see Appendix A.

3-Nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic-(*N*-2-pyridyl) imide (4-1).

3-nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (2-2a, 5.0051 g, 12.60 mmol) and 2-aminopyridine (1.1998 g, 12.76 mmol) were placed in *o*-dichlorobenzene (50 mL) and isoquinoline (5 drops) and stirred for 1 hour in a 3-necked rounded bottom flask fitted with a nitrogen inlet and Dean-Stark trap, after which it was set to reflux overnight. The homogeneous solution was cooled and poured into pentane (600 mL), the yellow precipitate was collected and dried in vacuo (100 °C, 5 mmHg) overnight; 5.25 g (88% yield); mp 234 - 236 °C; IR (KBr, C=O) 1769, 1713 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.73 (d, 1H), 8.24 (s, 1H), 7.92 (t, 1H), 7.81 (d, 1H), 7.47 (d, 1H), 7.20-7.45 (m, 5H), 7.07 (d, 1H), 6.98 (t, 1H), 4.24 (m, 2H), 2.95-3.25 (m, 4H), 2.61 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 166.8, 149.6, 146.9, 146.2, 140.8, 140.5, 140.0, 139.7, 139.5, 139.3, 138.2, 137.0, 132.6, 130.9, 130.5, 129.3, 128.2, 127.2, 126.3, 125.9, 123.4, 122.9, 122.2, 120.9, 28.5, 28.4, 23.9, 23.9 ppm; MS (EI, m/e, relative intensity %) 473 (M⁺, 100); HRMS calcd for C₂₉H₁₉N₃O₄ 473.1375, found 473.1374.

3-Amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic-(*N*-2-pyridyl) imide (4-2).

3-Nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic-(*N*-2-pyridyl) imide (**4-1**, 1.30 g, 2.74 mol) was dissolved in THF (50 mL) and acetic acid (0.5 mL) over PtO₂ (100 mg) and hydrogenated (60 psi) for 45 min. The solution was dried (MgSO₄) and removed to give a red solid which was dried in vacuo (100 °C, 5 mmHg) overnight: 1.21 g (99 % yield); m.p. 175 °C (dec); IR (KBr) 3457, 3372 (NH₂) 1761, 1710 (C=O) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.6 (bm, 2H), 2.9 (bm, 4H), 4.2 (bm, 2H), 6.27 (d, 1H), 6.60 (s, 1H), 6.69 (d, 1H), 7.00 (d, 1H), 7.17 (t, 1H), 7.28-7.38 (m, 2H), 7.44 (d, 1H), 7.87 (t, 1H), 8.70 (d, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 24.12, 24.29, 28.62, 28.79, 112.75, 113.44, 122.22, 123.14, 124.14, 124.26, 125.60, 125.80, 127.68, 128.07, 129.77, 131.76, 134.01, 137.94, 138.10, 138.48, 139.07, 139.39, 140.11, 140.98, 146.53, 146.81, 149.53, 167.36, 167.45 ppm; MS (EI, m/e, relative intensity %) 443 (M⁺, 100); HRMS calcd for C₂₉H₂₁N₃O₂ 443.1634, found 443.1623.

3, 12-Dinitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic-(*N*-2-pyridyl) imide (4-8).

3.12-Dinitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (2-3, 1.5022 g, 3.39 mmol) and 2-aminopyridine (0.3360 g, 3.57 mmol) were placed in *o*-dichlorobenzene (15 mL) and isoquinoline (3 drops) and stirred for 1 hour in a 3-necked rounded bottom flask fitted with a nitrogen inlet and Dean-Stark trap, after which it was set to reflux overnight. The homogeneous solution was cooled and poured into pentane (200 mL), the yellow precipitate was collected and dried in vacuo (100 °C, 5 mmHg) overnight; 1.74 g (99% yield); mp >300 °C; IR (KBr, C=O) 1769, 1713 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.73 (d, 1H), 8.28 (s, 2H), 7.69 (t, 1H), 7.84 (d, 2H), 7.85 (d, 2H), 7.35-7.50 (m, 3H), 7.15-7.25 (m, 2H), 4.30 (d, 2H), 2.90-3.20 (m, 4H), 2.65 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 149.5, 147.4, 145.8, 140.8, 139.7, 138.9, 138.6, 138.3, 131.1, 130.5, 127.7, 127.5, 123.7, 123.4, 122.2, 121.3, 28.4, 23.7 ppm; MS (EI, m/e, relative intensity %) 518 (M⁺, 100); HRMS calcd for C₂₉H₁₈N₄O₆ 518.1226, found 518.1281.

3, 12-Diamino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic-(*N*-2-pyridyl) imide (4-9).

3,12-Dinitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic-(*N*-2-pyridyl) imide (**4-8**, 400 mg, 0.77 mmol) was dissolved in THF (30 mL) and acetic acid (0.5 mL) over PtO₂ (40 mg) and hydrogenated (60 psi) for 6 h. The solution was dried (MgSO₄) and removed to give a red solid which was dried in vacuo (100 °C, 5 mmHg) overnight. The solid was chromatographed on SiO₂ (1:1 CHCl₃:acetone); (24 % yield). Alternatively: 3,12-Dinitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic-(*N*-2-pyridyl) imide (**4-8**, 400 mg, 0.77 mmol) was dissolved in THF (5 mL) then EtOH (5 mL) and cyclohexene (0.5 mL) were added, the solution placed over Pd-C (10%, 200 mg) and set to reflux overnight. The solution was diluted with THF (15 mL), dried (MgSO₄) and removed to give a red solid which was dried in vacuo (100 °C, 5 mmHg) overnight. The solid was chromatographed on SiO₂ (1:1 CHCl₃:acetone); (19 % yield).

m.p. 135 °C (dec); IR (KBr) NH₂ 3455, 3372; C=O 1763, 1709 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 2.6 (bm, 2H), 2.9 (bm, 4H), 4.2 (bm, 2H), 7.5 (d, 2H), 7.8 (s, 2H), 8.3 (s, 2H), 8.7 (m, 2H), 9.3 (t, 1H), 9.9 (m, 1H) ppm.

4.5. References.

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Chapter 5. Dendritic aryl imides containing the tetrahydro[5]helicene unit.

5.1. Introduction.

Having explored the properties and characteristics of linear macromolecules containing the tetrahydro[5]helicene unit, it would now be of interest to study the properties of the same unit within a macromolecule having dendritic architecture.¹ The synthesis of regular dendritic aryl imides would allow not only for the study of such molecules, but gives a direct avenue for the comparison of such dendritic molecules with their linear analogues, which we have previously synthesized and studied. For example, the dendrimer should also possess a relatively lower glass transition temperature (T_g) as compared to its linear analogue. Disc-shaped dendritic poly(aryl ether)s have been previously used to modify the properties of poly(*p*-phenylene).² Furthermore, given the dendrimer's extended array of *o*-terphenyl moieties, one may expect these dendritic macromolecules to possess some unique and interesting electrochemical properties as compared to their monomeric and oligomeric counterparts. Therefore, dendritic aryl imides have been constructed containing the tetrahydro[5]helicene unit using a divergent synthetic methodology.

5.2. Discussion.

5.2.1. Synthesis.

The first generation dendron (**G1-den**, Scheme 5-1) could be made by reaction of compound **1** with ethanolamine in refluxing DMF. Assembly of this dendron around the trimesic acid (1,3,5-benzenetricarboxylic acid) core was accomplished by reaction with

1,3,5-benzenetricarbonyl trichloride in dichloromethane using DMAP as a base. After purification, the first generation dendrimer **G1** was obtained as a yellow glassy solid in good yield (65%).

Scheme 5-1. Synthesis of first-generation dendron (**G1-den**) and dendrimer (**G1**).

Conditions: (i) ethanolamine, DMF, reflux. (ii) 1,3,5-benzenetricarbonyl trichloride, DMAP, CH₂Cl₂.

Imidization of dinitro compound **2-3** with ethanolamine in chlorobenzene and DMF followed by reduction with iron powder gave compound **5-1** in moderate yield (Scheme 5-2). Imidization of compound **5-1** with compound **1** in *m*-cresol at 200 °C afforded the second generation dendron (**G2-den**) in good yield after purification by SEC (Scheme 5-2). Assembly of **G2** was accomplished by reaction of **G2-den** with 1,3,5-benzenetricarbonyl trichloride for 3 days in dichloromethane.

Synthesis of the third generation dendron (**G3-den**) began with imidization of compound **5-1** with compound **2-3**, followed by reduction with iron powder to give compound **5-2** (Scheme 5-2). Imidization of compound **5-2** with compound **1** in *m*-cresol at 200 °C gave the third generation dendron (**G3-den**, Scheme 5-2) in good yield (70%)

after purification by SEC. However, this dendron could not be assembled around the trimesic acid core, even after the coupling reaction was carried out for 28 days, under similar conditions used for the assembly of the second-generation dendrimer. The highest molecular weight compound, isolated from the reaction mixture by SEC, had a mass corresponding to a trimesic acid core having only two dendrons assembled around it ($m/e = 5289$, MALDI-TOF-MS, dithranol/silver trifluoroacetate matrix). It is postulated that due to steric crowding **G3-den** can not get close enough in space to the trimesic acid core to couple.

Scheme 5-2. Synthesis of higher generation dendrons (**G2-den**, **G3-den**). Conditions: (i) 1, *m*-cresol, 200 °C. (ii) 1. **2-3**, *m*-cresol, 200 °C. 2. Fe, HCl. (iii) 1, *m*-cresol, 200 °C.

5.2.2. Structural characterization.

Gel permeation chromatography (GPC) was performed on each dendron from generation one (**G1-den.** Scheme 5-1) to three (**G3-den.** Scheme 5-2) that showed an increase in apparent molecular weight for increasing generation and the expected monodispersity. However, comparing these molecular weight profiles against polystyrene standards provided no useful information regarding molecular weight. This is not unexpected given the obvious difference in molecular conformation between polystyrene and these rigid aryl dendrites. Figure 5-1 illustrates both stick and space-filled molecular models of **G3-den.** From this model the conformation of each of the tetrahydro[5]helicene units as well as the shape and conformation of the dendron itself is illustrated.

Figure 5-1. Stick (left) and space-filled (right) molecular models of the third generation dendron (**G3-den.**).

The identity of each dendron and dendrimer was confirmed using IR spectroscopy and its mass was confirmed using MALDI-TOF mass spectrometry. In each case the mass spectrum was used as the primary means for structural determination since for every dendron and dendrimer higher than generation one, the ^1H NMR spectra were cluttered and not easily interpretable. A single peak was observed in the MALDI-TOF mass spectrum, corresponding to the mass of the parent molecular species plus Li^+ (from the matrix) except for **G2-den**, which had only its parent molecular ion.

5.2.3. Physical Properties.

In order to compare the physical properties of these dendritic aryl imides with analogous linear imides, oligoimides were needed of approximately the same molecular weight which contained only the tetrahydro[5]helicene unit. Consequently, the synthesis of oligoimide **5-3** was accomplished and is described in Appendix F. A fraction was obtained that had a distribution of oligomers corresponding to oligoimide **5-3** with 4-10 repeat units, which was confirmed by its MALDI-TOF mass spectrum (Figure 5-2). The distribution of molecular weights for oligoimide **5-3** was centered around $n = 7$ and a mass of $m/e = 2461$, which were close to that of **G3-den** ($n = 7$, $m/e = 2489$).

Scheme 5-3. Synthesis of oligoimide **5-3** ($n = 4-10$). (i) *m*-cresol, 200 °C, time controlled, fractionated from $\text{CHCl}_3/\text{MeOH}$.

Figure 5-2. MALDI-TOF mass spectra (dithranol/silver trifluoroacetate matrix) of oligoimide **5-3**. Peaks indicated are $M+Ag^+$ for a given number (n).

Figure 5-3 illustrates GPC traces of oligoimide **5-3** and **G3-den**. Both compounds have similar absolute molecular weights by MALDI-TOF. However, oligoimide **5-3** showed a higher apparent molecular weight, which can be attributed to its rigid-rod conformation and consequently larger hydrodynamic volume. This difference in hydrodynamic volume is a direct indication that the presented dendritic aryl imides would have a lower solution and melt viscosity when compared with their linear counterparts. These observations further confirm a widely held opinion for which there has only recently been direct evidence.³ DSC measurements showed that **G3-den** possessed a detectable glass transition (T_g) at 346 °C, whereas oligoimide **5-3** did not show a glass transition up to 450 °C. The measured lower T_g suggests that the dendritic aryl imide is

more flexible than the linear aromatic oligoimide. Both of these properties suggest that dendritic aryl imides could be used to modify the properties of traditional linear polyimides.

Figure 5-3. GPC traces of **G3-den** and oligoimide **5-3**.

5.2.4. Fluorescence Study.

Figure 5-4a illustrates the UV-Vis absorption spectra of the dendrons **G1-den**, **G2-den** and **G3-den** as well as oligoimide **5-3**, taken in dichloromethane solution at a concentration of 3×10^{-5} M.[‡] Each compound exhibits two maximum absorptions at about 290 nm and 370 nm. The repeat unit equivalent molar extinction coefficients for

[‡] The absorptions and emissions have been corrected by a factor equal to the repeat unit equivalent molar concentration for each compound.

each dendron at each $\lambda_{\text{max,abs}}$ are approximately equal. However, when the same series of compounds are irradiated at either wavelength they fluoresce and both the wavelength and intensity of the fluorescent emission vary widely among the compounds (Figure 4b). For example, the emission intensity of **G1-den** ($\lambda_{\text{max,em}} = 480 \text{ nm}$) is over 30 times greater than the emission intensity of **G2-den** ($\lambda_{\text{max,em}} = 477 \text{ nm}$) which is itself 5 times larger than that of **G3-den** ($\lambda_{\text{max,em}} = 501 \text{ nm}$). The shift of the fluorescent emission of **G3-den** compared to **G2-den** indicates a loss of radiant energy by some pathway. Furthermore, there is a progressive decrease in the emission intensity with increasing dendron generation. Additionally, the linear oligoimide **5-3** exhibits larger emission intensity (although shifted to longer wavelength) than **G3-den**. Coupling these observations leads to the conclusion that within the higher generation dendrons intermolecular quenching of the emitted radiation takes place. One may expect these observations, given the dendritic structure and conformation of **G3-den**. It would be more likely to undergo intramolecular quenching, as compared to its linear rod-like analogue, given that any intermolecular quenching would have to be a result of the *o*-terphenyl moieties overlapping and interacting in solution.

Figure 5-4. Normalized absorption (a) and emission (b) spectra of G1-den, G2-den, G3-den and oligoimide 5-3 as taken in dichloromethane solution ($3 \times 10^{-5} \text{ M}$).

5.2.5. Electrochemical Behavior.

Given the indication that the tetrahydro[5]helicene units of the higher generation dendrons are capable of interacting in solution, it would be of interest to see whether or not there exists a redox activity, not observed in isolated *o*-terphenyl moieties, tetrahydro[5]helicene units or an imide functionalities, that does exist within the higher generation dendrons (**G2-den** and **G3-den**). Thus, cyclic voltammetry was performed in DMF solution, using tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte, in order to examine the electrochemical behaviour of the dendritic aryl imides (**G1-den**, **G2-den** and **G3-den**).

All the three dendrons exhibited electrochemical activity, although only one reversible redox couple[§] was observed for **G1-den** (at -1.28 V) whereas two were observed for **G2-den** and **G3-den** (Figure 5-5, Table 5-1). The first reversible redox couple at approximately -1.28 V was consistently present for all the dendrons. If **G1-den** was submitted to potentials more negative than -1.3 V a second redox couple was observed. However, under these conditions neither the first nor the second redox couples were reversible, indicating that chemical degradation occurred at the more negative potentials.

[§] Reversible couple is defined in this work as the ability of the molecule to undergo identical redox couples (ie. superimposable CV waves) over 12 consecutive scans within the applied potential range.

Figure 5-5. Cyclic voltammograms of **G3-den** (a) and oligoimide **5-3** (b).

In order to explain these observations and the nature of this electrochemical behaviour, cyclic voltammograms for a series of compounds (Figure 5-6) containing both *o*-terphenyl and anhydride moieties were obtained. Within compound **1** the *o*-terphenyl moiety is bridged and held in place by the ethylene unit (at positions 5-6 and 9-10). The twist angle of the *o*-terphenyl moiety within compound **1** is approximately 32° as shown by x-ray diffraction analysis of a single crystal (see Chapter 2). Compounds **5-5**, **5-6** and **5-7** differ in the degree of conjugation within the *o*-terphenyl moiety, brought about by the difference in the number of bridging carbon atoms as compared with compound **1**. The *o*-terphenyl moiety within compound **5-7** is not bridged at all and therefore is least conjugated within this series. Whereas, compound **2-11** ([5]helicene-7,8-dicarboxylic anhydride) contains an *o*-terphenyl moiety which is bridged by a vinylene group and is therefore the most conjugated within the series. Therefore this series of compounds can be thought to undergo a shift in the degree of conjugation of the *o*-terphenyl moiety as follows: $2-11 \geq 5-5 > 1 > 5-6 > 5-7 \approx o\text{-terphenyl}$.

Figure 5-6. Analogs of compound **1**, containing both *o*-terphenyl and anhydride moieties.

All the compounds illustrated in Figure 5-6 exhibited electrochemical activity, with redox couples in the range of -0.70 to -2.00 V vs. SCE (Table 5-1) whereas *o*-terphenyl itself did not. For compounds **1**, **5-6**, and **5-7**, only one reversible redox couple was observed. Compounds **2-11** and **5-5** exhibited two reversible redox couples with the second couple at more negative potential. The first redox couple is shifted to more positive potentials as the degree of conjugation increases, in the order **2-11** > **5-5** > **1** > **5-6** > **5-7**. Furthermore, when compound **1** was submitted to higher negative potentials it underwent an additional reductive process at approximately -1.9 V. However, this reduction was not reversible and resulted in the degeneration of the measured current over consecutive scans and a shift of the reduction potential for both the first and second redox couples, behaviour similar to that observed for **G1-den**.

Table 5-1. Electrochemical Data for **G1-den**, **G2-den**, **G3-den**, **1** and **2-11**, **5-5**, **5-6**, **5-7**.

Compound	$E_{1/2}$ reduction (V vs. SCE)	
	1 st	2 nd
G1-den	-1.28	
G2-den	-1.24	-1.93
G3-den	-1.24	-1.92
11	-1.23 ^a	
1	-1.10	
6	-0.78	-1.55
7	-1.09	-1.18
8	-1.20	
9	-1.25	
o-terphenyl	— ^b	

^a – measured in NMP solution. ^b – not observed

Based on these observations and by analogy to compounds **1** and **2-11**, **5-5**, **5-6**, **5-7**, the electrochemical behaviour of the tetrahydro[5]helicene containing dendrons (**G1-den**, **G2-den** and **G3-den**) can be partially explained. The presence and approximate position of the first redox couple is consistent within the dendrons (**G1-den**, **G2-den** and **G3-den**) and the model compounds (**1**, **2-11**, **5-5**, **5-6**, **5-7**). The potential of the first redox couple is invariant with generation. Therefore, the first redox couple must be attributed to a redox process occurring at the anhydride/imide functionality. This is consistent with the reported findings from the electrochemical study of soluble linear polyimides.⁴ Since the first redox couple moves to more negative potential in the series **2-11** > **5-5** > **1** > **5-6** > **5-7**, its position is directly proportional to the degree of conjugation present within the *o*-terphenyl moiety (which is attached to the anhydride/imide functionality). The lower the degree of conjugation within the aromatic ring system, the more difficult the reduction of the anhydride carbonyl group becomes. For compounds **2-11** and **5-5** a second reversible redox couple at more negative potential was also observed. These two compounds possess the highest degree of conjugation within the series of model compounds. Thus, this second redox couple must originate within the *o*-terphenyl moiety and is stabilized within these compounds due to their increased degree of π -conjugation.

Two reversible reductive processes were observed for the higher generation dendrons (**G2-den** and **G3-den**, Figure 5-5). Although within these dendrons, there is an extended array of tetrahydro[5]helicene units (and consequently the *o*-terphenyl moieties) they can not be in a state of extended conjugation because of the imide functionality. Given the presence of a non-reversible reductive process at approximately -1.90 V for

compound **1** and **G1-den**, the second reduction of the higher dendrons at -1.93 V and -1.92 V, for **G2-den** and **G3-den** respectively, must originate within the *o*-terphenyl moiety. Furthermore, due to its reversibility, the intermediate of the second reduction must be stabilized by interaction with other *o*-terphenyl moieties within the dendritic structure itself. This is consistent with the observations made using fluorescence spectroscopy which indicated an interaction between tetrahydro[5]helicene units of the higher generation dendrons in solution. Further to this, linear oligoimide **5-3**, which on average has the same number of repeat units as **G3-den**, exhibits only one, albeit broad, redox couple at -1.23 V when measured in NMP solution (Table 1, Figure 5-5). The presence of only one redox couple for linear oligomer **5-3** further implies that the second redox couple observed for **G3-den** is attributed to the dendritic structure of the molecule. Further spectroelectrochemical investigation of the higher dendrons may help determine the exact nature of the second redox couple.

5.3. Conclusion.

In conclusion, dendritic aryl imides from generation one to three, containing the tetrahydro[5]helicene unit have been synthesized. First and second generation dendrons could be assembled around a trimesic acid core to give first and second generation dendrimers, **G1** and **G2** respectively. In each case, MALDI-TOF-MS and spectroscopic methods were used to confirm the identity of each dendron and dendrimer. Each of the dendrons underwent either one or two electrochemical reductions on the range -1.2 V to -2.1 V vs. SCE. When a dendritic aryl imide was compared with its linear analog,

differences were found in the hydrodynamic volumes, glass transition temperatures, and fluorescence and electrochemical behaviour.

5.4. Experimental.

Nomenclature. **G1-den** (Scheme 5-1), **G2-den** (Scheme 5-2) and **G3-den** (Scheme 5-2) refer to the first, second and third generation dendrons, respectively. **G1** and **G2** refer to the first and second generation dendrimers, respectively.

Materials. Compound **5-5** was made according to the established synthesis for compound **1**. Compounds **5-6**⁵ and **5-7**⁶ are known. Chlorobenzene and *N,N*-dimethylformamide (DMF) were reagent grade (Aldrich) and dried over 4Å molecular sieves prior to use. Ethanolamine, iron powder, *m*-cresol, isoquinoline, 1,3,5-benzenetricarbonyl trichloride, *N,N*-dimethyl-4-aminopyridine (DMAP) and toluene were reagent grade (Aldrich) and used as received. Spectrophotometric grade DMF (Aldrich), NMP (1-methyl-2-pyrrolidinone, Aldrich) and Bu₄NPF₆ (Sigma) were used as received. Purification of dendrons and dendrimers was done using a gravity fed preparative size exclusion chromatography (SEC) column packed with Bio-Beads SX-3 (purchased from Bio-Rad). Flash chromatography was performed using standard grade silica gel (Merck).

Characterization. For general experimental methods see Appendix A.

G1-den.

To a suspension of compound **1** (6.0 g, 15.0 mmol) in DMF (60 mL) was added ethanolamine (2.0 mL, 30 mmol). After stirring at room temperature for 1 h, the solution was clear and homogeneous at which point it was set to reflux overnight. The solution was cooled to room temperature and added dropwise with vigorous stirring to an HCl aqueous solution (10%, 300 mL). The resulting yellow precipitate was filtered, washed with water (until the washings were neutral to litmus) and dried *in vacuo* overnight (80 °C, 5 mmHg) to give **G1-den**: 5.8 g (97 % yield): m.p. >300 °C: IR (KBr) 3536 (OH), 1757, 1706 (C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, 2H), 7.15-7.25 (m, 4H), 6.95 (t, 2H), 4.1 (b, 2H), 3.9 (m, 2H), 2.9 (m, 4H), 2.5 (b, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 176.6, 170.1, 139.8, 139.51, 134.18, 130.9, 129.09, 128.44, 126.5, 119.3, 62.2, 41.3, 29.2, 24.9 ppm; MS (EI, m/e, relative intensity %) 395 (M^+ , 100); HRMS calcd for $\text{C}_{26}\text{H}_{21}\text{NO}_3$ 395.1521, found 395.1512.

G1.

A solution of **G1-den** (2.7415 g, 6.94 mmol), 1,3,5-benzenetricarbonyl chloride (0.6142 g, 2.27 mmol) and DMAP (1.3866 g, 11.40 mmol) in dichloromethane (50 mL) was set to stir under argon atmosphere overnight. The dichloromethane solution was washed with

HCl (1M, 2 x 50 mL) and water (2 x 50 mL). The insoluble materials were filtered and the filtrate was dried and concentrated to give **G1** as a yellow glass: 2.54 g (65% yield); IR (KBr) 1759, 1732, 1704 (C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.67 (s, 1H), 7.22 (d, 2H), 7.03-7.12 (m, 4H), 6.82 (t, 1H), 4.41-4.50 (m, 2H), 3.92-3.97 (m, 4H), 2.78-2.87 (m, 4H), 2.3-2.5 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 170.1, 169.2, 139.8, 139.6, 139.4, 135.7, 134.2, 131.6, 130.9, 129.1, 128.4, 126.7, 126.4, 63.5, 37.1, 29.2, 24.9 ppm; MS (MALDI-TOF-MS, dithranol/LiBr matrix, m/e, relative intensity %) calcd for $\text{C}_{87}\text{H}_{63}\text{N}_3\text{O}_{12}$ 1341.4, found 1348.0 ($\text{M}+\text{Li}^+$, 100).

G2-den.

To a solution of compound **2-3** (2.00 g, 4.52 mmol) in chlorobenzene (25 mL) in a round-bottomed flask fitted with a Dean-Stark trap, was added ethanolamine (0.41 g, 1.5 equiv, 6.80 mmol) in DMF (0.3 mL). The solution was stirred at room temperature for 1 h, and then set to reflux overnight. The chlorobenzene solution was concentrated, then precipitated into n-pentane and the resulting yellow solid was filtered (2.06 g, 95%). IR, ^1H and ^{13}C NMR and MS confirmed the identity of the product. This imide product (4.70

g, 9.5 mmol) was placed in a mixture of THF (80 mL), ethanol (40 mL), water (20 mL) and conc. HCl (1 mL). To this was added iron powder (18 g) and the mixture was sonicated at 60 °C (water bath) for 1 h. The iron/oxide powders were filtered and then washed with boiling ethyl acetate (150 mL). The combined solutions were partitioned and the aqueous layer was extracted with ethyl acetate (2 x 50 mL). The combined organic phases were dried over MgSO₄ and concentrated to give a red solid which was further purified by flash column chromatography (60/40 v/v ethyl acetate/hexane then ethyl acetate) to give compound **5-1** (1.57 g, 39%). IR, ¹H and ¹³C NMR and MS confirmed the identity of the product. Compounds **5-1** (1.06 g, 2.5 mmol) and **1** (1.98 g, 5.6 mmol, 2.2 equiv) were dissolved in *m*-cresol (15 mL) with isoquinoline (0.5 mL) and heated at 200 °C under argon flow overnight. The reaction mixture was precipitated into methanol (50 mL) and the resulting yellow precipitate was filtered. The yellow compound was further purified by preparative SEC (toluene). Removal of the solvent and drying overnight (80 °C, 5 mmHg) gave **G2-den**: 1.79 g (65% yield); IR (KBr) 3439 (OH), 1756, 1710 (C=O) cm⁻¹; ¹³C NMR (50 MHz, CDCl₃) δ 169.3, 167.7, 140.1, 139.4, 139.2, 138.9, 138.6, 133.5, 132.7, 131.8, 130.8, 130.4, 130.3, 128.5, 127.8, 126.4, 126.1, 125.9, 125.8, 125.7, 125.6, 124.1, 28.7, 28.6, 24.2, 24.1 ppm; MS (MALDI-TOF-MS, dithranol/LiBr matrix, m/e, relative intensity %) calcd for C₇₄H₅₁N₃O₇ 1093.3, found 1093.1 (M⁺, 100).

G2. A solution of **G2-den** (0.602 g, 0.55 mmol), 1,3,5-benzenetricarbonyl chloride (50.1 mg, 0.18 mmol) and DMAP (0.1284 g, 1.00 mmol) in dichloromethane (20 mL) was stirred at room temperature for 3 days under argon atmosphere. The dichloromethane

solution was washed with aqueous HCl solution (1M, 2 x 50 mL), water (2 x 50 mL) dried over MgSO_4 and concentrated to give a yellow-orange glassy compound. The compound was further purified by preparative SEC (toluene). Removal of the solvent and drying overnight gave **G2** as a yellow-orange glass: 0.428 g (68% yield): IR (KBr) 1760, 1734, 1706 (C=O) cm^{-1} ; MS (MALDI-TOF-MS, dithranol/LiBr matrix, m/e, relative intensity %) calcd for $\text{C}_{231}\text{H}_{153}\text{N}_9\text{O}_{24}$ 3436.1, found 3445.0 ($\text{M}+1+\text{Li}^+$, 100).

G3-den.

As described for the synthesis of **G2-den**, compound **3** was imidized with **4** in *m*-cresol at 200 °C, followed by reduction with iron powder to give compound **5**. Subsequent imidization of **1** with **5** afforded **G3-den** in 70% yield after purification by SEC (toluene). IR (KBr) 3442 (OH), 1763, 1711 (C=O) cm^{-1} ; MS (MALDI-TOF-MS, dithranol/LiBr

matrix, m/e, relative intensity %) calcd for $C_{170}H_{111}N_7O_{15}$ 2489.8, found 2496.1 ($M+Li^+$, 100); $T_g = 346\text{ }^\circ\text{C}$.

5.5. References.

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- ⁶ (a) Allen, C.F.H.; Van Allan, J.; *J. Am. Chem. Soc.*, **1942**, *64*, 1260. (b) Synthesis adapted from: Gray, F.W.; *J. Chem. Soc.*, **1909**, 2131 and Grummit, O.; *Org. Synth., Coll. Vol. 3*, 807.

Chapter 6. Polyimides derived from AA-type diamine monomers.

6.1. The use of the precursor approach for the introduction of a [5]helicene unit into linear polyimides.

6.1.1. Introduction.

The application of the precursor strategy in polymer synthesis has recently attracted much attention. It is often employed when a desired polymer can not be obtained by direct polymerization because of the lack of a suitable monomer or insolubility of the resulting polymer. In this case, a high molecular weight polymer is synthesized first as a precursor and subsequently converted into the desired polymer by a simple transformation. The transformation may be effected by a chemical process,¹ a photochemical process² or a thermal (heating) process.³ Protecting or masking groups can also be used in obtaining a soluble precursor polymer and later removed to yield the targeted insoluble polymer. Examples include poly(*p*-phenylene),⁴ poly(phenylene sulfide),⁵ poly(*p*-phenylene terephthalamide),⁶ poly(ether ether ketone),⁷ and aromatic polyimides from poly(amic ester)s.⁸

The precursor approach has some advantages particularly if the transformation can be done on the precursor polymer as a thin film or bulk part. Thus, the precursor polymer is processed to the desired form and transformed (or cured) to the final polymer product that often has improved solvent resistance and increased thermal stability compared to its precursor. However, there are certain requirements that should be considered. The process should ideally be simple, clean and leave no residue or by-

product. If by-products are generated, as is likely in the case of chemical transformation, then they should be easily removed from the polymer. The transformation should not cause polymer degradation or unwanted cross-linking. Ideally, the transformation should be done in the solid state by a thermal process within the polymer processing temperature window.

All attempts to polymerize monomers containing a [5]helicene unit produced low molecular weight materials.⁹ This has been attributed to the lack of both solubility and mobility in the polymerization solvent. However, these desired materials can be made using a precursor approach. High molecular weight linear polyimides containing the tetrahydro[5]helicene unit can be obtained and oxidized post-polymerization to produce [5]helicene containing polyimides. The oxidation can be done using elemental bromine or atmospheric oxygen.

6.1.2. Discussion.

Monomer Synthesis.

The mononitration of **2-5c** and **2-5d**, is the key step in the synthetic route (Scheme 6-1). Imidization of **1** before nitration was chosen in the early stages of our work with these compounds because the dinitro compounds **6-1a** and **6-1b** were easier to purify than the mono-nitrated product **2-2a**. However later on it was found that compounds **6-1a** and **6-1b** could also be made by imidization of **2-2a** with *m*- and *p*-nitroaniline respectively. The pure dinitro derivatives **6-1a** and **6-1b** were not very soluble in common organic solvents, making spectroscopic characterization difficult. Subsequent reduction with tin(II) chloride gave the unsymmetric diamines **6-2a** and **6-2b**

in good yields. The diamines were bright orange amorphous solids and decomposed at 290 °C. They could be handled and purified in air for a prolonged period of time without showing signs of deterioration (i.e. no color change). The diamines **6-2a** and **6-2b** gave spectral data in excellent agreement with the proposed structures, including high-resolution mass spectrometry. The chemical shifts of the amino hydrogens were around 5.3 ppm and 5.5 ppm, therefore even though **6-2a** and **6-2b** are unsymmetric, each amino-group can be thought to have almost equal reactivity based on the chemical shift of the amino-protons.¹⁰ This leads to the formation of three possible diads (ca. head-to-head, tail-to-tail or tail-to-head) in the polyimide backbone.¹¹

Scheme 6-1. Synthesis of unsymmetric diamines (**6-2a**, **6-2b**) containing the tetrahydro[5]helicene unit. Conditions: (i) nitroaniline, DMF, AcOH, reflux. (ii) HNO₃, H₂SO₄, AcOH, CHCl₃. (iii) SnCl₂, THF.

Polymer synthesis.

It is known that in general tetrahydro[5]helicene containing polyimides have good solubility in organic solvents. Therefore, one-step polymerizations were performed in *m*-cresol at 210 °C. Two dianhydrides (6FDA and *s*-BPDA) were selected for polymerization with **6-2a** and **6-2b**. They were chosen as they are thought to have the highest probability of producing soluble polyimides. Both polymerized successfully with both **6-2a** and **6-2b** to produce a series of high molecular weight polyimides **6-3a,b** and **6-4a,b** (Figure 6-1). Polymerization reactions were stopped 2 h after a piece of flexible film could be cast from the polymerization solution. For the polyimides derived from 6FDA (**6-3a**, **6-4a**), which were chloroform soluble, the polymerization reaction was complete after approximately 6 h, as indicated by GPC.

Figure 6-1. Polyimides containing the tetrahydro[5]helicene unit (**6-3a,b** and **6-4a,b**).

All the polyimides were obtained as slightly yellow fibrous powders. The UV/VIS spectra of representative polymers **6-3a** and **6-4a** showed a maximum absorption at 370 nm in TCE confirming the presence of the tetrahydro[5]helicene moiety. The cast thin films from TCE solution after drying were slightly darker and closer to yellow/orange in color. Table 6-1 lists the solubilities and inherent viscosities of polyimides **6-3a.b** and **6-4a.b**. The measured inherent viscosities (0.41 - 0.48 dL/g @ 0.5 g/dL in NMP) indicate that the polyimides are of high molecular weight. The polyimides showed good solubility in common organic solvents like TCE and NMP. The 6F-containing polyimides **6-3a** and **6-4a** were even soluble in chloroform and pyridine at ambient temperatures. GPC analysis showed a weight-average molecular weight of 80000 for polyimide **6-3a** (**6-2a**/6FDA), relative to polystyrene standards. The apparent weight-average molecular weight (35300) of polyimide **6-4a** (**6-2b**/6FDA) was relatively lower, even though their inherent viscosities were almost the same (0.48 dL/g for **6-3a** and 0.41 dL/g for **6-4a**).

Figure 6-2. Endcapped polyimide **6-5** from diamine **6-2a** and 6FDA.

Table 6-1. Solubilities and solution viscosities of tetrahydro[5]helicene-containing polyimides **6-3a,b** and **6-4a,b**.

polymer	6-3a	6-3b	6-4a	6-4b
$[\eta]_{\text{inh}}^{\text{a}}$ (dL/g)	0.48	0.55	0.41	n/m
CHCl ₃	+	±	+	–
TCE	+	+	+	+
NMP	+	+	+	±
DMF	+	±	+	–
DMAc	+	±	+	±
DMSO	+	–	+	–
Pyridine	+	+	+	±
Chlorobenzene	±	–	±	–

^a measured in NMP solution (0.5 g/dL) at 30.0 °C; n/m: not measured due to low solubility in NMP; key: soluble (+), partially soluble (±), not soluble (–) at ambient temperatures (0.5 g/dL)

To estimate absolute molecular weight, endcapped polyimide **6-5** was synthesized using 4-*t*-butyl phthalic anhydride as an end-capping agent (Figure 6-2). Polymer **6-5** had the same inherent viscosity as the corresponding uncapped polymer **6-3a** (0.48 dL/g in NMP @ 30.0 °C) and the same apparent molecular weight by GPC ($M_w = 71900$, $M_n = 40900$). The resonance at 1.40 ppm in the ¹H NMR spectrum (400 MHz, TCE-d₂) of polymer **6-5** was assigned to the *t*-butyl group, supported by correlation (using HETCOR spectroscopy) with the *t*-butyl resonance in the ¹³C NMR spectrum. The *t*-butyl resonance was integrated relative to the resonance at 4.16 ppm corresponding to one proton in each of the ethylene bridges of the tetrahydro[5]helicene unit (or two protons

per repeat unit). Based on the NMR data, calculation showed that polyimide **6-5** on average contained 69 repeat units or had a number-average molecular weight of 60500. Since the polyimides **6-3a**, **6-4a** and **6-5** derived from **6-2a** had similar solution viscosities they should have number-average molecular weights of about 60000.

Table 6-2. Thermal properties and Young's moduli of polyimides **6-3a,b** and **6-4a,b**.

polymer		6-3a	6-3b	6-4a	6-4b
T_d^a (°C)	N ₂	471	498	490	491
	air	439	463	432	--- ^g
T_g (°C)	TMA ^b	--- ^c	380	386	--- ^f
	ODSC ^c	371	365	384	--- ^g
E'^d (GPa)		1.99	0.40	0.59	--- ^f

^a onset temperature for 5% weight loss, as assessed by TG at a heating rate of 10 °C/min; ^b taken as a maximum of $\tan \delta$ and measured on a 2 x 10 mm thin film at a heating rate of 3 °C/min; ^c observed on the C_p curve of the ODSC scan; ^d Young's modulus at 25 °C measured by TMA on a 2 x 10 mm thin film in static air; ^e a maximum of $\tan \delta$ was not observed; ^f thin film was too brittle for measurement; ^g not measured

The thermal and mechanical properties of **6-3a,b** and **6-4a,b** (Table 2) were assessed by oscillating differential scanning calorimetry (ODSC), thermogravimetry (TG), and thermomechanical analysis (TMA). Polyimide **6-4b** could not produce a solution cast film because of limited solubility. The glass transition temperatures (T_g) for these polyimides were not detectable using standard DSC experiments, but were detectable in the deconvoluted ODSC scan and were also detected by DMA. During the DMA experiment a loss of modulus could clearly be seen in the E' curve and the T_g was

taken as a maximum in the $\tan \delta$ curve. The T_g values were in the range of 368 °C to 386 °C by ODSC and DMA. For polymer **6-3b** (**6-2a**/s-BPDA) only a very weak $\tan \delta$ peak was observed, presumably because of its rigid structure. The T_g values taken as a maximum of $\tan \delta$ in the TMA experiment were in good agreement with the T_g values observed by ODSC, with the exception of one case. A maximum of $\tan \delta$ could not be observed for polymer **6-3a** (**6-2a**/6FDA) because of a change in modulus that occurred at the glass transition. The E' curve shows clearly a loss of modulus followed by a sharp increase in modulus above T_g . While this behavior was characteristic for this series of polymers, this was the only case where an increase in modulus occurred before a maximum of $\tan \delta$ was observed. This increase in modulus was not retained upon slow cooling of the polymer film to room temperature.

All four polyimides (**6-3a.b** and **6-4a.b**) showed high thermal stability in nitrogen and decreased thermooxidative stability in air (Table 6-2). An isothermal aging experiment was conducted on polymer **6-3a** (**6-2a**/6FDA) for 4 days in nitrogen (200 mL/min). On extended heating at 400 °C, the resulting rate of mass loss was found to be 1.5 %/day (0.06%/h).

Young's modulus measurements at 25 °C showed that polyimides **6-3b** and **6-4a** had unusually low moduli ($E' = 0.40$ - 0.59 GPa), whereas polymer **6-3a** had a Young's modulus of 1.99 GPa (Table 6-2) comparable to most known polyimides. The thin film of **6-3b** (**6-2a**/s-BPDA) was somewhat brittle and could not be folded or creased without breaking.

A [5]helicene containing polyimide.

As a basis for comparison, a diamine monomer containing a [5]helicene moiety (**6-7**) was synthesized and completely characterized (Scheme 6-2). Aromatization of *m*-dinitro derivative **6-1a** with elemental bromine gave compound **6-6** which could be reduced with tin(II)chloride to give [5]helicene containing diamine **6-7**. Subsequent polymerization in *m*-cresol with 6FDA gave polyimide **6-8a**. Polyimide **6-8a** was of low molecular weight ($[\eta] = 0.23 \text{ dL g}^{-1}$) and had a Td of 493 °C in nitrogen.

Scheme 6-2. Synthesis and polymerization of an unsymmetric diamine containing the [5]helicene unit **6-7**. Conditions: (i) Br₂(*l*), TCE, reflux. (ii) SnCl₂, THF, reflux. (iii) 6FDA, *m*-cresol, isoquinoline, 200 °C.

Polymer transformation: Chemical transformation.

It has previously been shown that elemental bromine at elevated temperatures can effect the chemical transformation of tetrahydro[5]helicene to [5]helicene. The technique has been shown by elemental analysis not to leave residual bromine within the polyimide. The two precursor polymers **6-3a,b** were chosen in this work because they were of high

molecular weight and were soluble enough to cast into a thin film from TCE solution. The resulting [5]helicene-containing polyimides **6-8a,b** were otherwise unattainable at high molecular weight by direct polymerization of a [5]helicene-containing diamine and a dianhydride. For example, as indicated above, polycondensation 6FDA with the [5]helicene containing diamine (**6-7**) afforded only oligomeric **6-8a**.

Scheme 6-3. Chemical and thermal transformation of precursor polyimides **6-3a,b** to [5]helicene containing polyimides **6-8a,b**. Conditions: (i) $\text{Br}_2(l)$, 150 °C, TCE or $\text{Br}_2(g)$, 180 °C or Air, 400 °C.

Bromine was effective in quantitatively transforming precursor polyimides **6-3a,b** to [5]helicene-containing polyimides **6-8a,b** (Scheme 6-3). The transformation could be effected by treatment of either the polyimide thin film with an excess of gaseous bromine at 180 °C or a TCE solution of the polyimide with a slight excess of liquid bromine. The complete conversion of the tetrahydro[5]helicene unit in the precursor polymers was verified by IR spectroscopy. Upon aromatization, the corresponding [5]helicene polyimides showed the complete disappearance of the C-H aliphatic stretch (near 2800 cm^{-1}) in their IR spectra.

It is expected that the wholly aromatic [5]helicene-based polyimide would possess a greater thermal stability than the precursor polyimides containing aliphatic moieties. There was only a slight increase in the thermal stability of polyimides **6-8a,b** in nitrogen atmosphere, but a rather large increase in air (Tables 6-3) as compared to **6-3a,b**. For example, the thermooxidative stability increased quite dramatically upon chemical transformation of **6-3a** to **6-8a**, as indicated by the onset temperature for 5% weight loss in air increasing from 439 °C for **6-3a** to 512 °C for **6-8a**.

Table 6-3. Comparison of thermal stabilities of polyimides **6-3a,b** and **6-8a,b**.

Polyimide		6-3a	6-8a	ΔT	6-3b	6-8b	ΔT
T_d^a (°C)	N ₂	471	515	44	498	529	31
	air	439	515	76	463	531	68

^a onset temperature for 5% weight loss as assessed by TGA

There was no change in the Young's modulus of **6-3a** upon transformation to **6-8a** (1.99 GPa) indicating that the polymer transformation did not result in any chain cleavage or crosslinking. Due to the meta catenation and 6F linkage, polyimide **6-8a** can be expected to be the most flexible in this series of polyimides. For the more rigid **6-8b**, the film after chemical transformation became very brittle and the modulus could not be measured. This is an indication that the introduction of the wholly aromatic [5]helicene unit can greatly increase the stiffness of the polyimide backbone.

Certainly, bromine is not the only reagent that can convert tetrahydro[5]helicene to [5]helicene. It is known that 9,10-dihydrophenanthrene, which constitutes part of the tetrahydro[5]helicene unit, can be oxidized to phenanthrene using a variety of oxidizing

agents. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and nitrobenzene or elemental oxidizing agents such as S, Se and Te have been used in the aromatization of 9,10-dihydrophenanthrene and its analogues.¹² In the case of dehydrogenation using sulfur, the mechanism is thought to involve radical abstraction of the benzylic hydrogen by a sulfur radical. A similar mechanism likely plays a role in the aromatization of tetrahydro[5]helicene, using bromine. At elevated temperatures, bromine homolytically cleaves to generate a bromine radical, which can abstract a benzylic hydrogen atom and substitute at the same position. Thermal elimination of HBr results in aromatization. It has also been shown that the same transformation can be effected using a stoichiometric amount of N-bromosuccinimide in TCE solution at 140 °C.

Polymer transformation: Thermal transformation.

It is likely that oxygen may also effect the transformation of tetrahydro[5]helicene to [5]helicene, given that oxygen at high temperature would also abstract a benzylic hydrogen atom. To this end, 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**1**) was placed in a sealed tube containing air and heated at 300 °C for 2.5 h. Compound **1** was converted to [5]helicene-7,8-dicarboxylic anhydride (**2-11**) in high yield in the presence of oxygen. Confirmation of the thermal transformation was done using ¹H NMR. The details of which are supplied in Chapter 2.

Simple heating in air was also sufficient to transform tetrahydro[5]helicene containing polyimides **6-3a,b** to [5]helicene containing polyimides **6-8a,b**. The transformation was confirmed using FTIR. The IR spectra of the transformed polymer powder of **6-3a** shows the characteristic disappearance of the aliphatic C-H stretch

around 2800 cm^{-1} . When the IR spectrum of polyimide **6-8a**, made by thermal treatment of **6-3a**, is compared with oligomeric **6-8a** (made by solution polymerization) the fingerprint region of **6-8a** is superimposable on the same region of oligomeric **6-8a** (obtained by direct polycondensation). Furthermore, a powder of polyimide **6-3a** was shown to be unaffected by heating in nitrogen at $400\text{ }^{\circ}\text{C}$ for 15 min, as confirmed by IR.

Figure 6-3. TMA curves of polyimide **6-3a**. (a) first scan and (b) second scan.

Thermal transformation also occurred, when a film of **6-3a** was subjected to repeated heating to $450\text{ }^{\circ}\text{C}$ in static air during DMA analyses (Figure 6-3). In the first

scan (from 25 °C to 450 °C), polyimide **6-3a** displayed a glass transition as indicated by a loss of modulus and an increase in the $\tan \delta$ curve. On second scanning no glass transition was observed, however the film still showed a large increase in modulus (Figure 6-3). It is known that oligomeric **6-8a** made by solution polymerization had no glass transition below 450 °C by ODSC analysis. The IR spectrum of the thin film of **6-3a** after the first DMA measurement did not show the characteristic aliphatic C-H bands at 2800 cm^{-1} . Similar results were obtained using polyimide **6-3b** which could also be converted by heating in air to **6-8b**, as confirmed by IR.

6.1.3. Conclusions.

The tetrahydro[5]helicene-containing polyimides derived from diamines **6-2a** and **6-2b** showed good solubility in common solvents and good thermal properties. These precursor polyimides were then transformed into polyimides containing the more rigid [5]helicene unit by chemical treatment (in solution or solid state) or by heating (in the solid state) at temperatures around 400 °C in air. The transformed polyimides showed a marked increase in thermooxidative stability and solvent resistance. This thermooxidative transformation method may be applicable to other air oxidizable systems.

6.1.4. Experimental.

Materials. *m*-Cresol, isoquinoline, *m*-nitroaniline, *p*-nitroaniline and bromine were purchased from Aldrich Chemical Co. and used as received. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) were polymer grade as purchased from ChrisKev Company. 4-*t*-Butylphthalic anhydride (TBPA) was purchased from TCI America and used as received. 1,1,2,2-Tetrachloroethane (TCE), dimethylsulfoxide (DMSO), N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidinone (NMP), N,N-dimethylformamide (DMF) and other common organic solvents (Aldrich) were reagent grade, unless otherwise stated, and used as received. TCE-d₂ was purchased from CIL Isotopes and used as received.

Characterization. For general experimental methods see Appendix A.

Monomer Synthesis

Compounds **6-1a** and **6-1b**.

The imide **2-5c** or **2-5d** (10.0 g, 21.0 mmol) was dissolved in 160 mL of chloroform. To this solution 32 mL of acetic acid was added with stirring and the homogeneous solution was cooled to 10 °C. To this stirred solution a chilled (0 °C) mixture of 12.7 g of HNO₃

(70%), 16.2 g of H_2SO_4 (96%) and 12.5 mL of acetic acid was added dropwise over a period of 1 h. The reaction mixture was then allowed to warm to room temperature and the two-phase reaction medium was stirred vigorously. The reaction was followed by TLC (SiO_2 , 10% acetone in hexane) and was stopped when TLC showed no starting imide (3-6 h). The reaction mixture was placed in a separatory funnel without partitioning and washed with water (3 x 150 mL). The organic phase was dried over sodium sulfate and concentrated under vacuum to yield a yellow solid (two spots on TLC). Two successive precipitations of the crude product in 95% ethanol from hot chloroform solution gave the desired dinitro product in 80% yield. The dinitro product was reduced without further purification. **6-1a**: m.p. > 300 °C: MS (EI, m/e, relative intensity %) 517 ($\text{M}^{+\bullet}$, 100.0). **6-1b**: m.p. > 300 °C: MS (EI, m/e, relative intensity %) 517 ($\text{M}^{+\bullet}$, 100.0).

Diamines **6-2a** and **6-2b**.

The dinitro compound **3a** or **3b** (21.0 g, 40.0 mmol) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (94.5 g, 0.40 mol) were placed in 300 mL of THF. After reflux for 5 h the initially yellow and heterogeneous mixture had turned to a homogenous blood red solution. The solution was poured slowly into an aqueous solution containing 50 g of sodium carbonate. A white precipitate was formed and was filtered from the blood red solution. The red filtrate was

placed in a separatory funnel and extracted with 200 mL of chloroform. The aqueous phase was then extracted with 200 mL of chloroform. The white precipitate was stirred with THF (200 mL) and filtered. The THF washings and chloroform extracts were combined and concentrated under reduced pressure. The residual solution (100 mL) was then passed through a pad of silica gel to remove remaining inorganic salts. The filtrate was concentrated under reduced pressure to yield a red solid, which was dissolved in a minimum amount of TCE and loaded onto a column packed with silica gel (6 cm x 20 cm). The column was first eluted with 4 L of dichloromethane and then with 8 L of chloroform. The chloroform fraction was collected and concentrated under vacuum to give the diamine **4a** or **4b** as a red solid.

4a: 9.1 g (50%); m.p. 290 °C (dec.); IR (KBr) 3466 cm^{-1} , 3374 cm^{-1} (NH_2), 1754 cm^{-1} , 1703 cm^{-1} (C=O imide); ^1H NMR (400 MHz, DMSO-d_6) 2.4 (m, 2H), 2.8 (m, 4H), 3.9-4.0 (m, 2H), 5.29 (s, 2H), 5.48 (s, 2H), 6.16 (d, 1H), 6.4 (m, 2H), 6.55 (t, 1H), 6.61 (d, 1H), 6.78 (d, 1H), 7.00 (t, 1H), 7.12 (t, 1H), 7.18 (t, 1H), 7.26 (d, 1H), 7.35 (d, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) 23.64, 23.93, 27.74, 28.08, 111.45, 111.97, 112.89, 113.35, 114.70, 120.62, 123.28, 125.35, 125.49, 127.63, 127.71, 128.79, 128.90, 130.96, 132.61, 133.78, 135.86, 136.85, 137.92, 138.56, 139.70, 140.24, 149.14, 149.31, 167.27, 167.37; HRMS calcd for $\text{C}_{30}\text{H}_{23}\text{N}_3\text{O}_2$ 457.1790, found 457.1784.

4b: 10.0 g (55%); m.p. 290 °C (dec.); IR (KBr) 3460 cm^{-1} , 3371 cm^{-1} (NH_2); 1754 cm^{-1} , 1698 cm^{-1} (C=O imide); ^1H NMR (400 MHz, DMSO-d_6) 2.35 (m, 2H), 2.8 (m, 4H), 3.9 (m, 2H), 5.33 (s, 1H), 5.51 (s, 1H), 6.16 (d, 1H), 6.50 (s, 1H), 6.64 (m, 2H), 6.77 (d, 1H), 7.0 (m, 3H), 7.17 (t, 1H), 7.25 (d, 1H), 7.33 (d, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) 23.71, 24.00, 27.837, 28.18, 111.51, 112.04, 113.50, 119.87, 120.72, 123.42, 125.53,

127.72, 128.42, 128.87, 131.02, 133.86, 135.80, 136.75, 137.81, 138.62, 139.62, 140.30, 148.64, 149.32, 167.89, 167.91; HRMS calcd for $C_{30}H_{23}N_3O_2$ 457.1790, found 457.1821.

Diamine **6-7**.

A red powder: 3.85 g (84%); mp 278 °C (dec): ^1H NMR (400 MHz, DMSO- d_6) δ 8.90 (1 H, d), 8.78 (1 H, d), 8.33 (1 H, d), 8.16 (1 H, d), 8.05 (1 H, d), 7.89 (2 H, t), 7.60 (1 H, t), 7.33 (1 H, t), 7.18 (1 H, t), 6.99 (1 H, d), 6.6 - 6.7 (4 H, m), 5.94 (2 H, s), 5.35 (2 H, s); ^{13}C NMR (100 MHz, DMSO- d_6) δ 168.22, 168.18, 149.25, 135.30, 132.55, 132.35, 132.06, 130.29, 130.04, 129.74, 129.18, 129.08, 129.00, 128.02, 127.87, 127.67, 126.11, 125.98, 125.18, 123.44, 122.53, 121.17, 120.79, 120.71, 115.64, 114.79, 113.42, 112.96, 106.81; MS (EI, m/e, relative intensity %) 453 (M^+ , 100); HRMS calcd for $C_{30}H_{19}N_3O_2$ 453.1477, found 453.1488.

Typical procedure for polymerization

Diamine **6-2a** (1.381 g, 3.000 mmol) and 6FDA (1.341 g, 3.000 mmol) were placed in a 100 mL three-necked round-bottomed flask equipped with a N_2 inlet and a Dean-Stark trap fitted with a N_2 outlet, followed by 45 mL of *m*-cresol and 24 drops of isoquinoline under a strong N_2 stream. The flask was then placed in a preheated oil bath at 210 °C. The initially red solution quickly faded to give a yellow-orange solution. Polymerization

was stopped after 6-8 h by pipetting the hot solution into 600 mL of vigorously stirred methanol. The resulting fibrous polyimide was collected by filtration and washed twice with methanol (600 mL), filtered and finally washed with methanol (600 mL) overnight. Polymer **6-3a** was dried under vacuum (5 mmHg) for 4 days at 150 °C.

Endcapped polyimide 7

Diamine **6-2a** (0.458 g, 1.000 mmol), 6FDA (0.4273 g, 0.960 mmol) and TBPA (8.5 mg, 0.040 mmol) were polymerized as above. After 6 h the hot solution was poured into 300 mL of vigorously stirred methanol. The resulting fibrous polymer was filtered and washed with methanol (300 mL), filtered and finally washed with methanol (300 mL) overnight. Polyimide **6-5** was dried under vacuum (5 mmHg) for 4 days at 150 °C.

Model thermal transformation of compound 1.

See Chapter 2.

Polymer Transformation.

1. Chemical transformation using gaseous bromine (typical procedure).

A thin film of **6-3a** (0.01 - 0.03 mm thick, 50 mm x 10 mm) was placed in a glass tube (3 cm I.D. x 15 cm) fitted with a vacuum outlet and a bromine inlet. The tube was evacuated with water aspiration and placed in a preheated oil bath at 180 °C and allowed to stand for 1 h. The vacuum source was disconnected and gaseous bromine (~50 mL) was let into the tube. Bromine and HBr were evacuated and bromine was refilled every hour for a period of 4 h. After 4 h, IR showed the reaction to be complete and the tube

was evacuated for a further 2 h, while maintained at 180 °C. The tube was cooled to room temperature and the film was removed.

2. Chemical transformation using bromine in solution (typical procedure).

Polyimide **6-3a** (300 mg, 0.34 mmol) was dissolved in 15 mL of TCE in a 50 mL round-bottomed flask fitted with a dropping funnel and a reflux condenser. To this refluxing solution, a solution of bromine (130 mg, 0.72 mmol) in 5 mL of TCE was added dropwise over 30 min. White fumes evolved which were acidic to moist litmus. After 2 h, IR spectroscopy confirmed the reaction to be complete and the hot reaction mixture was poured into 200 mL of methanol. The resulting powder was filtered and stirred in 200 mL of methanol overnight. Polyimide **6-6a** (298 mg, 100%) was collected by filtration and dried under vacuum overnight (100 °C, 5 mmHg).

3. Thermal transformation (general procedure, powder or thin film)

The polyimide (100 mg) in a Pyrex dish (5 cm I.D., 0.75 cm deep) was placed in a preheated oven at 400 °C for 15 min. after which time the IR spectroscopy showed the reaction to be complete. The sample was removed and cooled to room temperature. The yield was quantitative.

6.1.5. References.

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6.2. Soluble linear copolyimides containing the tetrahydro[5]helicene unit.

6.2.1. Introduction.

It has been shown in the previous section that diamine monomers **6-2a** and **6-2b** were readily polymerized with 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) to yield polyimides **6-3a,b** and **6-4a,b**. All four polyimides were of high molecular weight and soluble in some common organic solvents. The tetrahydro[5]helicene unit in diamines **6-2a,b** is deemed to play a role in the ease of polyimide formation and good solubility observed for **6-3** and **6-4**. However, 6FDA and BPDA are expected to show high reactivity and contain structural moieties that can impart greater solubility to the corresponding polyimides. Specifically, the 6F moiety in 6FDA is known to interact well with polar and chlorinated solvents¹ and BPDA's non-planar bent conformation introduces a kink in the polyimide backbone.

At the molecular level, high solubility of a condensation polyimide can be either attributed to structural features contained within the dianhydride or the diamine monomer(s). Therefore, it is of interest to know whether the high solubility observed for polyimides **6-3a,b** and **6-4a,b** can be attributed to the structural features of the dianhydrides previously used (6FDA and BPDA) or to the diamine monomers **6-2a,b**. This can be probed by using dianhydrides which are structurally different from 6FDA and BPDA, such as 3,3',4,4'-benzophenonetetracarboxylic anhydride (BTDA), 3,3,4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA), and rigid pyromellitic dianhydride (PMDA).

Furthermore, molecular modeling is used to examine the molecular structure and conformation of diamines **6-2a** and **6-2b** in three dimensional space, with respect to the structural features which may lead to the observed solubilities of the presented polyimides.

6.2.2. Discussion.

Polyimide Synthesis and Characterization

Three commercially available dianhydrides were chosen for polycondensation with diamines **6-2a** and **6-2b**; BTDA, PMDA and SDPDA (Scheme 6-4). BTDA is structurally related to 6FDA with a difference at the connecting group ($C=O$ vs $C(CF_3)_2$); DSDA is known to be less reactive than other dianhydrides and therefore gives an indication of the reactivity of diamines **6-2a** and **6-2b**; rigid PMDA is likely to produce the polyimides with poor solubility and thus allows one to probe the brute ability of the tetrahydro[5]helicene unit to enhance the solubility of a polyimide.

Scheme 6-4. Synthesis of perfectly alternating copolyimide containing the tetrahydro[5]helicene unit (**6-9a,b**, **6-10a,b**, **6-11a,b**). Conditions: (i) *m*-Cresol, isoquinoline, 210 °C.

One-step polymerizations in *m*-cresol were performed using a small amount of isoquinoline at 210 °C. BTDA, DSDA and PMDA were polymerized with both **6-2a** and **6-2b** to produce polyimides **6-9a,b**, **6-10a,b** and **6-11a,b** respectively. With the exception of **6-11b** (**6-2b** with PMDA) which formed an insoluble gel after a short period of time, high molecular weight polyimides were readily obtained over 8 h. Diamines **6-2a** and **6-2b** appeared to be quite reactive, because high molecular weight polyimides were readily formed even with less reactive DSDA. Except for **6-11b**, all the polyimides were obtained as slightly yellow fibrous powders. Inherent viscosities of polyimides **6-9a,b**, **6-10a,b** and **6-11b** were measured at 0.5 g/dL in NMP to be in the range of 0.38-1.18 dL/g (Table 6-4), indicating that the polyimides are of high molecular weight. The

tetrahydro[5]helicene-containing polyimides showed the expected thermal stability in nitrogen atmosphere, having onset temperatures (T_d) for 5% weight loss in the range of 425 °C (**6-9a**) to 472 °C (**6-11a**). None of the polyimides showed a glass transition temperature or any other phase transitions between 25 °C and 400 °C as measured by DSC in normal or oscillating heating mode. All the polyimides showed good solubility in common organic solvents like TCE, NMP, DMAc and pyridine, except polyimide **6-11b** which formed a practically insoluble gel on polymerization. In sharp contrast to the polyimide derived from PMDA and 4,4'-oxydianiline (ODA), polyimide **6-11b** (PMDA with **6-2b**) was completely soluble in NMP and pyridine. This is an indication that the high solubility previously observed with tetrahydro[5]helicene containing polyimides **6-3a,b** and **6-4a,b** was not exclusively due to the flexible linkages within the dianhydride unit but at least partially due to the tetrahydro[5]helicene unit.

Table 6-4. Inherent viscosities and thermal stabilities of polyimides containing the tetrahydro[5]helicene unit.

	6-4a	6-4b	6-9b	6-10b	6-11b	6-3a	6-3b	6-9a	6-10a	6-11a
$[\eta]_{inh}$ (dL/g) ^a	0.41	n.m.	1.18	0.38	n.m.	0.48	0.55	0.47	0.46	0.46
T_d (°C) ^b	480	482	458	430	471	471	482	457	425	472

^a measure in NMP solution (0.5 g/dL) at 30.0 °C; ^b measured from 25 °C to 800 °C at a heating rate of 10 °C/min and taken as 5% weight loss in N₂ atmosphere; n.m. - polymer was not soluble enough to measure solution viscosity at 0.5 g/dL.

Diamine Conformation and Structure

It has been previously shown that perfectly alternating copolyimides can be made to higher molecular weight and can possess greater solubility than their random counterparts.² By design, the structure of diamines **6-2a** and **6-2b** leads to the formation of perfectly alternating copolyimides containing the tetrahydro[5]helicene unit, *m*- or *p*-phenylene diamine and the corresponding dianhydride moieties. In contrast to random copolymers which may form a short block within the polymer backbone, perfectly alternating polyimides derived from **6-2a** and **6-2b** should show greater solubility. As well, assuming that each amino group has similar reactivity, given that the ¹H chemical shifts are similar for the amino protons, the unsymmetric nature of diamines **6-2a** and **6-2b** leads to the formation of all three possible diads in the polyimide backbone. Such an irregular microstructure is deemed to increase the solubility of polyimides, due to the reduced interchain interaction.

However, these structural features can not be the only contributions leading to marked increase in solubility observed in this series of copolyimides. There are other features, such as spatial volume and preferred catenation, that can be described using computer aided molecular modeling. For a polymer, modeling allows for the accurate translation of structural properties of monomer or oligomer into observable polymer properties and conversely allows for the prediction of polymer properties based on computed monomer and oligomer structures.³

Figure 6-4. Stick models of diamines **6-2a** (top, right) and **6-2b** (top, left) and calculated ΔH_f surfaces (bottom) for the rotation about the imide bond.

Figure 6-4 illustrates energy minimized molecular models of diamines **6-2a** and **6-2b**, respectively, which were constructed using HyperChem version 4.0. These models were made by first optimizing the raw input structure using the MM+ (enhanced MM2⁴) molecular mechanics force field with final refinement done using the AM1⁵ semi-empirical method. The models show the expected helical conformation of the tetrahydro[5]helicene unit which results from spatial overlapping of the terminal aromatic rings. This spatial overlapping causes the tetrahydro[5]helicene unit to occupy approximately a volume of 335 Å³, nearly 100 Å³ more than if the structure is a planar

aromatic system. The spatial volume occupied by the tetrahydro[5]helicene unit is nearly equal to that occupied by the rigid helical [5]helicene. Therefore, the increase in solubility must be due not only to the spatial volume occupied by tetrahydro[5]helicene but also its ability to be flexible and move within that volume. Having these structural features, the tetrahydro[5]helicene unit once placed in a polymer environment should be able to inhibit chain-chain interactions and hinder polymer chain packing. Consequently, the solubility of the polyimide increases, as shown in our case.

Figure 6-4 also shows the relationship between the torsion angle about the imide (C-N) bond (illustrated) and $\Delta H_f^\ddagger$ for diamines **6-2a** and **6-2b**. The ΔH_f values were calculated as single points by incremental rotation of the imide bond, of the previously optimized structures. Maximum torsional energy occurs at 0° , when the phenylene ring is planar to the imide group and the *ortho*-protons are close in space to the carbonyl group; whereas a maximum at 180° occurs when there is no conjugation between the phenylene ring and the imide group. As expected, there exists potential energy minima for torsion angles of $\pm 30^\circ$ and $\pm 60^\circ$. For diamine **6-2b**, due to its *para* catenation, there is no difference between these two conformations, however because of the *meta* catenation of **6-2a** there exists the possibility for the introduction of further irregularity within the polymer backbone. It is for this reason that there is a marked increase in the solubility of the polyimides made from **6-2a** as opposed to polyimides from **6-2b**.

[‡] Since $\Delta G = \Delta H - T\Delta S$, and $-T\Delta S$ is negligible for this rotation, ΔH_f can be considered to be equal to ΔG_f .

6.2.3. Conclusion.

Diamines **6-2a** and **6-2b** containing the tetrahydro[5]helicene core have been proved to be able to impart great solubility to the polyimides derived from a variety of dianhydrides including rigid PMDA. The enhanced solubility observed for these tetrahydro[5]helicene containing polyimides can be attributed to the presence of diads in the polymer backbone, alternating repeat units, large spatial volume occupied by the tetrahydro[5]helicene unit and its structural mobility.

6.2.4. Experimental.

Materials. *m*-Cresol and isoquinoline were purchased from Aldrich Chemical Co. and used as received. 3,3,4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA) was polymer grade as purchased from ChrisKev Company. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) and pyromellitic dianhydride (PMDA) were polymer grade and obtained as gift from Allco Company. 1,1,2,2-Tetrachloroethane (TCE), dimethylsulfoxide (DMSO), N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidinone (NMP), N,N-dimethylformamide (DMF) and other common organic solvents (Aldrich) were reagent grade, unless otherwise stated, and were used as received.

Characterization. For general experimental methods see Appendix A.

Molecular Modeling. Molecular modeling was performed on a personal computer using HyperChem version 4.0. Models were first optimized using the MM+ (enhanced MM2) molecular mechanics forcefield with a convergence gradient of 0.01 kcal/Å mol using the Polak-Ribieue conjugate gradient algorithm. These models were then further optimized using the AM1 semi-empirical method utilizing the same convergence method and parameters.

Typical procedure for polymerization.

Diamine **6-2b** (1.381 g, 3.000 mmol) and BTDA (0.966 g, 3.000 mmol) were placed in a 100 mL, three-necked, round-bottomed flask equipped with a N₂ inlet and a Dean-Stark

trap fitted with a N₂ outlet, followed by 45 mL of *m*-cresol and 24 drops of isoquinoline under a strong N₂ stream. The flask was then placed in a preheated oil bath at 210 °C.

The initially red solution quickly faded to give a yellow-orange solution. Polymerization was stopped after 6-8 h by pipetting the hot solution into 600 mL of vigorously stirred methanol. The resulting fibrous polyimide was collected by filtration and washed twice with methanol (600 mL), filtered and finally stirred in methanol (600 mL) overnight.

Polymer **6-9b** was dried under vacuum (5 mmHg) for 4 days at 150 °C.

6.2.5. References.

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6.3. Poly(ether imide)s containing helically locked *o*-terphenyl subunits.

6.3.1. Introduction.

Traditional polyimides are made from a rather limited stock of commercially available monomers. Frequently these monomers are linear in nature with diamines made from para-substituted anilines and dianhydrides made from 4-substituted phthalic anhydrides. Variation in the chemical group linking the aniline and phthalic functionalities can result in monomers that impart highly desirable properties (such as enhanced solubility, improved mechanical properties and changes in dielectric constant) into the polyimides of which they are a part. However, these monomers retain the same basic spacial arrangement of their core functionality and are generally symmetric, as a result most polyimides are considered to be akin to rigid rods in both solution and the solid state. Variations on this theme have been restricted (at the commercial level) to meta-substituted diamines and 3-substituted phthalic anhydrides.¹

We have previously shown that the incorporation of a helically locked *o*-terphenyl moiety into the polymer backbone of a poly(ether sulfone) can have a dramatic effect on its glass transition temperature with no noticeable effect on the copoly(ether sulfone)'s solubility in organic solvents.²

It would now be of interest to study the effects the presence of a helical locked *o*-terphenyl moiety has on the physical properties of other high temperature polymers. Herein the synthesis and characterization of copoly(ether imide)s derived from a monomer containing a helically locked *o*-terphenyl moiety 3,12-diamino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic(*N*-*n*-butyl) imide is described (6-13, Scheme 6-5).

6.3.2. Discussion.

Monomer Synthesis.

Imidization of compound **2-3** with *n*-butylamine in the presence of isoquinoline in *o*-dichlorobenzene gave compound **6-12** in high yield. *n*-Butylamine was chosen to block the anhydride functionality instead of an aromatic amine, so as to prevent the possibility of a transimidization reaction occurring, in the presence of an aryl amine, during the subsequent polymerization step.

Scheme 6-5. Synthesis of helical diamine **6-13**. Conditions: (i) *n*-butylamine, chlorobenzene, isoquinoline, reflux. (ii) H₂, PtO₂, AcOH (cat), THF. (iii) phthalic anhydride, *m*-cresol, isoquinoline.

Subsequent hydrogenation of compound **6-12** to give diamine monomer **6-13** (Scheme 1) using Adam's catalyst (PtO₂) in the presence of a small amount of acetic acid proceeded with high yield. This monomer exhibited the characteristic imide and amino stretching frequencies in its IR spectra (1747, 1694 (C=O); 3463, 3372 (NH₂) cm⁻¹) and

the observed peak in its high-resolution mass spectrum was in good agreement with the calculated exact molecular mass (calculated 437.2103, found 437.2088). The ^1H NMR spectrum showed the expected resonances for the aliphatic *n*-butyl group (δ 3.50, 1.55, 1.24, 0.87 ppm) as well as the chemical shift for the protons within the amino group at δ 5.33 ppm (as measured in DMSO- d_6 solution). Figure 6-5 shows a molecular model of diamine monomer **6-13**. From this rendering (energy minimized using the AM1 semi-empirical method) the general shape and spacial arrangement of *o*-terphenyl moiety and the amino groups within monomer **6-13** can be seen.

Figure 6-5. Molecular model of diamine monomer **6-13**.

6-14a, $n = 0.05$; **6-14b**, $n = 0.10$; **6-14c**, $n = 0.20$; **6-14d**, $n = 0.50$; **6-14e**, $n = 1.00$

Figure 6-6. Random copoly(ether imide) **6-14** (molar percentage of unit containing monomer **6-13** in feed is indicated).

Polymer Synthesis.

Copolymers.

A variety of copoly(ether imide)s containing monomer **6-13**, BAPP and ODPA[‡] with feed ratios of 5, 10, 20 and 50 mol% of **6-13** (**6-14a-d**, Figure 6-6, Table 6-5) were prepared, as well as the homopolymer of **6-13** and ODPA (**6-14e**). Due to the chemical shift difference of the amino protons (δNH_2 , as measured in DMSO- d_6 solution) of monomer **6-13** (5.33 ppm) and BAPP (4.95 ppm) each polymer was made by a sequential addition polymerization method, as described in the experimental section.³ This was done to ensure that each polymer had diamine **6-13** distributed as randomly as possible within the polymer backbone. Furthermore, each copoly(ether imide) was endcapped with phthalic anhydride to ensure no free amino groups remained within the polymer, as the presence of such groups is known to lower the decomposition temperature. The molar percentage incorporation ratios could not be determined by any means. For instance, the distinct UV absorption of the disubstituted tetrahydro[5]helicene unit can be

[‡] ODPA/BAPP poly(ether imide) was chosen as the parent polymer because it exhibits a clear and measurable glass transition temperature at 258 °C. See Chapter 4.

observed at $\lambda_{\text{max}} = 368$ nm. However, this absorption in the UV spectrum is obscured by the tail end of the massive $\pi\text{-}\pi^*$ absorption at $\lambda_{\text{max}} = 287$ nm and therefore its true intensity could not be determined.

Macrocyclic formation.

For the series of copoly(ether imide)s **6-14a-e**, it was observed that on increasing the mol% of monomer **6-13** within the copolymer there was a notable increase in the amount of low molecular weight materials being formed. Figure 6-7 illustrates GPC traces of poly(ether imide)s **6-14a-e**. The intensity of the peak to the far right side of the chromatogram can be seen increasing with increased content of monomer **6-13**. The trend is seen until the point where (in the case of the homopolymer of **6-13** and ODPA, **6-14e**) no high molecular weight polymer was formed. A MALDI-TOF MS spectrum was obtained of polymer **6-14e** and is illustrated in Figure 6-8. It clearly shows that the lowest molecular weight material formed contains two repeat units ($n=2$) and has characteristic mass peaks at 1428.5 ($M+\text{Li}^+$), 1460.3 ($M+\text{Li}^++\text{CH}_3\text{OH}$) and 1492.4 ($M+\text{Li}^++2\text{CH}_3\text{OH}$). The methanol molecules have apparently become trapped within the macrocyclic structure even though this polymer was dried in vacuo at elevated temperatures for a significant period of time.

Table 6-5. Properties of poly(ether imide)s **6-14a-e**.

Molar feed ratio of monomer 6-13	Td (°C, N ₂)	Tg (°C)	M _w ^a (amu)	M _n ^a (amu)	M _w /M _n	[n] (NMP, dL g ⁻¹)	Film formation
5%	499	226	10,575	5,300	1.99	0.34	√
10%	504	226	10,216	5,056	2.02	0.36	√
20%	493	225	6,458	3,589	1.79	0.22	x
50%	484	256	7,699	2,466	2.46	0.22	x
100%	477	341	--- ^b	--- ^b	--- ^b	--- ^c	x
ODPA/BAPP	499	258	--- ^b	--- ^b	--- ^b	--- ^c	√

a – relative to polystyrene standards

b – not calculated

c – not measured

√ – yes

x – no

Figure 6-7. GPC traces of poly(ether imide)s **6-14a-e** showing increase in low molecular weight material being formed on increasing content of monomer **6-13**.

Figure 6-8. MALDI-TOF MS of cyclic poly(ether imide) **6-14e** from homopolymerization of monomer **6-13** and ODPA.

Characterization.

The physical properties of the presented poly(ether imide)s **6-14a-e** are outlined in Table 6-5. The apparent molecular weights obtained by comparison with narrow dispersed polystyrene molecular weight standards, on first glance, appear to be low. However, the ability of the poly(ether imide)s **6-14a** and **6-14b** to form polymer films indicates that they are of higher molecular weight than indicated by comparison with the polystyrene standards. Furthermore, the inherent viscosities also indicate that the poly(ether imide)s synthesized are of good molecular weight as they are in the range of 0.22 – 0.34 dL g⁻¹ (as measured in NMP solution at 0.5 g dL⁻¹).

As can be seen in Table 6-5 there is a noticeable change in the measured glass transition temperatures (T_g) of copoly(ether imide)s **6-14a-e** as a function of feed mol% monomer **6-13**. For feed ratios of 5, 10 and 20 mol% monomer **6-13** there was a measured decrease in the glass transition for these copolymers as compared to the parent polymer. Whereas, the 50 mol% copolymer had a nearly identical T_g (256 °C) to the parent polymer (258 °C) and the homopolymer **6-14e** had a T_g of 341 °C. Although polymer **6-14e** has been shown to consist of macrocyclic material, it did not display any other thermal transitions, other than a glass transition, by DSC. This change in the glass transition temperature that the incorporation of monomer **6-13** had on copolymers **6-14a-d** is in stark contrast to the observed effect that a similar unit had on the poly(ether sulphone) copolymers for which it was a part. In that case the incorporation of the monomer resulted in an linear increase in the measured glass transition temperature. Furthermore, it is well understood that the glass transition temperatures for a series of copolymers should fall between the glass transition temperatures of each of the

homopolymers and this is not the case for copolymers **6-14a-c**. Therefore, one must conclude that the cause for the changes in measured glass transition temperatures for copolymer **6-14a-c** is not understood.

Copoly(ether imide)s **6-14a-d** are fluorescent and their emission spectra are shown in Figure 6-9 along with that of compound **6-15** (the bis-phthalimide of diamine **6-13**). The emission spectra were obtained from irradiation of solutions of **6-14a-d** and **6-15** in chloroform at 365 nm and are normalized to the monomer equivalent concentration of **6-13** within the poly(ether imide). Each spectra shows an emission maximum at 485 – 490 nm (blue/green) and the molar emission intensity decreases with increasing mol% of **6-13** present. This can be attributed to the higher probability of inter-monomer-unit quenching taking place in the copoly(ether imide)s containing higher mol% diamine **6-13**.

Figure 6-9. Fluorescence emission spectra of copoly(ether imide)s **6-14a-e**. Emissions are corrected to monomer **6-13** equivalent concentration.

6.3.3. Conclusions.

A diamine monomer containing a *o*-terphenyl unit (**6-13**) has been synthesized and copolymerized with ODPA and BAPP to form a series of copoly(ether imide)s. The tendency of the copolymers to be of lower molecular weight and form macrocyclic materials at higher molar percentage of monomer **6-14** has been demonstrated. Each copolymer was fluorescent and the molar emission was shown to decrease on increasing molar percentage of monomer **6-13**.

6.3.4. Experimental.

Materials. *n*-Butylamine, chlorobenzene, platinum(IV)oxide, tetrahydrofuran (HPLC grade, inhibitor free), *m*-cresol and isoquinoline were purchased from Aldrich Chemical Co. and used as received. Oxydiphthalic dianhydride (OPDA) and 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) were polymer grade as purchased from ChrisKev Company. Common solvents and reagents (Aldrich) were reagent grade, unless otherwise stated, and were used as received.

Characterization. For general experimental methods see Appendix A.

Monomer synthesis.

3,12-Dinitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic(*N*-*n*-butyl) imide (6-12).

2.2198 g (5.02 mmol) of 3,12-dinitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**2**) and *n*-butylamine (2 mL) were set to stir in chlorobenzene (40 mL) containing isoquinoline (5 drops) for 1 h in a 3-necked rounded bottom flask fitted with a nitrogen inlet and Dean-Stark trap, after which it was set to reflux overnight. The homogeneous solution was cooled and poured into pentane (200 mL), the yellow precipitate was collected and dried in vacuo (100 °C, 5 mmHg) overnight; 2.30 g (92% yield); mp >300 °C; IR (KBr, C=O) 1762, 1702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ

8.25 (s, 2H), 7.81 (d, 2H), 7.17 (d, 2H), 4.23 (m, 2H), 3.70 (t, 2H), 3.06 (m, 4H), 2.57 (m, 2H), 1.68 (m, 2H), 1.39 (m, 2H), 0.96 (t, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 168.2, 147.3, 140.8, 139.0, 138.8, 137.6, 131.0, 127.8, 123.3, 121.2, 37.8, 30.6, 28.5, 23.7, 20.1, 13.6 ppm; MS (EI, m/e, relative intensity %) 497 (M^+ , 100); HRMS calcd for $\text{C}_{24}\text{H}_{23}\text{N}_3\text{O}_6$ 497.1586, found 497.1487.

3,12-Diamino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic(*N*-*n*-butyl) imide (6-13).

2.2501 g (4.52 mmol) of 3,12-dinitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic(*N*-*n*-butyl) imide (**3**) was dissolved in THF (35 mL) and acetic acid (0.5 mL) over PtO_2 (200 mg) and hydrogenated (60 psi) for 45 min. The solution was dried (MgSO_4) and removed to give a red solid which was dried in vacuo (100 °C, 5 mmHg) overnight; 1.95 g (99% yield); mp >300 °C; IR (KBr) 1747, 1694 ($\text{C}=\text{O}$), 3463, 3372 (NH_2) cm^{-1} ; ^1H NMR (400 MHz, DMSO-d_6) δ 6.90 (d, 2H), 6.44 (s, 2H), 6.16 (d, 2H), 5.30 (s, 4H, NH_2), 3.9 (bm, 4H), 3.50 (t, 2H), 2.65 (m, 4H), 2.2 (bm, 2H), 1.55 (m, 2H), 1.24 (m, 2H), 0.87 (t, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.4, 148.6, 139.8, 137.2, 136.5, 130.1, 123.4, 121.5, 111.9, 111.4, 36.5, 30.1, 28.4, 23.9, 19.5, 13.4 ppm; MS (EI, m/e, relative intensity %) 437 (M^+ , 100); HRMS calcd for $\text{C}_{28}\text{H}_{27}\text{N}_3\text{O}_2$ 437.2103, found 437.2088.

3,12-Diamino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic(*N*-*n*-butyl) imide-bis-phthalimide (6-15).

Diamine **4** (0.100 g, 0.23 mmol) and phthalic anhydride (70 mg, 0.47 mmol) were set to stir in *m*-cresol (1 mL) at 200 °C under Ar overnight. The following morning the solution was precipitated into methanol. The resulting red/brown powder was dried in vacuu (150 °C, 10 mmHg). 0.150 g (94% yield); mp >300 °C; IR (KBr, C=O) 1756, 1722, 1695 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.92 (m, 4H), 7.77 (m, 4H), 7.44 (s, 2H), 7.35 (d, 2H), 7.09 (d, 2H), 4.1 (m, 2H), 3.65 (t, 2H), 2.9 (m, 4H), 2.6 (m, 2H), 1.65 (m, 2H), 1.40 (m, 2H), 0.96 (t, 3H) ppm; ¹³C NMR (50 MHz, CDCl₃) δ 169.16, 167.42, 140.49, 138.73, 138.43, 134.77, 133.20, 131.93, 131.69, 131.20, 126.72, 125.72, 124.07, 37.88, 30.99, 28.99, 24.25, 20.45, 14.00 ppm; MS (FAB, m/e, relative intensity %) 698 (M+H⁺, 1.0).

Polymer synthesis.

Typical procedure is as follows. In a 3-necked rounded bottom flask fitted with a Dean Stark trap and argon inlet, monomer **6-13** (0.30 mmol, 10 mol%) and ODPA (3.00 mmol, 100 mol%) were placed in *m*-cresol (7.5% total final solids content) with a catalytic amount of isoquinoline (5 drops). The resulting solution was heated at 200 °C under Ar

gas flow for 4 h. After which BAPP (2.70 mmol, 90 mol%) was added as a powder and the polymerization continued overnight. Phthalic anhydride (100 mg) was added to endcap any remaining amine groups and after 2 h the reaction was precipitated while hot into methanol (800 mL) with vigorous stirring. The resulting fibrous precipitate was collected, Soxhlet extracted with ethanol for 2 days and dried in vacuo (150 °C, 10 mmHg).

6.3.5. References.

- ¹ Wilson, D.; Stenzenberger, H.D.; Hergenrother, P.M.: editors. Polyimides. **1990**. Chapman and Hall, New York, USA.
- ² (a) MacKinnon, S.M.; Wang Z.Y.; *Macromolecules*. **1998**, *31*, 7970.
- ³ The chemical shift of the amino protons in DMSO-d₆ solution is directly related to the reactivity of the amino group. See: (a) Ando, S.; Matsuura, T.; Sasaki, S.; *J. Polym. Sci., Pt A: Polym. Chem.*, **1992**, *30*, 2285. (b) Okude, K.; Miwa, T.; Tochigi, K.; Shimanoki, H.; *Polym. Prep.*, **1991**, *32*(1), 61.

Summary.

A single core molecule, the tetrahydro[5]helicene unit, has been chemically derivatized to produce a series of compounds suitable for incorporation into a variety of macromolecules having different molecular architecture.¹ The result is a series of macromolecules which all share a root functionality yet differ drastically in their macromolecular architectures.

The chemical reactivity, structural conformation and chirality of the tetrahydro[5]helicene unit has been explored. For example, spectroscopic evidence supported by computer aided molecular modeling has shown that the tetrahydro[5]helicene unit, although it is chiral, can not be resolved at ambient temperatures. The calculated racemization barrier for the unit was shown to be on the order of the energy available at room temperature.

The tetrahydro[5]helicene unit has been derivatized to produce an AB-type amino anhydride monomer. This monomer is stable at ambient and moderate temperatures yet becomes activated to polymerization at elevated temperatures. This monomer also has a tendency to self-assemble in the solid state through the formation of a hydrogen bond between its amino and anhydride functions. Simple thermal treatment in the solid state results in a collapse of this hydrogen bond and formation of an imide bond, thus its polymerization occurs readily in the solid state.² Furthermore, the solid state

¹ Bender, T.P.; MacKinnon, S.M.; Wang, Z.Y.; *Polymer News*, **1999**, 24(4), 115.

² (a) Wang, Z.Y.; Qi, Y.; Bender, T.P.; Gao, J.P.; *Macromolecules*, **1997**, 30, 764. (b) Bender, T.P.; Wang, Z.Y.; Wayner, D.M.M.; *J. Am. Chem. Soc.*, **1999**, submitted.

polymerization is unaffected by the presence of certain inorganic species and has been used to form polyimide-inorganic hybrid materials.³

It has been acknowledged that this may be the only case of a stable AB-type amino anhydride monomer and as a result methodology has been developed that can be used to form polyimides when the target AB-monomer is not stable. The tetrahydro[5]helicene unit has been derivatized to form an AX-type amino imide monomer which undergoes a transimidization reaction at elevated temperatures. The resulting polyimide contains reactive endgroups and therefore has been used in the synthesis of segmented polyimide block copolymers.⁴

The tetrahydro[5]helicene unit has also been incorporated into a series of dendritic aryl imides from generation one to three. The higher generation dendrimers exhibited unique electrochemical and fluorescent behaviours not seen in the first generation dendron or a series of model compounds. A mechanism has been proposed to account for these observations. Furthermore, on comparison of the third generation dendron with a linear analogue, there were observable differences in both its hydrodynamic volume and its glass transition temperature.⁵

Two unsymmetric diamines containing the tetrahydro[5]helicene unit have been synthesized and polymerized with a series of commercial monomers. They could be used as precursor polymers to [5]helicene containing polyimides which were otherwise

³ Bender, T.P.; Wang, Z.Y.; *Chem. Mater.*, **1999**, submitted.

⁴ (a) Bender, T.P.; Wang, Z.Y.; *Proc. Amer. Chem. Soc.: Division of Polymeric Materials Science and Engineering*, **1999**, in press. (b) Bender, T.P.; Wang, Z.Y.; *Macromolecules*, **1999**, submitted.

unobtainable by direct polymerization.⁶ Furthermore, this series of perfectly alternating copolyimides was shown to be remarkably soluble. The increase in solubility can be attributed to the presence of the tetrahydro[5]helicene unit with the polyimides and molecular modeling has been used to explain the observation.⁷

A helical-turn diamine monomer based on the tetrahydro[5]helicene unit has been synthesized and incorporated, by random copolymerization, into a poly(ether imide). Its presence within the molecular backbone has been shown to effect the glass transition temperature dramatically, having a variation over 120 °C.⁸

Contributions to knowledge.

This work represents the first time a complex and multifunctional molecule has been used as a core or basis for the rational design of new monomers and new macromolecules. This has been done by specific and selective chemical derivatization of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**1**) to produce an array of new monomers for incorporation into variety of macromolecules all within the framework of a polyimide. A detailed study of compound **1** using molecular modeling has been done in order to correlate experimental observations and measurements with the molecular structure and molecular motion inherent in the tetrahydro[5]helicene unit. Results

⁵ Bender, T.P.; Qi, Y.; Desjardins, P.; Wang, Z.Y.; *Can. J. Chem.*, **1999**, in press.

⁶ Bender, T.P.; Qi, Y.; Gao, J.P.; Wang, Z.Y.; *Macromolecules*, **1997**, 30, 6001.

⁷ Bender, T.P.; Wang, Z.Y.; *J. Polym. Sci., Part. A: Polym. Chem.*, **1998**, 1349.

⁸ Bender, T.P.; MacKinnon, S.M.; Wang, Z.Y.; *J. Polym. Sci., Part. A: Polym. Chem.*, **1999**, submitted.

obtained using molecular modeling and have been supported by obtaining the x-ray determined structure of compound **1** within a single crystal.

Compound **1** produces an assortment of monomers with specific spacial arrangements of their functionalities about its core. It is this variety in spacial arrangements and the tetrahydro[5]helicene unit's unique helical conformation that has allowed for the use of compound **1** in the synthesis of dendritic aryl imides (Chapter 5), soluble linear polyimides (Chapter 6.1, Chapter 6.2) and helical-turn copolyimides (Chapter 6.3). Furthermore, compound **1** can be selectively derivatized at its 3-position. As a result the tetrahydro[5]helicene unit has been used to study new methods in polyimide formation from AB-type amino anhydride and AX-type amino imide type monomers (Chapter 3 and Chapter 4 respectively).

Although this is the first instance of a functional core molecule of such versatility this approach can be used for the rational design of other polymeric systems based on other core molecules. Furthermore, as polymer scientists begin to think differently the current predominant focus of polymers as structural materials will shift to a focus on their use as functional materials. In other words the hypothesis "how do we make the glass transition low?" or "how do we make this polymer more wear resistant?" will change to include "how do we incorporate this moiety of known functionality into a polymer and use that polymer in its place?" When this happens, the need for an emphasis on a rational and versatile approach to the synthesis of these materials will become more evident and it will no longer be commonplace to make polymers because you can and the chemistry is easy.

Appendix A.

General experimental and characterization methods.

Characterization. ^1H and ^{13}C NMR spectra were recorded on a Bruker-400 instrument using tetramethylsilane as an internal reference. Infrared measurements were performed on a Bomem Michelson 120 FTIR spectrometer. Low (EI) and high resolution mass spectra were obtained on VG 7070E and Kratos Concept IIF spectrometers, respectively. UV-Vis absorption spectra were obtained on a Varian Cary3 spectrophotometer. Fluorescence measurements were made on a Shimadzu RF-1501 spectrofluorophotometer. Melting points were obtained with a Fisher-Johns apparatus and are uncorrected. Gel permeation chromatography (GPC) was performed using chloroform at ambient temperature at a flow rate of 1.0 mL per min; a UV detector set at 254-nm wavelength was used for detection. Apparent M_w and M_n were calculated relative to narrowly distributed polystyrene molecular weight standards. Inherent viscosities were measured in chloroform solution at $25 \pm 0.1^\circ\text{C}$ using an Ubbelohde dilution viscometer. The glass transition temperatures were determined on a Seiko 220C DSC at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen flow (50 mL/min). Thermal stabilities of the polymer samples were determined using a Seiko 120 TG/DTA analyzer run from 25°C to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen flow (200 mL/min). Thin films were cast from TCE solution, dried at $200\text{--}250^\circ\text{C}$ under vacuum (5 mmHg) over 14 days, and cut into strips (length = 10 mm, width = 2 mm, thickness = 0.01-0.03 mm). Young's moduli of thin films were obtained on a Seiko TMA/SS 120C TMA/SS analyzer. The films were tested by measuring the stress and strain while applying a sinusoidal load program. For Young's modulus at 25°C , the parameters were set as: offset load = 20 g, load amplitude = 10 g and cycling frequency = 0.05 Hz. Young's

moduli were obtained from the slope of the linear portion of the stress-strain plots (E'). After the data was collected, the same film was used without changing the parameters to measure Young's modulus variation with temperature by heating to 450 °C at a rate of 3 °C/min in static air. After cooling the film slowly to room temperature, a second measurement of Young's modulus variation with temperature was performed on the same film without changing the parameters, by heating to 450 °C at a rate of 3 °C/min in static air. MALDI-TOF mass spectra were obtained on a Kratos Kompact MALDI 3 time-of-flight mass spectrometer, using a dithranol/lithium bromide (20:1 by weight) or dithranol/silver trifluoroacetate (20:1 by weight) matrix.

Appendix B.

X-ray data for 5,6,9,10-tetrahydro[5]helicene-7,8,-dicarboxylic anhydride (compound **1**).

Table 1. Crystal data and structure refinement for ww001.

Identification code	ww001
Empirical formula	C ₂₄ H ₁₆ O ₃
Formula weight	352.37
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Ibca
Unit cell dimensions	a = 6.7083(9) Å alpha = 90 deg. b = 17.980(2) Å beta = 90 deg. c = 27.577(4) Å gamma = 90 deg.
Volume	3326.2(8) Å ³
Z, Calculated density	8, 1.407 Mg/m ³
Absorption coefficient	0.092 mm ⁻¹
F(000)	1472
Crystal size	0.3 x 0.3 x 0.02 mm
Theta range for data collection	2.27 to 28.73 deg.
Limiting indices	0 ≤ h ≤ 9, 0 ≤ k ≤ 23, 0 ≤ l ≤ 36
Reflections collected / unique	13006 / 2045 [R(int) = 0.0851]
Completeness to theta = 28.73	94.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2045 / 0 / 124
Goodness-of-fit on F ²	1.010
Final R indices [I > 2σ(I)]	R ₁ = 0.0465, wR ₂ = 0.0964
R indices (all data)	R ₁ = 0.0920, wR ₂ = 0.1077
Extinction coefficient	0.0014(3)
Largest diff. peak and hole	0.340 and -0.202 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ww001.

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	5000	2500	5706(1)	40(1)
O(2)	5055(2)	1258(1)	5591(1)	44(1)
C(1)	5018(2)	1865(1)	5414(1)	34(1)
C(2)	4997(2)	2112(1)	4905(1)	28(1)
C(3)	4888(2)	1700(1)	4481(1)	28(1)
C(4)	4808(2)	2111(1)	4045(1)	28(1)
C(5)	4130(2)	1709(1)	3605(1)	29(1)
C(6)	2917(3)	2056(1)	3259(1)	34(1)
C(7)	2161(3)	1658(1)	2876(1)	38(1)
C(8)	2589(3)	907(1)	2828(1)	40(1)
C(9)	3735(3)	553(1)	3176(1)	36(1)
C(10)	4497(2)	942(1)	3570(1)	31(1)
C(11)	5622(3)	578(1)	3977(1)	35(1)
C(12)	4839(3)	859(1)	4461(1)	34(1)

Table 3. Bond lengths [Å] and angles [deg] for ww001.

O(1)-C(1)#1	1.3953(19)
O(1)-C(1)	1.3953(19)
O(2)-C(1)	1.1958(19)
C(1)-C(2)	1.473(2)
C(2)-C(3)	1.384(2)
C(2)-C(2)#1	1.397(3)
C(3)-C(4)	1.413(2)
C(3)-C(12)	1.514(2)
C(4)-C(4)#1	1.421(3)
C(4)-C(5)	1.483(2)
C(5)-C(6)	1.401(2)
C(5)-C(10)	1.404(2)
C(6)-C(7)	1.374(2)
C(7)-C(8)	1.386(2)
C(8)-C(9)	1.385(2)
C(9)-C(10)	1.391(2)
C(10)-C(11)	1.501(2)
C(11)-C(12)	1.522(2)
C(1)#1-O(1)-C(1)	109.73(19)
O(2)-C(1)-O(1)	120.83(17)
O(2)-C(1)-C(2)	131.51(17)
O(1)-C(1)-C(2)	107.65(14)
C(3)-C(2)-C(2)#1	122.31(9)
C(3)-C(2)-C(1)	130.14(14)
C(2)#1-C(2)-C(1)	107.48(9)
C(2)-C(3)-C(4)	116.15(13)
C(2)-C(3)-C(12)	124.45(15)
C(4)-C(3)-C(12)	119.40(15)
C(3)-C(4)-C(4)#1	120.51(9)
C(3)-C(4)-C(5)	116.90(13)
C(4)#1-C(4)-C(5)	122.35(9)
C(6)-C(5)-C(10)	119.44(15)
C(6)-C(5)-C(4)	121.26(14)
C(10)-C(5)-C(4)	118.77(15)
C(7)-C(6)-C(5)	120.53(15)
C(6)-C(7)-C(8)	120.21(17)
C(9)-C(8)-C(7)	119.81(17)
C(8)-C(9)-C(10)	120.99(16)
C(9)-C(10)-C(5)	118.91(16)
C(9)-C(10)-C(11)	123.31(15)
C(5)-C(10)-C(11)	117.72(15)
C(10)-C(11)-C(12)	109.71(13)
C(3)-C(12)-C(11)	110.84(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1/2, z+0

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ww001.

The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	40(1)	49(1)	31(1)	0	0	-6(1)
O(2)	41(1)	47(1)	42(1)	14(1)	-5(1)	-3(1)
C(1)	23(1)	41(1)	39(1)	2(1)	-2(1)	-4(1)
C(2)	22(1)	33(1)	31(1)	4(1)	1(1)	1(1)
C(3)	23(1)	26(1)	36(1)	3(1)	-1(1)	0(1)
C(4)	25(1)	24(1)	34(1)	-1(1)	0(1)	2(1)
C(5)	29(1)	24(1)	34(1)	-1(1)	2(1)	-3(1)
C(6)	37(1)	26(1)	38(1)	1(1)	-2(1)	-2(1)
C(7)	42(1)	35(1)	36(1)	1(1)	-6(1)	-5(1)
C(8)	45(1)	35(1)	39(1)	-6(1)	-2(1)	-7(1)
C(9)	37(1)	26(1)	45(1)	-5(1)	2(1)	-3(1)
C(10)	28(1)	26(1)	38(1)	-1(1)	3(1)	-2(1)
C(11)	34(1)	22(1)	49(1)	0(1)	0(1)	2(1)
C(12)	34(1)	25(1)	43(1)	8(1)	-5(1)	0(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ww001.

	x	y	z	U(eq)
H(6A)	2622	2559	3289	40
H(7A)	1359	1893	2647	45
H(8A)	2109	642	2563	47
H(9A)	3998	48	3146	43
H(11A)	7031	692	3948	42
H(11B)	5462	43	3958	42
H(12A)	3481	687	4507	41
H(12B)	5648	658	4722	41

Appendix C.

Coordinate files for molecular models obtained for 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (Compound 1) using various computational methods (PDB format).

PDB file of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (Compound 1)

calculated using MM+ molecular mechanics method from HyperChem ver 5.01.

HETATM	1	C	1	-3.852	-1.707	-1.010
HETATM	2	C	2	-2.646	-2.356	-1.264
HETATM	3	C	3	-3.830	-0.410	-0.501
HETATM	4	C	4	-2.617	0.229	-0.219
HETATM	5	C	5	-1.395	-0.433	-0.412
HETATM	6	C	6	-1.439	-1.715	-0.982
HETATM	7	C	7	-2.612	1.633	0.322
HETATM	8	C	8	-1.483	2.396	-0.372
HETATM	9	C	9	-0.193	1.627	-0.234
HETATM	10	C	10	-0.176	0.220	-0.134
HETATM	11	C	11	1.036	-0.481	0.093
HETATM	12	C	12	1.074	-1.792	0.613
HETATM	13	C	13	2.213	-2.595	0.437
HETATM	14	C	14	3.378	-2.051	-0.344
HETATM	15	C	15	3.584	-0.595	0.078
HETATM	16	C	16	2.284	0.158	-0.058
HETATM	17	C	17	0.037	-2.309	1.404
HETATM	18	C	18	0.080	-3.603	1.924
HETATM	19	C	19	1.192	-4.408	1.689
HETATM	20	C	20	2.260	-3.892	0.957
HETATM	21	C	21	1.051	2.245	-0.304
HETATM	22	C	22	2.241	1.537	-0.234
HETATM	23	C	23	1.378	3.549	-0.465
HETATM	24	O	24	2.726	3.687	-0.490
HETATM	25	C	25	3.243	2.443	-0.345
HETATM	26	O	26	4.435	2.245	-0.316
HETATM	27	O	27	0.636	4.496	-0.586
HETATM	28	H	28	-2.648	-3.363	-1.716
HETATM	29	H	29	-4.784	0.113	-0.324
HETATM	30	H	30	-0.517	-2.241	-1.277
HETATM	31	H	31	-2.443	1.588	1.424
HETATM	32	H	32	-3.585	2.150	0.146
HETATM	33	H	33	-1.411	3.402	0.103
HETATM	34	H	34	-1.704	2.534	-1.457
HETATM	35	H	35	3.140	-2.120	-1.432
HETATM	36	H	36	4.311	-2.635	-0.159
HETATM	37	H	37	4.377	-0.162	-0.574
HETATM	38	H	38	3.925	-0.533	1.138
HETATM	39	H	39	-0.829	-1.689	1.688
HETATM	40	H	40	-0.750	-3.979	2.546
HETATM	41	H	41	3.151	-4.522	0.794
HETATM	42	H	42	-4.811	-2.201	-1.239
HETATM	43	H	43	1.241	-5.429	2.105
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CONECT	5	4	6	10		
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CONECT	41	20			
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CONECT	43	19			
END					

PDB file of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (Compound 1)

calculated using AM1 semi empirical method from HyperChem ver 5.01.

HETATM	1	C	1	-3.945	-1.692	-0.904
HETATM	2	C	2	-2.765	-2.377	-1.191
HETATM	3	C	3	-3.890	-0.390	-0.411
HETATM	4	C	4	-2.657	0.227	-0.186
HETATM	5	C	5	-1.460	-0.483	-0.414
HETATM	6	C	6	-1.531	-1.776	-0.951
HETATM	7	C	7	-2.584	1.650	0.242
HETATM	8	C	8	-1.451	2.351	-0.486
HETATM	9	C	9	-0.172	1.606	-0.341
HETATM	10	C	10	-0.177	0.184	-0.179
HETATM	11	C	11	1.010	-0.490	0.144
HETATM	12	C	12	1.062	-1.871	0.631
HETATM	13	C	13	2.226	-2.636	0.410
HETATM	14	C	14	3.388	-2.005	-0.271
HETATM	15	C	15	3.541	-0.568	0.194
HETATM	16	C	16	2.268	0.187	0.048
HETATM	17	C	17	0.024	-2.422	1.394
HETATM	18	C	18	0.110	-3.729	1.869
HETATM	19	C	19	1.238	-4.502	1.593
HETATM	20	C	20	2.296	-3.952	0.872
HETATM	21	C	21	1.040	2.258	-0.345
HETATM	22	C	22	2.262	1.541	-0.195
HETATM	23	C	23	1.391	3.685	-0.515
HETATM	24	O	24	2.795	3.802	-0.504
HETATM	25	C	25	3.360	2.524	-0.322
HETATM	26	O	26	4.578	2.470	-0.307
HETATM	27	O	27	0.764	4.722	-0.651
HETATM	28	H	28	-2.804	-3.393	-1.610
HETATM	29	H	29	-4.820	0.163	-0.210
HETATM	30	H	30	-0.603	-2.321	-1.187
HETATM	31	H	31	-2.416	1.700	1.351
HETATM	32	H	32	-3.549	2.179	0.024
HETATM	33	H	33	-1.331	3.397	-0.093
HETATM	34	H	34	-1.699	2.434	-1.581
HETATM	35	H	35	3.233	-2.033	-1.383
HETATM	36	H	36	4.332	-2.569	-0.049
HETATM	37	H	37	4.356	-0.060	-0.391
HETATM	38	H	38	3.849	-0.551	1.276
HETATM	39	H	39	-0.868	-1.817	1.623
HETATM	40	H	40	-0.714	-4.149	2.464
HETATM	41	H	41	3.199	-4.550	0.677
HETATM	42	H	42	-4.919	-2.172	-1.081
HETATM	43	H	43	1.299	-5.539	1.956
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CONECT	41	20			
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CONECT	43	19			
END					

PDB file of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (Compound 1)

calculated using Merck molecular mechanics method from Spartan ver 5.

HEADER

REMARK Spartan exported Thu Apr 29 10:01:10 1999

HETATM	1	H	UNK	0001	3.649	3.601	0.163
HETATM	2	C	UNK	0001	2.753	3.111	0.536
HETATM	3	C	UNK	0001	0.492	1.839	1.544
HETATM	4	C	UNK	0001	2.374	1.852	0.047
HETATM	5	C	UNK	0001	1.999	3.729	1.529
HETATM	6	C	UNK	0001	0.879	3.086	2.045
HETATM	7	C	UNK	0001	1.194	1.220	0.496
HETATM	8	C	UNK	0001	3.236	1.136	-0.960
HETATM	9	H	UNK	0001	2.298	4.699	1.917
HETATM	10	H	UNK	0001	0.304	3.550	2.842
HETATM	11	C	UNK	0001	0.813	-0.110	-0.069
HETATM	12	H	UNK	0001	-0.374	1.358	1.994
HETATM	13	C	UNK	0001	0.366	-2.800	-0.683
HETATM	14	C	UNK	0001	1.886	-0.939	-0.511
HETATM	15	C	UNK	0001	-0.529	-0.616	-0.141
HETATM	16	C	UNK	0001	-0.728	-2.013	-0.343
HETATM	17	C	UNK	0001	1.625	-2.277	-0.785
HETATM	18	C	UNK	0001	3.279	-0.361	-0.633
HETATM	19	C	UNK	0001	-1.761	0.226	-0.078
HETATM	20	C	UNK	0001	-2.119	-2.597	-0.222
HETATM	21	C	UNK	0001	2.523	-3.354	-1.166
HETATM	22	C	UNK	0001	0.444	-4.211	-1.022
HETATM	23	C	UNK	0001	-4.146	1.745	0.055
HETATM	24	C	UNK	0001	-2.967	-0.342	0.390
HETATM	25	C	UNK	0001	-1.819	1.543	-0.566
HETATM	26	C	UNK	0001	-2.992	2.300	-0.487
HETATM	27	C	UNK	0001	-4.139	0.422	0.486
HETATM	28	C	UNK	0001	-2.975	-1.800	0.768
HETATM	29	H	UNK	0001	-0.946	2.006	-1.021
HETATM	30	H	UNK	0001	-3.000	3.323	-0.854
HETATM	31	H	UNK	0001	-5.054	-0.017	0.874
HETATM	32	H	UNK	0001	-5.057	2.335	0.118
HETATM	33	H	UNK	0001	3.835	-0.851	-1.439
HETATM	34	H	UNK	0001	3.814	-0.536	0.308
HETATM	35	H	UNK	0001	-3.996	-2.200	0.759
HETATM	36	H	UNK	0001	4.258	1.532	-0.952
HETATM	37	H	UNK	0001	2.821	1.305	-1.962
HETATM	38	H	UNK	0001	-2.583	-2.604	-1.216
HETATM	39	H	UNK	0001	-2.587	-1.901	1.789
HETATM	40	H	UNK	0001	-2.078	-3.628	0.143
HETATM	41	O	UNK	0001	3.724	-3.290	-1.331
HETATM	42	O	UNK	0001	1.750	-4.462	-1.290
HETATM	43	O	UNK	0001	-0.468	-5.010	-1.070
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CONECT	43	22			

END

PDB file of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (Compound 1)

calculated using AM1 semi empirical method from Spartan ver 5.

```

HEADER
REMARK Spartan exported Thu Apr 29 10:01:26 1999
HETATM 1 H UNK 0001 3.589 3.596 0.135
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HETATM 3 C UNK 0001 0.389 1.932 1.466
HETATM 4 C UNK 0001 2.325 1.844 0.012
HETATM 5 C UNK 0001 1.893 3.723 1.475
HETATM 6 C UNK 0001 0.759 3.078 1.968
HETATM 7 C UNK 0001 1.144 1.215 0.459
HETATM 8 C UNK 0001 3.208 1.126 -0.946
HETATM 9 H UNK 0001 2.177 4.713 1.861
HETATM 10 H UNK 0001 0.154 3.550 2.756
HETATM 11 C UNK 0001 0.794 -0.107 -0.067
HETATM 12 H UNK 0001 -0.505 1.327 1.866
HETATM 13 C UNK 0001 0.331 -2.790 -0.678
HETATM 14 C UNK 0001 1.892 -0.926 -0.481
HETATM 15 C UNK 0001 -0.517 -0.600 -0.139
HETATM 16 C UNK 0001 -0.747 -1.994 -0.365
HETATM 17 C UNK 0001 1.644 -2.246 -0.778
HETATM 18 C UNK 0001 3.258 -0.350 -0.596
HETATM 19 C UNK 0001 -1.715 0.239 -0.040
HETATM 20 C UNK 0001 -2.117 -2.560 -0.248
HETATM 21 C UNK 0001 2.539 -3.346 -1.199
HETATM 22 C UNK 0001 0.434 -4.233 -0.989
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HETATM 25 C UNK 0001 -1.722 1.569 -0.482
HETATM 26 C UNK 0001 -2.882 2.336 -0.400
HETATM 27 C UNK 0001 -4.071 0.450 0.521
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HETATM 31 H UNK 0001 -5.001 0.004 0.905
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HETATM 34 H UNK 0001 3.793 -0.489 0.384
HETATM 35 H UNK 0001 -4.005 -2.168 0.738
HETATM 36 H UNK 0001 4.247 1.549 -0.920
HETATM 37 H UNK 0001 2.817 1.259 -1.991
HETATM 38 H UNK 0001 -2.610 -2.525 -1.259
HETATM 39 H UNK 0001 -2.551 -1.941 1.791
HETATM 40 H UNK 0001 -2.060 -3.640 0.056
HETATM 41 O UNK 0001 3.726 -3.446 -1.461
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HETATM 43 O UNK 0001 -0.346 -5.170 -1.025
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CONECT 2 1 5 4
CONECT 3 6 7 12
CONECT 4 7 2 8

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CONECT	42	21	22		
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END					

PDB file of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (Compound 1)

calculated using PM3 semi empirical method from Spartan ver 5.

HEADER

REMARK Spartan exported Thu Apr 29 10:01:39 1999

HETATM	1	H	UNK	0001	3.569	3.601	0.161
HETATM	2	C	UNK	0001	2.671	3.097	0.537
HETATM	3	C	UNK	0001	0.416	1.796	1.522
HETATM	4	C	UNK	0001	2.309	1.854	0.024
HETATM	5	C	UNK	0001	1.908	3.688	1.538
HETATM	6	C	UNK	0001	0.794	3.028	2.042
HETATM	7	C	UNK	0001	1.147	1.212	0.483
HETATM	8	C	UNK	0001	3.172	1.153	-0.970
HETATM	9	H	UNK	0001	2.195	4.667	1.938
HETATM	10	H	UNK	0001	0.210	3.478	2.852
HETATM	11	C	UNK	0001	0.794	-0.107	-0.062
HETATM	12	H	UNK	0001	-0.466	1.280	1.922
HETATM	13	C	UNK	0001	0.333	-2.783	-0.671
HETATM	14	C	UNK	0001	1.885	-0.918	-0.486
HETATM	15	C	UNK	0001	-0.516	-0.599	-0.139
HETATM	16	C	UNK	0001	-0.745	-1.988	-0.352
HETATM	17	C	UNK	0001	1.636	-2.240	-0.782
HETATM	18	C	UNK	0001	3.249	-0.327	-0.623
HETATM	19	C	UNK	0001	-1.718	0.246	-0.059
HETATM	20	C	UNK	0001	-2.119	-2.553	-0.206
HETATM	21	C	UNK	0001	2.529	-3.355	-1.205
HETATM	22	C	UNK	0001	0.446	-4.233	-0.994
HETATM	23	C	UNK	0001	-4.054	1.781	0.042
HETATM	24	C	UNK	0001	-2.914	-0.310	0.423
HETATM	25	C	UNK	0001	-1.729	1.554	-0.552
HETATM	26	C	UNK	0001	-2.889	2.317	-0.498
HETATM	27	C	UNK	0001	-4.069	0.466	0.492
HETATM	28	C	UNK	0001	-2.936	-1.753	0.799
HETATM	29	H	UNK	0001	-0.812	1.982	-0.975
HETATM	30	H	UNK	0001	-2.884	3.342	-0.881
HETATM	31	H	UNK	0001	-4.995	0.032	0.887
HETATM	32	H	UNK	0001	-4.963	2.389	0.098
HETATM	33	H	UNK	0001	3.830	-0.867	-1.397
HETATM	34	H	UNK	0001	3.799	-0.475	0.328
HETATM	35	H	UNK	0001	-3.974	-2.140	0.837
HETATM	36	H	UNK	0001	4.189	1.591	-0.993
HETATM	37	H	UNK	0001	2.755	1.298	-1.987
HETATM	38	H	UNK	0001	-2.613	-2.549	-1.200
HETATM	39	H	UNK	0001	-2.529	-1.875	1.822
HETATM	40	H	UNK	0001	-2.070	-3.615	0.105
HETATM	41	O	UNK	0001	3.699	-3.471	-1.459
HETATM	42	O	UNK	0001	1.775	-4.528	-1.313
HETATM	43	O	UNK	0001	-0.314	-5.164	-1.046
CONECT	1	2					
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CONECT	3	6	7	12			
CONECT	4	7	2	8			

CONECT	5	2	6	9	
CONECT	6	5	3	10	
CONECT	7	3	4	11	
CONECT	8	4	36	37	18
CONECT	9	5			
CONECT	10	6			
CONECT	11	7	15	14	
CONECT	12	3			
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CONECT	14	17	11	18	
CONECT	15	11	16	19	
CONECT	16	15	13	20	
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CONECT	33	18			
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CONECT	38	20			
CONECT	39	28			
CONECT	40	20			
CONECT	41	21			
CONECT	42	21	22		
CONECT	43	22			
END					

PDB file of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (Compound 1)

calculated using DFT method from Spartan ver 5.

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HEADER
REMARK  Spartan exported Wed May  5 09:57:35 1999
HETATM   1  H   UNK   0001   4.660   0.405   2.477
HETATM   2  C   UNK   0001   3.639   0.017   2.462
HETATM   3  C   UNK   0001   1.070  -1.008   2.386
HETATM   4  C   UNK   0001   2.840   0.262   1.353
HETATM   5  C   UNK   0001   3.164  -0.731   3.528
HETATM   6  C   UNK   0001   1.877  -1.256   3.482
HETATM   7  C   UNK   0001   1.524  -0.225   1.323
HETATM   8  C   UNK   0001   3.359   0.975   0.156
HETATM   9  H   UNK   0001   3.805  -0.925   4.390
HETATM  10  H   UNK   0001   1.504  -1.869   4.303
HETATM  11  C   UNK   0001   0.708  -0.005   0.126
HETATM  12  H   UNK   0001   0.065  -1.428   2.350
HETATM  13  C   UNK   0001  -0.691  -0.074  -2.263
HETATM  14  C   UNK   0001   1.415   0.113  -1.092
HETATM  15  C   UNK   0001  -0.708   0.005   0.126
HETATM  16  C   UNK   0001  -1.415  -0.113  -1.092
HETATM  17  C   UNK   0001   0.691   0.074  -2.263
HETATM  18  C   UNK   0001   2.895   0.250  -1.089
HETATM  19  C   UNK   0001  -1.524   0.225   1.323
HETATM  20  C   UNK   0001  -2.895  -0.250  -1.089
HETATM  21  C   UNK   0001   1.160   0.133  -3.643
HETATM  22  C   UNK   0001  -1.160  -0.133  -3.643
HETATM  23  C   UNK   0001  -3.164   0.731   3.528
HETATM  24  C   UNK   0001  -2.840  -0.262   1.353
HETATM  25  C   UNK   0001  -1.070   1.008   2.386
HETATM  26  C   UNK   0001  -1.877   1.256   3.482
HETATM  27  C   UNK   0001  -3.639  -0.017   2.462
HETATM  28  C   UNK   0001  -3.359  -0.975   0.156
HETATM  29  H   UNK   0001  -0.065   1.428   2.350
HETATM  30  H   UNK   0001  -1.504   1.869   4.303
HETATM  31  H   UNK   0001  -4.660  -0.405   2.477
HETATM  32  H   UNK   0001  -3.805   0.925   4.390
HETATM  33  H   UNK   0001   3.229   0.749  -2.010
HETATM  34  H   UNK   0001   3.349  -0.759  -1.110
HETATM  35  H   UNK   0001  -4.456  -1.032   0.191
HETATM  36  H   UNK   0001   4.456   1.032   0.191
HETATM  37  H   UNK   0001   2.984   2.013   0.130
HETATM  38  H   UNK   0001  -3.349   0.759  -1.110
HETATM  39  H   UNK   0001  -2.984  -2.013   0.130
HETATM  40  H   UNK   0001  -3.229  -0.749  -2.010
HETATM  41  O   UNK   0001   2.277   0.259  -4.116
HETATM  42  O   UNK   0001   0.000   0.000  -4.471
HETATM  43  O   UNK   0001  -2.277  -0.259  -4.116
CONNECT   1     2
CONNECT   2     1     5     4
CONNECT   3     6     7    12
CONNECT   4     7     2     8

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CONNECT	6	5	3	10	
CONNECT	7	3	4	11	
CONNECT	8	4	36	37	18
CONNECT	9	5			
CONNECT	10	6			
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CONNECT	12	3			
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CONNECT	17	13	14	21	
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CONNECT	28	24	39	20	35
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CONNECT	38	20			
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CONNECT	40	20			
CONNECT	41	21			
CONNECT	42	21	22		
CONNECT	43	22			
END					

PDB file of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (Compound 1)

calculated using STO-3G AB initio method from Spartan ver 5.

HEADER

REMARK Spartan exported Wed May 5 09:57:55 1999

HETATM	1	H	UNK	0001	0.292	-4.657	2.006
HETATM	2	C	UNK	0001	-0.078	-3.640	1.983
HETATM	3	C	UNK	0001	-1.077	-1.066	1.887
HETATM	4	C	UNK	0001	0.170	-2.850	0.869
HETATM	5	C	UNK	0001	-0.812	-3.148	3.049
HETATM	6	C	UNK	0001	-1.328	-1.863	2.991
HETATM	7	C	UNK	0001	-0.295	-1.531	0.830
HETATM	8	C	UNK	0001	0.868	-3.407	-0.368
HETATM	9	H	UNK	0001	-1.004	-3.774	3.912
HETATM	10	H	UNK	0001	-1.934	-1.481	3.802
HETATM	11	C	UNK	0001	-0.050	-0.703	-0.409
HETATM	12	H	UNK	0001	-1.501	-0.073	1.846
HETATM	13	C	UNK	0001	-0.026	0.692	-2.799
HETATM	14	C	UNK	0001	0.007	-1.416	-1.626
HETATM	15	C	UNK	0001	0.050	0.703	-0.409
HETATM	16	C	UNK	0001	-0.007	1.416	-1.626
HETATM	17	C	UNK	0001	0.026	-0.692	-2.799
HETATM	18	C	UNK	0001	0.083	-2.942	-1.613
HETATM	19	C	UNK	0001	0.295	1.531	0.830
HETATM	20	C	UNK	0001	-0.083	2.942	-1.613
HETATM	21	C	UNK	0001	0.059	-1.147	-4.240
HETATM	22	C	UNK	0001	-0.059	1.147	-4.240
HETATM	23	C	UNK	0001	0.812	3.148	3.049
HETATM	24	C	UNK	0001	-0.170	2.850	0.869
HETATM	25	C	UNK	0001	1.077	1.066	1.887
HETATM	26	C	UNK	0001	1.328	1.863	2.991
HETATM	27	C	UNK	0001	0.078	3.640	1.983
HETATM	28	C	UNK	0001	-0.868	3.407	-0.368
HETATM	29	H	UNK	0001	1.501	0.073	1.846
HETATM	30	H	UNK	0001	1.934	1.481	3.802
HETATM	31	H	UNK	0001	-0.292	4.657	2.006
HETATM	32	H	UNK	0001	1.004	3.774	3.912
HETATM	33	H	UNK	0001	0.561	-3.289	-2.526
HETATM	34	H	UNK	0001	-0.922	-3.366	-1.589
HETATM	35	H	UNK	0001	-0.903	4.492	-0.325
HETATM	36	H	UNK	0001	0.903	-4.492	-0.325
HETATM	37	H	UNK	0001	1.894	-3.043	-0.429
HETATM	38	H	UNK	0001	0.921	3.366	-1.589
HETATM	39	H	UNK	0001	-1.894	3.043	-0.429
HETATM	40	H	UNK	0001	-0.561	3.289	-2.526
HETATM	41	O	UNK	0001	0.123	-2.260	-4.720
HETATM	42	O	UNK	0001	0.000	0.000	-5.062
HETATM	43	O	UNK	0001	-0.123	2.260	-4.720
CONECT	1	2					
CONECT	2	1	5	4			
CONECT	3	6	7	12			
CONECT	4	7	2	8			

CONECT	5	2	6	9	
CONECT	6	5	3	10	
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CONECT	8	4	36	37	18
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CONECT	37	8			
CONECT	38	20			
CONECT	39	28			
CONECT	40	20			
CONECT	41	21			
CONECT	42	21	22		
CONECT	43	22			
END					

Appendix D.

Coordinate files for molecular models obtained for 5,6,9,10-tetrahydro[5]helicene.

[5]helicene and their transition states (PDB format).

PDB file of P-[5]helicene.

HETATM	1	C	1	-3.970	-1.590	0.944
HETATM	2	C	2	-2.778	-2.274	1.253
HETATM	3	C	3	-3.910	-0.332	0.384
HETATM	4	C	4	-2.661	0.268	0.095
HETATM	5	C	5	-1.462	-0.459	0.302
HETATM	6	C	6	-1.555	-1.720	0.943
HETATM	7	C	7	-2.598	1.634	-0.332
HETATM	8	C	8	-1.397	2.263	-0.432
HETATM	9	C	9	-0.174	1.546	-0.229
HETATM	10	C	10	-0.195	0.149	-0.037
HETATM	11	C	11	1.051	-0.563	-0.119
HETATM	12	C	12	1.171	-1.965	-0.453
HETATM	13	C	13	2.407	-2.627	-0.247
HETATM	14	C	14	3.552	-1.878	0.175
HETATM	15	C	15	3.484	-0.524	0.271
HETATM	16	C	16	2.245	0.165	0.069
HETATM	17	C	17	0.131	-2.687	-1.090
HETATM	18	C	18	0.274	-4.024	-1.397
HETATM	19	C	19	1.470	-4.701	-1.088
HETATM	20	C	20	2.523	-4.009	-0.532
HETATM	21	C	21	1.059	2.255	-0.196
HETATM	22	C	22	2.229	1.587	0.031
HETATM	23	H	23	-2.832	-3.253	1.752
HETATM	24	H	24	-4.830	0.231	0.170
HETATM	25	H	25	-0.629	-2.250	1.217
HETATM	26	H	26	-0.797	-2.159	-1.365
HETATM	27	H	27	-0.543	-4.568	-1.893
HETATM	28	H	28	3.477	-4.515	-0.318
HETATM	29	H	29	-4.939	-2.057	1.172
HETATM	30	H	30	1.559	-5.774	-1.312
HETATM	31	H	31	-3.542	2.164	-0.528
HETATM	32	H	32	-1.333	3.334	-0.680
HETATM	33	H	33	4.489	-2.421	0.372
HETATM	34	H	34	4.374	0.076	0.516
HETATM	35	H	35	1.043	3.348	-0.321
HETATM	36	H	36	3.179	2.129	0.153
CONECT	1	2	3	29		
CONECT	2	1	6	23		
CONECT	3	1	4	24		
CONECT	4	3	5	7		
CONECT	5	4	6	10		
CONECT	6	5	2	25		
CONECT	7	4	8	31		
CONECT	8	7	9	32		
CONECT	9	8	10	21		
CONECT	10	9	5	11		
CONECT	11	10	12	16		
CONECT	12	11	13	17		
CONECT	13	12	14	20		
CONECT	14	13	15	33		
CONECT	15	14	16	34		
CONECT	16	15	11	22		

CONECT	17	12	18	26
CONECT	18	17	19	27
CONECT	19	18	20	30
CONECT	20	19	13	28
CONECT	21	9	22	35
CONECT	22	21	16	36
CONECT	23	2		
CONECT	24	3		
CONECT	25	6		
CONECT	26	17		
CONECT	27	18		
CONECT	28	20		
CONECT	29	1		
CONECT	30	19		
CONECT	31	7		
CONECT	32	8		
CONECT	33	14		
CONECT	34	15		
CONECT	35	21		
CONECT	36	22		
END				

PDB file of [5]helicene racemization transition state.

HETATM	1	C		1	-3.769	-0.732	-1.522
HETATM	2	C		2	-3.276	-1.202	-0.294
HETATM	3	C		3	-3.279	0.457	-2.024
HETATM	4	C		4	-2.231	1.137	-1.362
HETATM	5	C		5	-1.548	0.524	-0.275
HETATM	6	C		6	-2.218	-0.564	0.326
HETATM	7	C		7	-1.963	2.507	-1.682
HETATM	8	C		8	-1.080	3.203	-0.924
HETATM	9	C		9	-0.209	2.519	-0.010
HETATM	10	C		10	-0.302	1.119	0.191
HETATM	11	C		11	0.887	0.433	0.636
HETATM	12	C		12	1.104	-1.005	0.720
HETATM	13	C		13	2.382	-1.524	0.368
HETATM	14	C		14	3.521	-0.656	0.372
HETATM	15	C		15	3.364	0.641	0.738
HETATM	16	C		16	2.053	1.216	0.835
HETATM	17	C		17	0.185	-1.949	1.228
HETATM	18	C		18	0.380	-3.310	1.081
HETATM	19	C		19	1.550	-3.799	0.478
HETATM	20	C		20	2.561	-2.911	0.170
HETATM	21	C		21	0.854	3.276	0.553
HETATM	22	C		22	1.978	2.628	0.973
HETATM	23	H		23	-3.756	-2.067	0.188
HETATM	24	H		24	-3.718	0.909	-2.926
HETATM	25	H		25	-1.983	-0.839	1.360
HETATM	26	H		26	-0.641	-1.611	1.863
HETATM	27	H		27	-0.372	-4.017	1.461
HETATM	28	H		28	3.532	-3.272	-0.202
HETATM	29	H		29	-4.568	-1.278	-2.042
HETATM	30	H		30	1.673	-4.877	0.306
HETATM	31	H		31	-2.534	2.982	-2.493
HETATM	32	H		32	-0.947	4.289	-1.048
HETATM	33	H		33	4.510	-1.081	0.144
HETATM	34	H		34	4.230	1.304	0.886
HETATM	35	H		35	0.776	4.373	0.576
HETATM	36	H		36	2.854	3.176	1.351
CONECT	1	2	3	29			
CONECT	2	1	6	23			
CONECT	3	1	4	24			
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CONECT	10	9	5	11			
CONECT	11	10	12	16			
CONECT	12	11	13	17			
CONECT	13	12	14	20			
CONECT	14	13	15	33			
CONECT	15	14	16	34			
CONECT	16	15	11	22			

CONNECT	17	12	18	26
CONNECT	18	17	19	27
CONNECT	19	18	20	30
CONNECT	20	19	13	28
CONNECT	21	9	22	35
CONNECT	22	21	16	36
CONNECT	23	2		
CONNECT	24	3		
CONNECT	25	6		
CONNECT	26	17		
CONNECT	27	18		
CONNECT	28	20		
CONNECT	29	1		
CONNECT	30	19		
CONNECT	31	7		
CONNECT	32	8		
CONNECT	33	14		
CONNECT	34	15		
CONNECT	35	21		
CONNECT	36	22		
END				

PDB file of M-[5]helicene.

HETATM	1	C	1	-3.691	-1.755	-1.793
HETATM	2	C	2	-2.470	-2.457	-1.772
HETATM	3	C	3	-3.729	-0.439	-1.385
HETATM	4	C	4	-2.557	0.207	-0.924
HETATM	5	C	5	-1.350	-0.525	-0.798
HETATM	6	C	6	-1.327	-1.855	-1.289
HETATM	7	C	7	-2.565	1.614	-0.660
HETATM	8	C	8	-1.401	2.265	-0.395
HETATM	9	C	9	-0.171	1.544	-0.261
HETATM	10	C	10	-0.170	0.134	-0.286
HETATM	11	C	11	1.026	-0.548	0.130
HETATM	12	C	12	1.059	-1.898	0.646
HETATM	13	C	13	2.303	-2.565	0.772
HETATM	14	C	14	3.518	-1.858	0.503
HETATM	15	C	15	3.488	-0.526	0.235
HETATM	16	C	16	2.242	0.167	0.101
HETATM	17	C	17	-0.097	-2.552	1.142
HETATM	18	C	18	-0.034	-3.841	1.628
HETATM	19	C	19	1.191	-4.536	1.649
HETATM	20	C	20	2.343	-3.902	1.237
HETATM	21	C	21	1.052	2.259	-0.129
HETATM	22	C	22	2.236	1.583	-0.035
HETATM	23	H	23	-2.433	-3.489	-2.151
HETATM	24	H	24	-4.667	0.135	-1.430
HETATM	25	H	25	-0.371	-2.403	-1.307
HETATM	26	H	26	-1.055	-2.007	1.159
HETATM	27	H	27	-0.941	-4.333	2.010
HETATM	28	H	28	3.313	-4.418	1.282
HETATM	29	H	29	-4.600	-2.258	-2.153
HETATM	30	H	30	1.220	-5.573	2.013
HETATM	31	H	31	-3.522	2.153	-0.721
HETATM	32	H	32	-1.375	3.359	-0.269
HETATM	33	H	33	4.469	-2.409	0.565
HETATM	34	H	34	4.416	0.051	0.105
HETATM	35	H	35	1.025	3.359	-0.142
HETATM	36	H	36	3.197	2.119	-0.027
CONECT	1	2	3	29		
CONECT	2	1	6	23		
CONECT	3	1	4	24		
CONECT	4	3	5	7		
CONECT	5	4	6	10		
CONECT	6	5	2	25		
CONECT	7	4	8	31		
CONECT	8	7	9	32		
CONECT	9	8	10	21		
CONECT	10	9	5	11		
CONECT	11	10	12	16		
CONECT	12	11	13	17		
CONECT	13	12	14	20		
CONECT	14	13	15	33		
CONECT	15	14	16	34		
CONECT	16	15	11	22		

CONNECT	17	12	18	26
CONNECT	18	17	19	27
CONNECT	19	18	20	30
CONNECT	20	19	13	28
CONNECT	21	9	22	35
CONNECT	22	21	16	36
CONNECT	23	2		
CONNECT	24	3		
CONNECT	25	6		
CONNECT	26	17		
CONNECT	27	18		
CONNECT	28	20		
CONNECT	29	1		
CONNECT	30	19		
CONNECT	31	7		
CONNECT	32	8		
CONNECT	33	14		
CONNECT	34	15		
CONNECT	35	21		
CONNECT	36	22		
END				

PDB file of P-tetrahydro[5]helicene.

HETATM	1	C	1	-3.961	-1.416	1.247
HETATM	2	C	2	-2.783	-2.032	1.667
HETATM	3	C	3	-3.900	-0.264	0.466
HETATM	4	C	4	-2.665	0.267	0.089
HETATM	5	C	5	-1.470	-0.385	0.459
HETATM	6	C	6	-1.547	-1.518	1.280
HETATM	7	C	7	-2.582	1.547	-0.664
HETATM	8	C	8	-1.424	2.383	-0.148
HETATM	9	C	9	-0.156	1.603	-0.121
HETATM	10	C	10	-0.187	0.201	0.062
HETATM	11	C	11	1.004	-0.535	-0.093
HETATM	12	C	12	1.059	-1.992	-0.239
HETATM	13	C	13	2.235	-2.674	0.135
HETATM	14	C	14	3.395	-1.888	0.633
HETATM	15	C	15	3.520	-0.590	-0.145
HETATM	16	C	16	2.233	0.160	-0.168
HETATM	17	C	17	0.017	-2.718	-0.832
HETATM	18	C	18	0.113	-4.100	-0.986
HETATM	19	C	19	1.255	-4.775	-0.558
HETATM	20	C	20	2.317	-4.061	-0.007
HETATM	21	C	21	1.060	2.266	-0.282
HETATM	22	C	22	2.254	1.551	-0.261
HETATM	23	H	23	-2.825	-2.924	2.308
HETATM	24	H	24	-4.828	0.240	0.155
HETATM	25	H	25	-0.621	-2.006	1.623
HETATM	26	H	26	-2.436	1.328	-1.756
HETATM	27	H	27	-3.537	2.128	-0.563
HETATM	28	H	28	-1.303	3.289	-0.799
HETATM	29	H	29	-1.654	2.744	0.892
HETATM	30	H	30	3.251	-1.664	1.725
HETATM	31	H	31	4.344	-2.477	0.533
HETATM	32	H	32	4.324	0.042	0.316
HETATM	33	H	33	3.833	-0.813	-1.202
HETATM	34	H	34	-0.885	-2.191	-1.179
HETATM	35	H	35	-0.715	-4.655	-1.448
HETATM	36	H	36	3.231	-4.587	0.307
HETATM	37	H	37	-4.936	-1.830	1.542
HETATM	38	H	38	1.325	-5.867	-0.668
HETATM	39	H	39	1.075	3.359	-0.413
HETATM	40	H	40	3.215	2.082	-0.330
CONECT	1	2	3	37		
CONECT	2	1	6	23		
CONECT	3	1	4	24		
CONECT	4	3	5	7		
CONECT	5	4	6	10		
CONECT	6	5	2	25		
CONECT	7	4	8	26	27	
CONECT	8	7	9	28	29	
CONECT	9	8	10	21		
CONECT	10	9	5	11		
CONECT	11	10	12	16		
CONECT	12	11	13	17		

CONECT	13	12	14	20	
CONECT	14	13	15	30	31
CONECT	15	14	16	32	33
CONECT	16	15	11	22	
CONECT	17	12	18	34	
CONECT	18	17	19	35	
CONECT	19	18	20	38	
CONECT	20	19	13	36	
CONECT	21	9	22	39	
CONECT	22	21	16	40	
CONECT	23	2			
CONECT	24	3			
CONECT	25	6			
CONECT	26	7			
CONECT	27	7			
CONECT	28	8			
CONECT	29	8			
CONECT	30	14			
CONECT	31	14			
CONECT	32	15			
CONECT	33	15			
CONECT	34	17			
CONECT	35	18			
CONECT	36	20			
CONECT	37	1			
CONECT	38	19			
CONECT	39	21			
CONECT	40	22			
END					

PDB file of tetrahydro[5]helicene racemization transition state.

HETATM	1	C	1	-4.131	-0.508	0.705
HETATM	2	C	2	-3.459	-1.202	-0.296
HETATM	3	C	3	-3.620	0.712	1.151
HETATM	4	C	4	-2.408	1.188	0.655
HETATM	5	C	5	-1.628	0.395	-0.225
HETATM	6	C	6	-2.232	-0.737	-0.775
HETATM	7	C	7	-1.981	2.591	0.908
HETATM	8	C	8	-1.370	3.138	-0.378
HETATM	9	C	9	-0.200	2.290	-0.747
HETATM	10	C	10	-0.281	0.884	-0.560
HETATM	11	C	11	0.915	0.139	-0.563
HETATM	12	C	12	1.071	-1.286	-0.228
HETATM	13	C	13	2.132	-1.638	0.646
HETATM	14	C	14	3.205	-0.637	0.894
HETATM	15	C	15	3.420	0.154	-0.392
HETATM	16	C	16	2.141	0.831	-0.754
HETATM	17	C	17	0.318	-2.327	-0.774
HETATM	18	C	18	0.443	-3.634	-0.295
HETATM	19	C	19	1.368	-3.931	0.700
HETATM	20	C	20	2.241	-2.936	1.142
HETATM	21	C	21	0.986	2.903	-1.139
HETATM	22	C	22	2.167	2.167	-1.142
HETATM	23	H	23	-3.895	-2.118	-0.722
HETATM	24	H	24	-4.188	1.314	1.876
HETATM	25	H	25	-1.788	-1.239	-1.642
HETATM	26	H	26	-2.857	3.221	1.211
HETATM	27	H	27	-1.228	2.629	1.739
HETATM	28	H	28	-2.135	3.128	-1.199
HETATM	29	H	29	-1.052	4.201	-0.223
HETATM	30	H	30	2.912	0.055	1.727
HETATM	31	H	31	4.158	-1.145	1.192
HETATM	32	H	32	4.235	0.908	-0.241
HETATM	33	H	33	3.743	-0.537	-1.216
HETATM	34	H	34	-0.335	-2.150	-1.636
HETATM	35	H	35	-0.189	-4.428	-0.718
HETATM	36	H	36	3.035	-3.180	1.862
HETATM	37	H	37	-5.076	-0.893	1.113
HETATM	38	H	38	1.441	-4.950	1.108
HETATM	39	H	39	1.001	3.976	-1.379
HETATM	40	H	40	3.123	2.654	-1.385
CONECT	1	2	3	37		
CONECT	2	1	6	23		
CONECT	3	1	4	24		
CONECT	4	3	5	7		
CONECT	5	4	6	10		
CONECT	6	5	2	25		
CONECT	7	4	8	26	27	
CONECT	8	7	9	28	29	
CONECT	9	8	10	21		
CONECT	10	9	5	11		
CONECT	11	10	12	16		
CONECT	12	11	13	17		

CONNECT	13	12	14	20	
CONNECT	14	13	15	30	31
CONNECT	15	14	16	32	33
CONNECT	16	15	11	22	
CONNECT	17	12	18	34	
CONNECT	18	17	19	35	
CONNECT	19	18	20	38	
CONNECT	20	19	13	36	
CONNECT	21	9	22	39	
CONNECT	22	21	16	40	
CONNECT	23	2			
CONNECT	24	3			
CONNECT	25	6			
CONNECT	26	7			
CONNECT	27	7			
CONNECT	28	8			
CONNECT	29	8			
CONNECT	30	14			
CONNECT	31	14			
CONNECT	32	15			
CONNECT	33	15			
CONNECT	34	17			
CONNECT	35	18			
CONNECT	36	20			
CONNECT	37	1			
CONNECT	38	19			
CONNECT	39	21			
CONNECT	40	22			
END					

PDB file of M-tetrahydro[5]helicene.

HETATM	1	C	1	-4.034	-1.609	-0.674
HETATM	2	C	2	-2.886	-2.304	-1.052
HETATM	3	C	3	-3.923	-0.325	-0.144
HETATM	4	C	4	-2.667	0.261	0.027
HETATM	5	C	5	-1.499	-0.460	-0.295
HETATM	6	C	6	-1.628	-1.733	-0.868
HETATM	7	C	7	-2.538	1.664	0.503
HETATM	8	C	8	-1.428	2.372	-0.254
HETATM	9	C	9	-0.159	1.593	-0.221
HETATM	10	C	10	-0.194	0.183	-0.120
HETATM	11	C	11	1.011	-0.517	0.088
HETATM	12	C	12	1.088	-1.916	0.515
HETATM	13	C	13	2.238	-2.668	0.196
HETATM	14	C	14	3.351	-2.005	-0.534
HETATM	15	C	15	3.524	-0.579	-0.039
HETATM	16	C	16	2.237	0.170	-0.069
HETATM	17	C	17	0.099	-2.503	1.316
HETATM	18	C	18	0.217	-3.827	1.733
HETATM	19	C	19	1.328	-4.583	1.363
HETATM	20	C	20	2.340	-4.000	0.603
HETATM	21	C	21	1.060	2.266	-0.287
HETATM	22	C	22	2.254	1.552	-0.255
HETATM	23	H	23	-2.970	-3.306	-1.498
HETATM	24	H	24	-4.828	0.237	0.130
HETATM	25	H	25	-0.727	-2.286	-1.176
HETATM	26	H	26	-2.308	1.664	1.603
HETATM	27	H	27	-3.502	2.220	0.361
HETATM	28	H	28	-1.266	3.389	0.193
HETATM	29	H	29	-1.738	2.522	-1.324
HETATM	30	H	30	3.123	-2.000	-1.634
HETATM	31	H	31	4.309	-2.570	-0.391
HETATM	32	H	32	4.286	-0.057	-0.676
HETATM	33	H	33	3.917	-0.591	1.014
HETATM	34	H	34	-0.779	-1.911	1.619
HETATM	35	H	35	-0.571	-4.274	2.358
HETATM	36	H	36	3.232	-4.585	0.332
HETATM	37	H	37	-5.026	-2.065	-0.807
HETATM	38	H	38	1.414	-5.632	1.682
HETATM	39	H	39	1.076	3.362	-0.377
HETATM	40	H	40	3.213	2.079	-0.366
CONECT	1	2	3	37		
CONECT	2	1	6	23		
CONECT	3	1	4	24		
CONECT	4	3	5	7		
CONECT	5	4	6	10		
CONECT	6	5	2	25		
CONECT	7	4	8	26	27	
CONECT	8	7	9	28	29	
CONECT	9	8	10	21		
CONECT	10	9	5	11		
CONECT	11	10	12	16		
CONECT	12	11	13	17		

CONECT	13	12	14	20	
CONECT	14	13	15	30	31
CONECT	15	14	16	32	33
CONECT	16	15	11	22	
CONECT	17	12	18	34	
CONECT	18	17	19	35	
CONECT	19	18	20	38	
CONECT	20	19	13	36	
CONECT	21	9	22	39	
CONECT	22	21	16	40	
CONECT	23	2			
CONECT	24	3			
CONECT	25	6			
CONECT	26	7			
CONECT	27	7			
CONECT	28	8			
CONECT	29	8			
CONECT	30	14			
CONECT	31	14			
CONECT	32	15			
CONECT	33	15			
CONECT	34	17			
CONECT	35	18			
CONECT	36	20			
CONECT	37	1			
CONECT	38	19			
CONECT	39	21			
CONECT	40	22			
END					

Appendix E.

X-ray determined atomic coordinates for 3-amino-5,6,9,10-tetrahydro[5]helicene-7,8,-
dicarboxylic anhydride (compound **3-1**).

Formula: $C_{24}H_{17}NO_3 \cdot CHCl_3$

Point group: $P2(1)/c$

Crystal cell: $a=8.4530$ $b=23.8540$ $c=11.0902$ $\alpha=90.000$ $\beta=103.275$ $\gamma=90.000$

Atomic Coordinates (hydrogen positions are calculated)

Atom	X(Cryst)	Y(Cryst)	Z(Cryst)	X(Orth)	Y(Orth)	Z(Orth)
CL1	0.55458	0.25284	0.04981	4.56104	6.03126	0.53762
CL2	0.70315	0.21948	0.29592	5.19017	5.23566	3.19417
CL3	0.80319	0.16887	0.09103	6.55765	4.02828	0.98255
O1	0.15423	0.96337	0.02237	1.24676	22.98070	0.24147
O2	0.13191	0.89979	0.16667	0.69057	21.46409	1.79901
O3	0.13862	0.85499	0.34594	0.29080	20.39524	3.73400
N1	0.14191	1.30417	0.37979	0.23239	31.11031	4.09935
C1	0.16127	0.95368	0.12934	1.03384	22.74968	1.39605
C2	0.15800	0.89832	0.29642	0.58071	21.42895	3.19950
C3	0.20262	0.95450	0.34299	0.83934	22.76913	3.70216
C4	0.19996	0.98975	0.24123	1.07597	23.60995	2.60378
C5	0.22138	1.04614	0.25312	1.22673	24.95503	2.73218

C6	0.22172	1.08493	0.14615	1.50204	25.88038	1.57749
C7	0.32459	1.13613	0.18878	2.26301	27.10171	2.03770
C8	0.26159	1.16487	0.28956	1.47388	27.78737	3.12546
C9	0.23696	1.22146	0.29188	1.25980	29.13725	3.15048
C10	0.16281	1.24665	0.37768	0.41449	29.73816	4.07661
C11	0.11315	1.21211	0.46316	-0.22300	28.91429	4.99931
C12	0.14088	1.15574	0.46402	0.00920	27.56949	5.00859
C13	0.21896	1.13012	0.38003	0.88314	26.95855	4.10197
C14	0.24166	1.06940	0.37426	1.08966	25.50995	4.03968
C15	0.26878	1.03256	0.47877	1.05281	24.63131	5.16779
C16	0.32940	1.05322	0.60841	1.23504	25.12392	6.56714
C17	0.42244	1.10106	0.63799	1.94623	26.26512	6.88633
C18	0.47516	1.11915	0.76022	2.08061	26.69677	8.20567
C19	0.43475	1.08863	0.85528	1.49690	25.96865	9.23182
C20	0.34956	1.04007	0.82748	0.84762	24.81047	8.93173
C21	0.29177	1.02114	0.70606	0.66834	24.35870	7.62112
C22	0.20083	0.96744	0.67652	-0.02523	23.07775	7.30232
C23	0.26110	0.93706	0.57435	0.74442	22.35306	6.19948
C24	0.24393	0.97522	0.46298	0.88295	23.26350	4.99733
C26	0.73826	0.22997	0.14904	5.86108	5.48591	1.60872
H6A	0.13031	1.09668	0.11793	0.80120	26.16084	1.27291
H6B	0.27409	1.06344	0.09487	2.07530	25.36782	1.02400
H7A	0.31763	1.15933	0.12901	2.35638	27.65530	1.39254
H7B	0.43566	1.12355	0.21848	3.12632	26.80180	2.35821
H9	0.26910	1.24242	0.24564	1.64915	29.63723	2.65140
H11	0.06016	1.22931	0.52633	-0.83180	29.32452	5.68112
H12	0.09522	1.13445	0.51034	-0.49474	27.06166	5.50858
H17	0.45652	1.12555	0.56712	2.41482	26.84934	6.12138
H18	0.53620	1.15566	0.77952	2.54749	27.56769	8.41398
H19	0.49383	1.10001	0.96496	1.71709	26.24030	10.41562
H20	0.34478	1.01773	0.88001	0.67339	24.27745	9.49876
H22A	0.07721	0.97223	0.65215	-1.00808	23.19203	7.03919
H22B	0.21800	0.94087	0.74134	-0.04510	22.44408	8.00189
H23A	0.21672	0.89725	0.55613	0.41573	21.40337	6.00282
H23B	0.36912	0.92805	0.60132	1.58885	22.13819	6.49061
H26	0.82461	0.27006	0.15983	6.56353	6.44205	1.72514
NH1	0.02723	1.31503	0.41660	-0.83070	31.36942	4.49670
NH2	0.12340	1.31787	0.28309	0.32224	31.43704	3.05558

Appendix F.

Oligoimides from AB-amino anhydride monomer.

Oligoimides of the type shown were made by time controlled polymerization using standard conditions (*m*-cresol at 200 °C in the presence of iosquinoline). The produced oligoimides were fractionated into 4 parts (1-4) by reverse precipitation using chloroform (good solvent) and methanol (bad solvent). GPC traces for each are shown in Figure F-1. Analysis by MALDI-TOF MS provided exact distribution of the molecular mass for each sample. WAXD was performed on each sample.

Figure F-1. GPC analysis of oligoimides 1-4 and their summation.

Oligoimide 1.

Z-Wang-1-dith-Li

Data: <none> 2 21 Jul 97 16:20 Cal: TOF 18 Jun 97 16:16

Kratos Kompact MALDI 3 V4.0.0: + Reflectron High Power: 97

%Int. 100% = 21 mV [sum= 889 mV] Shots 79-120 Smooth Av 27

Oligoimide 2.

Z-Wang-2-dith-Li

Data: <none> 6 21 Jul 97 16:51 Cal: TOF 18 Jun 97 16:16

Kratos Kompact MALDI 3 V4.0.0: + Reflectron High Power: 97

%Int. 100% = 29 mV [sum= 2002 mV] Shots 1-67 Smooth Av 27

Oligoimide 3.

Z-Wang-3-dith-Ag

Data: Wa-30001.13 21 Jul 97 17:09 Cal: TOF 18 Jun 97 16:16

Kratos Kompact MALDI 3 V4.0.0: + Reflectron High Power: 97

%Int. 100% = 9 mV (sum= 684 mV) Shots 1-75 Smooth Av 27

Oligoimide 4.

Z-Wang-4-dith-Li

Data: <none> 16 21 Jul 97 17:14 Cal: TOF 18 Jun 97 16:16

Kratos Kompact MALDI 3 V4.0.0: + Reflectron High Power: 97

%Int. 100% = 23 mV (sum= 1957 mV) Shots 36-120 Smooth Av 27