THE CONSTRUCTION OF SUBSTITUTED ANTHRACENES AND THEIR PHOTOCHEMICAL APPLICATIONS

by

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ABSTRACT

The photodimerisation of anthracene is a reversible bimolecular process. Once dimerised, the monomeric anthracene may be reformed either thermally or photochemically. In the past, this dimerisation process has exhibited poor selectivity: when mixtures of substituted anthracenes are irradiated together a mixture of dianthracene products are formed.

The research in this thesis describes the development of substituted anthracene systems that allow for an effective control over this dimerisation process. When irradiated, pairs of anthracenes yield only a single cross-cyclomer photoproduct. Two techniques to achieve this desired reactivity were developed: the first is based on the use of orthogonal steric bulk, and the second exploits the differences in the UV-absorbances of the compounds to allow selective excitation of only a single reacting species. Both of these routes achieved the desired results yielding only the one desired cyclomer. Studies examining the reversibility of these structures were also undertaken. The structures were found to be reversible both thermally and photochemically.

To achieve this desired reactivity, novel anthracenes with peripherally-substituted phenyl groups were required. Two complementary methods for preparing the anthraquinone precursors were developed. These anthraquinones could then be reduced to the desired anthracenes. The first method utilised a Diels-Alder style addition of thiophene dioxides to benzo- and naphthoquinones to afford anthraquinones. This method allowed both phenyl- or bromo-groups to be placed at the 2-,3-,6- and 7-positions of the anthraquinone. To facilitate the preparation of lower symmetry derivatives, a complementary synthetic route using cyclopentadienones as the reactive species was developed. This methodology permitted three different substituent groups to be placed on the anthraquinone.

Keywords: Anthracene, Selective-Photochemistry, Cyclopentadienone, Thiophene Dioxide, Anthraquinone

Dedicated to the most wonderful discovery I made in the laboratory:
Laura

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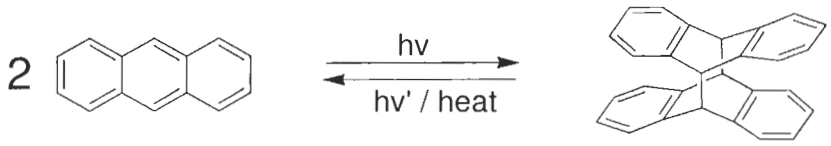
ABBREVIATIONS USED IN THIS THESIS

^{1}H NMR	proton nuclear magnetic resonance
^{13}C NMR	carbon nuclear magnetic resonance
AcOH	acetic acid
aq	aqueous
°C	degree(s) centigrade
calcd.	calculated
CI	chemical ionisation
cm^{-1}	wavenumber(s)
m-CPBA	meta-chloroperoxybenzoic acid
D	deuterium
d	doublet
dd	doublet of doublets
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
decomp	decomposed/decomposition
DFT	density functional theory
DMDO	dimethyldioxirane
DME	1,2-dimethoxyethane
DMSO	dimethylsulfoxide
e^{-}	electron(s)
Elec	electrophile
EDG	electron donating group(s)
EWG	electron withdrawing group(s)
EA	elemental analysis
EI	electron impact
EtOAc	ethyl acetate
EtOH	ethanol
equiv	equivalent(s)
FAB	fast atom bombardment
FT-IR	Fourier transform infrared
h	hour(s)
hh	head to head
ht	head to tail

HOMO	highest occupied molecular orbital
HR-MS	high resolution mass spectrometry
Hz	Hertz
irrad.	irradiation
J	coupling constant
LUMO	lowest unoccupied molecular orbital
m	multiplet
MALDI-TOF	matrix assisted laser desorption/ionisation time of flight
Me	methyl
MeOH	methanol
min	minute
mL	milliliter
mol	mole(s)
MP	melting point
MS	mass spectrometry
m/z	mass to charge ratio
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NOESY	nuclear Overhauser effect spectroscopy
Nu	nucleophile
Ox	oxidation
PAH	polyaromatic hydrocarbon
Ph	phenyl
pp.	pages
ppm	parts per million
pres.	pressure
Red	reduction
rel.	relative
RT	room temperature
rxn	reaction
s	singlet
THF	tetrahydrofuran
p-TsOH	p-toluenesulfonic acid
UV	ultraviolet
Vis	visible
wt.	weight

CHAPTER 1: INTRODUCTION

1.1 History of Anthracene Photochemistry

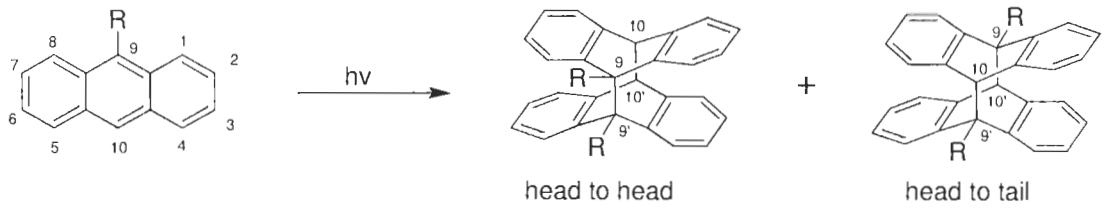


Scheme 1.1 Reversible photodimerisation of anthracene

Discovered in 1866, the photodimerisation of anthracene (Scheme 1.1) was one of the first photochemical reactions to have been observed.[1] Fritzsche noted that upon exposure to sunlight, saturated solutions of a soluble coal-tar distillate that he termed "Photene" became the insoluble "Paraphotene". Surprisingly, upon heating, this insoluble product reverted to its soluble form. Later studies would establish the identity of "Photene" and "Paraphotene" as anthracene and dianthracene, respectively.[1] By 1891, it was determined by molecular weight determination that this transformation was a dimerisation, and by the turn of the century, the correct structure of "Paraphotene" was proposed.[2] In 1932 the first crude X-Ray analysis of dianthracene was obtained, although it was not until 1966 that the dianthracene structure was fully refined.[3] Unlike the thermal

reversion that was discovered concurrently with the photodimerisation, the photochemical reversion of dianthracene to anthracene was only discovered in 1924 by Taylor and Lewis.[4]

By the mid 1950s, research into the photochemistry of substituted anthracenes began in earnest, focusing primarily on the reactions of 9- and 9,10-substituted anthracenes. During this period, it was observed that the reactions generally involved a [4+4]-cycloaddition across the central rings and resulted in head to tail dimeric structures (Scheme 1.2).[2]



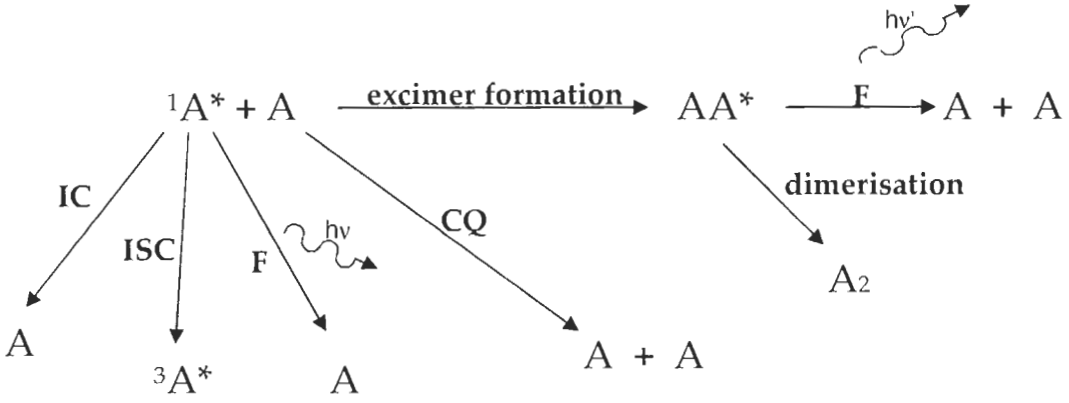
Scheme 1.2 Dimerisation modes of 9-substituted anthracene derivatives

In the past 60 years there has been considerable research exploring the scope of these reactions, especially in regards to the compatability of substituent groups with the photodimerisation. While the earliest mechanistic studies were done in 1905 by Luther and Weigert, it was only in the mid to late 1950s that systematic research into the mechanism of anthracene photodimerisation was undertaken.[5,6,7] The discovery of excimers in 1954 by Förster, as well as the

development of the Woodward-Hoffmann rules in 1965 helped garner interest in photochemical transformations such as the anthracene dimerisation.[3,8,9,10,11] During the 1970's further research into the mechanism of the dimerisation was undertaken, focusing on the role of excimers (*vide infra*) and the energy profile during dimerisation.[3] In the 1980's and 1990's substantial work into alternative, non-classical dimerisation modes as well as novel reactivity of irradiated anthracene molecules was undertaken.[12,13,14,15,16,17] By the 1990s research into material applications of this reaction became more common, and the dimerisation of anthracene was applied to diverse applications such as: the construction of cross-linked polymers,[18] creation of dynamic receptors,[19] and as a means of attenuating magnetic interactions.[20,21]

In this thesis, novel methods for achieving selective and controllable photo-cycloadditions between anthracene molecules will be described. It is anticipated that improved control over the photoreactivity will enable the development of new and useful applications of anthracene photochemistry. New synthetic methods that were required to produce the anthracene derivatives will also be described.

1.2 Anthracene Dimer Formation



IC = internal conversion ISC = intersystem crossing
F = fluorescence CQ = concentration quenching

Scheme 1.3 Relaxation routes available to an anthracene excited to the singlet state (modified from reference 7)

Irradiating solutions of anthracene derivatives with UV radiation (generally at wavelengths 250 nm < λ < 450 nm) leads to an excited singlet state that may relax through a variety of either radiative or nonradiative pathways (Scheme 1.3). Following is a brief discussion of these relaxation routes.

One of the most prevalent means for the excited state to relax is through fluorescence. The quantum yields of fluorescence vary greatly depending on the nature of the substituent, from near unity for 9,10-di(phenylethynyl)anthracene to about 0.01 for 9-bromoanthracene.[2] It has been suggested that halogens

increase the propensity of intersystem crossing to occur, thereby reducing the quantum yield of flourescence.[22] In addition, the first singlet state of anthracene lies 2 kcal/mol higher in energy than the second triplet state,[2] which allows for very efficient intersystem crossing to the triplet state. For many anthracene systems, it has been shown that the tendency towards intersystem crossing and fluorescence essentially exclude internal conversion as a relaxation route.[2] This, however, is not always the case; 9-(*t*-butyl)anthracene, for example, has quite a low quantum yield of fluorescence due to competition from internal conversion and an intramolecular chemical reaction (see Scheme 1.11). The efficiency of these processes result in intersystem crossing not being observed as a relaxation route.[23]

While the fluorescence of anthracenes is the most studied relaxation route from the singlet excited state, the photocycloaddition of these species with a second non-excited anthracene is the focus of the research described within this thesis. These photocycloaddition reactions are generally believed to occur *via* excited states arising from π-π^* transitions.[3]

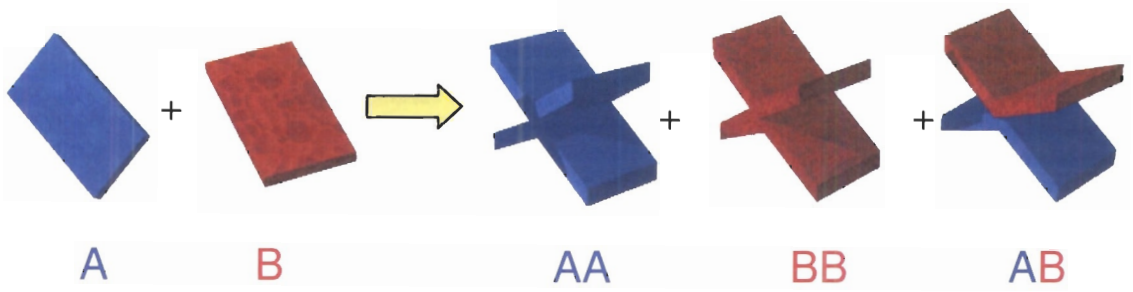
Measurements of the rate constants of anthracene dimerisations (which are generally in the range of 0.5 - 2.3 x 10^{-9} M^{-1} s^{-1}) have shown that the rate of these reactions is consistent with the lifetime of a singlet excited state (4-13

ns).[24,25,26] An anthracene in its excited singlet state may also form an excimer if it comes into contact with another anthracene molecule in its ground-state. An excimer (excited dimer) is a short-lived dimer (nanoseconds) consisisting of one molecule in an excited state and one in its ground state.[27] If the excimer is composed of two differing molecules it is more correctly termed an exciplex (excited complex), however the term excimer is often used to encompass both excimers and exciplexes. This excimer (or exciplex) is then capable of fluorescing. Excimer fluorescence is characterised by a broad undefined emission that is red-shifted relative to that of a solitary anthracene.

The exact relationship between excimer formation and photodimerisation has been the subject of some debate. Birks has termed photodimerisation as an "extreme case of excimer formation" and as result, he holds that if the dimerisation is inhibited the excimer fluorescence will increase.[27] Vember, alternatively proposed that excimer formation is a competitive pathway to dimerisation.[28] However, further studies throughout the mid 1970's all showed that excimer formation does appear to be an intermediate to photocyclomerisation.[29,30,31,32,33] Despite this, excimer fluorescence is rarely observed during irradiation experiments. A comparison of the rates of the processes involved in the photodimerisation may be used to explain this. It was found that the rate constant of excimer fluorescence (~2 x 10^6 s^{-1}), was an order of

magnitude less than both photoreactivity (140-500 x 10^6 s^{-1}), and non-radiative decay (260-430 x 10^6 s^{-1}).[7]

1.3 Controlling Anthracene Photocycloaddition

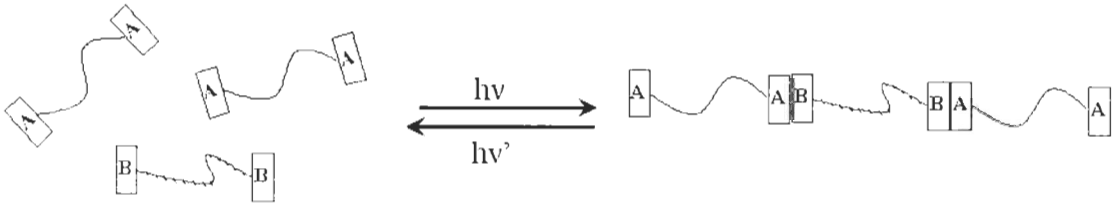


Scheme 1.4 A representation of cyclomers that may form during photochemical reactions between substituted anthracenes

Since the photochemical reaction of anthracene is a bimolecular process, it can be used to bring together two molecules. This property of anthracene has been exploited in the production of a variety of responsive systems (*vide infra*). Unfortunately, the dimerisation process tends to exhibit poor selectivity in mixed systems, and any anthracene derivative in solution may in general react with any other. Scheme 1.4 graphically represents two different anthracene species and the possible reactions that they may undergo. These anthracene derivatives may

differ in substitution pattern, the nature of the substituents or a combination of both. Irradiation of a mixture of two anthracenes (**A** and **B**) can give rise to three photoproducts: the homodimers **AA** and **BB** as well as the cross-cyclomer **AB**. Previous studies of substituted anthracenes have not been able to identify reliable methods to limit these reactions to form only desired **AB** cyclomer. Establishing generally applicable methods for achieving this type of selectivity is the ultimate goal of the research described within this thesis.

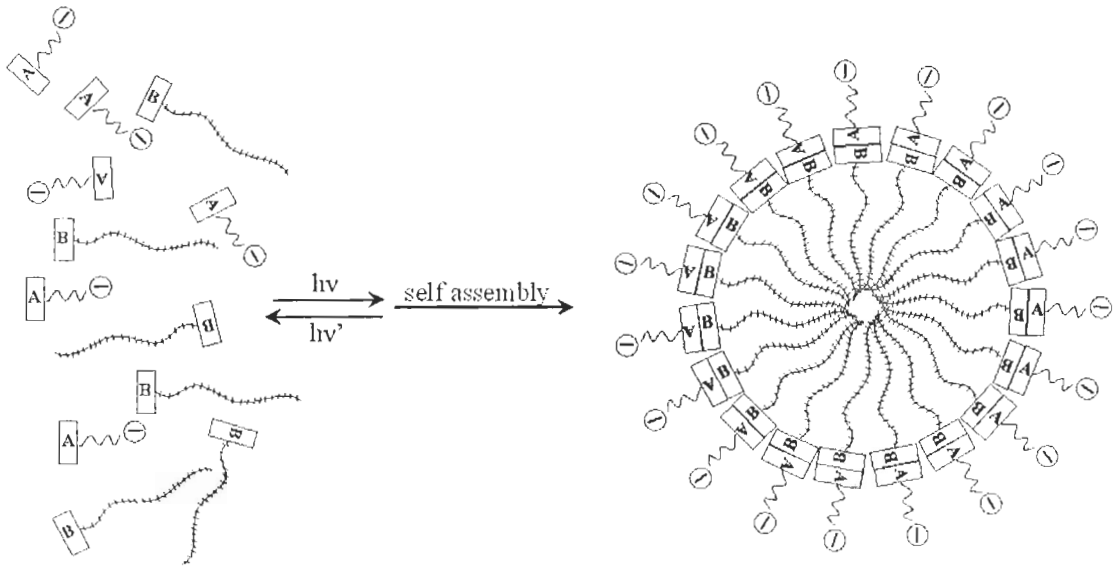
1.3.1 Potential Future Applications of Controllable Anthracene Photocycloaddition



Scheme 1.5 Formation of a reversible co-polymer using selective anthracene photochemistry

The motivation for attempting to gain this type of control over photocycloaddition reactions was the potential to significantly enhance the capabilities of many functional materials. A few possible applications are described below. The photocycloaddition reactions of anthracene molecules have been used in the context of polymers.[34] However, as it stands, this

methodology can only be applied to either crosslinking polymers or to the assembly of homopolymers or random copolymers. If greater selectivity were achieved, it would allow the construction of reversible block copolymers in which the alternation of blocks is strictly enforced (Scheme 1.5). Similar strategies could also be used in the construction of controllable multi-domain structures such as reversible micelles. Scheme 1.5 shows monomers with one of two anthracene end-caps "A" and "B". If for instance the "A" monomers are hydrophilic and the "B" monomers hydrophobic, selective photo-cycloaddition would yield covalently linked monomer pairs with both hydrophobic and hydrophilic ends, which could then self-assemble into micellar structures (Scheme 1.6). These systems could be assembled and disassembled through irradiation with light of the appropriate wavelength either to form the photo-cyclomers or to revert them to their component anthracenes. Structures such as this could be applied to drug delivery, small molecule sequestration, or catalyst delivery.[35]



Scheme 1.6 Formation of a micelle using selective anthracene photochemistry

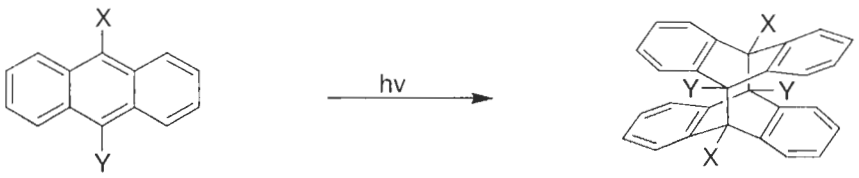
This selective anthracene photochemistry could also be used for reversible surface modification, in which small molecules could be alternatively bound and released from a surface using light. One could envision this being used to scavenge an expensive and/or toxic catalyst that one would want to recover. The catalyst could be attached to a polymer bead *via* a dianthracene linker. Irradiation would release the catalyst into the reaction mixture, and when the reaction was complete, irradiation at longer wavelengths could be used to reattach the catalyst to the bead, allowing for easy removal from the reaction mixture. A system such as this would combine the best features of both heterogeneous catalysts (*i.e.* facile removal of catalyst from reaction mixture) and

homogeneous catalysis (greater efficiency, lower catalyst loading), while potentially lowering costs and/or environmental impact.

Having an effective way of reversibly bringing two molecules together in a controlled manner could allow the production of many new functional materials, and even new classes of materials. However, except for the systems described in this thesis, there are few examples of reversible, externally controlled, and selective bimolecular reactions.

1.3.2 Previous Attempts to Control Anthracene Photocycloadditions

Tables 1.1 and 1.2 give a brief overview of the previous studies that have examined the photocycloaddition of substituted anthracenes. These examples were chosen to give an overview of the scope of the previous research, with a focus on molecules that were used in the studies described in this thesis.

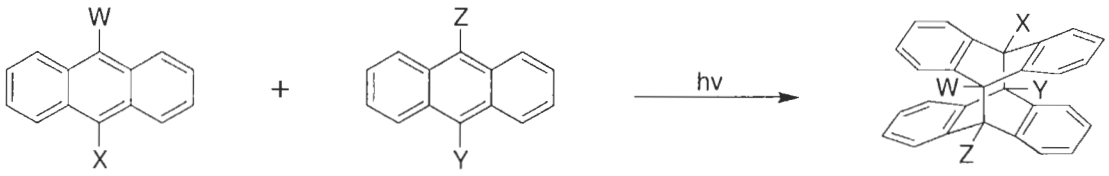


X	Y
C_6H_5	H
CF_3	H
COC_6H_5	H
$SiMe_3$	H
COONa	H
Me	H
CN	H
F	F
Me	Me

Table 1.1 A selection of previously-reported homodimers formed through photocycloadditions [3]

Table 1.1 lists a selection of centrally 9- and/or 10- substituted anthracenes that have proven capable of homodimerisation. Of particular note is the relative lack of disubstituted anthracenes in this list. While there are numerous examples of monosubstituted anthracenes that form homodimers when irradiated, the only reported cases of 9,10-disubstituted anthracenes dimerising are 9,10-dimethylanthracene and 9,10-difluoroanthracene. However, while 9,10-dimethylanthracene (**DMA**) has been shown to photodimerise, it will only do so under forcing conditions. Specifically, Bouas-Laurent showed that with a powerful light source (500W high-pressure mercury lamp) and extended reaction

times (8 h) the dimer 9,9′,10,10′-tetramethyldianthracene **DMA-DMA** could be formed in 80% yield (Table 1.1).[36] This product does not form in significant amounts when lower intensity light sources are used. For example, after 2 hours irradiation in a Rayonet Photochemical Reactor© with lamps emitting light centred at 350 nm, a 4 mM solution of **DMA** showed only very limited homodimerisation (~5%).

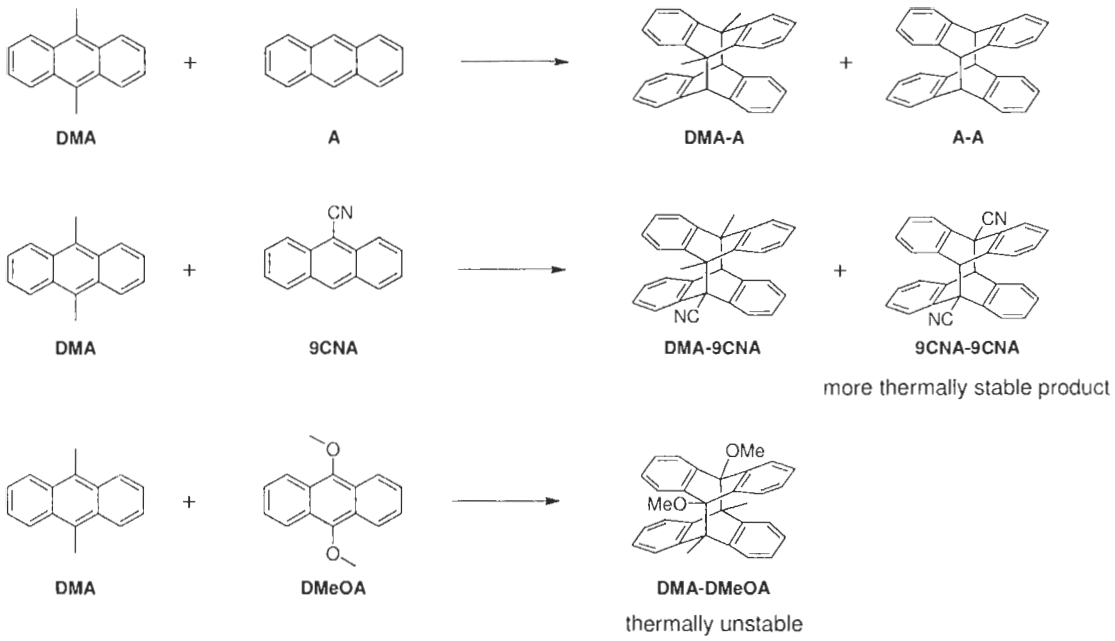


W	X	Y	Z
H	**H**	**Me**	**H**
H	**H**	***n*-Bu**	**H**
H	**H**	**Br**	**Br**
H	**H**	***n*-Pr**	***n*-Pr**
H	**H**	**OMe**	**OMe**
H	**H**	**Me**	**Me**
CN	**H**	**Me**	**Me**
Br	**H**	**Me**	**Me**
CN	**H**	**H**	**OMe**
Me	**Me**	**OMe**	**OMe**

Table 1.2 A selection of previously-reported cross-cyclomers formed through photocycloadditions [3]

Table 1.2 provides an overview of the dianthracene cross-cyclomers that have been previously synthesised. Most commonly, unsubstituted anthracene is

irradiated in solution with a partner that is centrally substituted at the 9- and/or 10-positions. These reactions invariably lead to a mixture of products: the crossed-cyclomer and one or possibly two dianthracene homodimers. There have only been a few examples of controlled anthracene photoreactions, in which only the cross-cycloaddition product is formed. The majority of these examples have been attributed to the electronic properties of the anthracene molecules, and primarily, on the premise of utilising a donor–acceptor motif. This is believed to promote the formation of charge-transfer complexes, which help to bring the molecules together in solution and allowing the cycloaddition to proceed more efficiently. These 'donor-acceptor' methodologies involve one of the chromophores possessing an electron-donating group and the other an electron-withdrawing group. Unfortunately, these approaches have met with only limited success, exhibiting either partial selectivity, transient products, or both.[37,38,39] All of these attempts have utilised **DMA** as one of the reactive species. While **DMA** is loathe to react with itself, it has been shown to readily undergo photochemical dimerisations with other anthracene derivatives (Scheme 1.7).

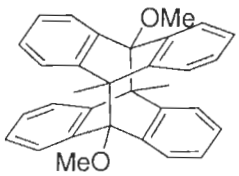


Scheme 1.7 Cross-photocycloadditions of some centrally substituted anthracenes

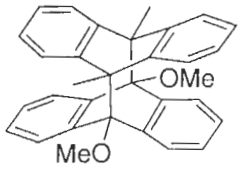
A solution of **DMA** and anthracene (top entry), when irradiated by a broad-band light source, yields a mixture of the dianthracene **A-A** and the cross-coupled 9,10-dimethyldianthracene **DMA-A**. The second entry of Scheme 1.7 shows a more promising attempt at a selective anthracene photoreactivity: the reaction of 9,10-dimethylanthracene with 9-cyanoanthracene. When irradiated together, these molecules preferentially form 9,10-dimethyl-9′-cyanodianthracene **DMA-9CNA**.[37] However, the head-to-tail dimer of 9-cyanoanthracene **9CNA-9CNA,** while not preferentially formed, has substantially higher stability than the cross-coupled product **DMA-9CNA**. This

homodimer is also preferred when the solvent is heated during the reaction or when polar solvents are used during irradiation. Hence, when the reaction is performed in ether at 30°C, the homodimer **9CNA-9CNA** is formed as 1% of the product mixture, while in methanol the percentage of this dimer increases to 35%, and at 80°C in benzene, it is the only observed product.[36] It is the donor-acceptor properties of these molecules (**DMA** donor, **9CNA** acceptor) that have been proposed as the source of their selectivity.[37]

The final example shown in Scheme 1.7 is the reaction between **DMA** and 9,10-dimethoxyanthracene **DMeOA,** which only produces one product: the cross-cyclomer 9,10-dimethyl-9′,10′-dimethoxydianthracene **DMA-DMeOA**. However, this compound quickly reverts back to its monomeric components. In comparison, the structurally similar photodimer 9,10′-dimethyl-9′10-dimethoxy-dianthracene **MMeOA-MMeOA** reverts to its constituent monomers 3-4 times slower than **DMA-DMeOA**.[40]



MMeOA-MMeOA

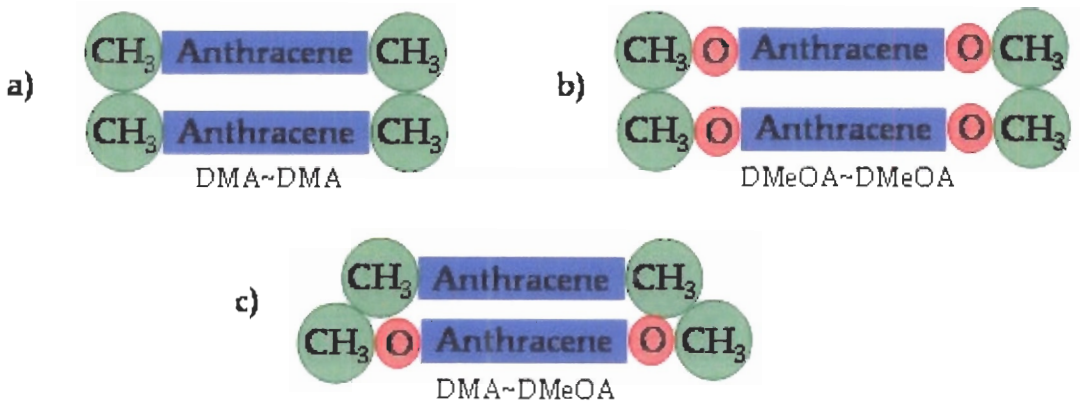


DMA-DMeOA

In this single reported case of a fully selective [4+4] photocycloaddition reaction, steric demands may have played an important role in the outcome. It

has been suggested that these molecules resist homodimerisation due to the steric interactions between the central substituents.[7] In the case of the reaction of **DMA** with **DMeOA**, the oxygen of the methoxy group may act as a spacer that causes the methoxy-methyl steric interactions to be less unfavourable than either the methoxy-methoxy or methyl-methyl repulsion (Scheme 1.8). However, electrostatic/charge complementary effects may also contribute to this reactivity.

A similar sterics-dominated effect has been observed when comparing the reactivity of 9-*t*-butylanthracene with that of 9-trimethylsilylanthracene. 9-*t*-butylanthracene does not dimerise, yet the trimethylsilyl derivative does.[41] This has been attributed to the longer C-Si bond length, which alleviates the steric crowding around the reactive centre.[3] These observations suggest it may be possible to control anthracene photoreactivity solely based on steric interactions.



Scheme 1.8 A representation of the approach of: a) two **DMA** molecules, b) two **DMeOA** molecules and c) a **DMA** molecule with a **DMeOA** molecule during photocycloaddition

1.3.3 Controlling Anthracene Photocycloaddition through Steric Demands

While the majority of attempts at selective cross-dimerisation between anthracene derivatives have been based on the electronic properties of the molecules, steric demands can also play a role (*vide supra*). While undergoing the [4+4] addition to form cyclomers, the molecules must come in close proximity to one another. It is quite conceivable that dimer formation may be suppressed by restricting access to the reactive central rings. This is consistent with studies of centrally substituted anthracenes that are symmetrically 9,10-disubstituted. Symmetrical 9,10-disubstituted anthracenes have been shown not to photodimerise when the groups at these positions are: phenyl, alkyl groups

larger than a methyl, alkoxy, chloro, bromo, or cyano groups. The only symmetrical 9,10-disubstituted anthracenes that were found to homodimerise were the dimethyl and the difluoro derivatives (*vide supra*). Presumably, two large centrally-substituted groups prevent dimerisation, while mono substituted anthracenes can undergo homodimerisation. This being said, very large substituents, such as the *t*-butyl group, are able to prevent homodimerisation even when only one group is present at the 9-position (*vide supra*).

Only relying on modifications to the central ring of anthracenes inherently restricts the options in controlling the photochemistry of these molecules. Opening the peripheral positions (such as the 2-, 3- ,6-, and 7-positions) to substitution may allow greater control of the photochemical properties of anthracene derivatives. The effects of functional groups at these peripheral positions have not been as extensively studied and therefore are not well understood. Of interest was whether bulky groups at these positions would allow the same control over the dimerisation process as the central substituents. One of the primary targets for these studies was 2,3,6,7-tetraphenylanthracene (**TPA**) see Figure 1.9.

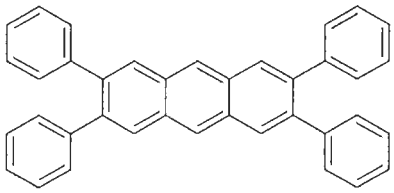


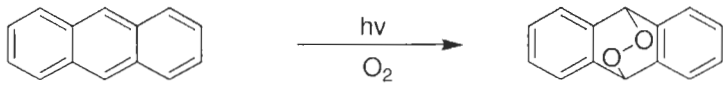
Figure 1.9 2,3,6,7-Tetraphenylanthracene **TPA**

It was hoped that by utilising the steric demands of the molecules, a pair of anthracenes could be designed that would only be capable of forming cross-cyclomers without any accompanying homodimer formation. In Chapter 4, a detailed discussion of the development and use of orthogonal steric demands to enforce this desired selectivity to yield cyclomers that do not readily decompose will be described.

1.4 Alternate Photoinduced Reactions of Substituted Anthracenes

While the primary focus of this thesis is the [4+4]-cycloaddition reaction across the 9,10-positions of the anthracene core, some anthracene derivatives are known to undergo other photochemical reactions. A few of these reactions are discussed below.

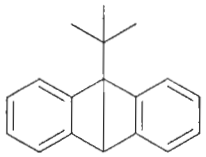
1.4.1 Endoperoxide Formation of Anthracenes

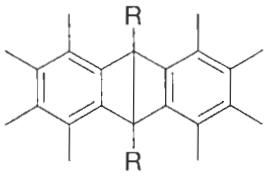


Scheme 1.10 Anthracene endoperoxide formation

When irradiated in the presence of molecular oxygen, anthracene derivatives may undergo an addition with either singlet or triplet oxygen.[3,42] The resulting endoperoxide can then release O_2 as either a singlet or triplet, or the endoperoxide oxygen-oxygen bond may undergo homolytic cleavage.[43] The singlet form of dioxygen is very reactive and may undergo unwanted reactions with compounds present in solution. For this reason, oxygen was excluded from all photochemical experiments described in this thesis. The efficiency of singlet O_2 production is dependent on both the nature of substituents and the solvent in which the experiment was conducted.[42,44] While it is most common for the endoperoxides to decompose quickly, releasing singlet oxygen, some are quite persistent. For example, the endoperoxide of 9-*t*-butylanthracene only breaks down at 219°C.[45]

1.4.2 Dewar Anthracene Formation





1

R = Me, OMe, OEt, O*i*-Pr

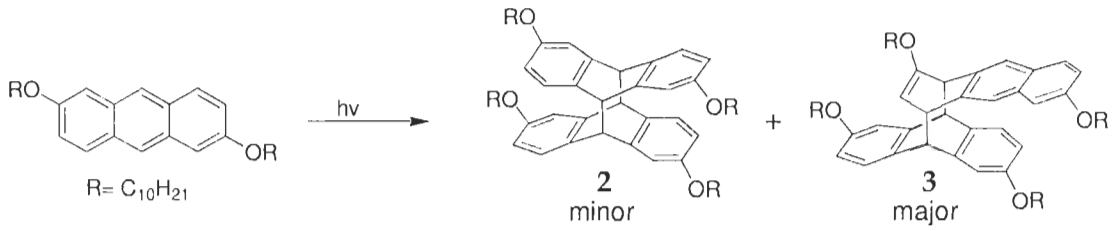
Scheme 1.11 Examples of Dewar anthracenes

Anthracene derivatives may also undergo valence isomerisation when irradiated, to form their Dewar equivalents (Scheme 1.11). However, this reaction only occurs in anthracenes with bulky groups that force the structure out of planarity.[2] The Dewar forms are thermally labile and commonly revert back to their Hückel forms quickly, even at low temperatures. For example, the most intransient of the studied alkoxy derivatives, compound **1** R = OMe, has only a one hour half-life at -30°C (Scheme 1.11).[46]

1.4.3 Non-Classical Photoadditions

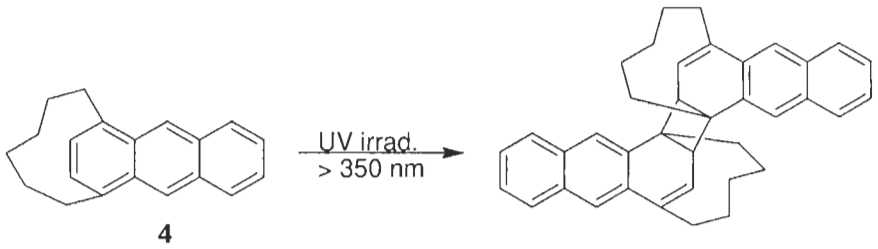
While the vast majority of anthracenes undergo cycloadditions across the central ring, there are examples of other dimerisation modes reported. Fages constructed a 2,6-dialkoxyanthracenes that, when irradiated, produced a mixture of two dimers, with the expected dimer **2** formed as the minor product, whereas

the major product was the cyclomer **3** (Scheme 1.12). This unusual reactivity was attributed to perturbation of the electron density distribution by the electron donating substituents.[47]



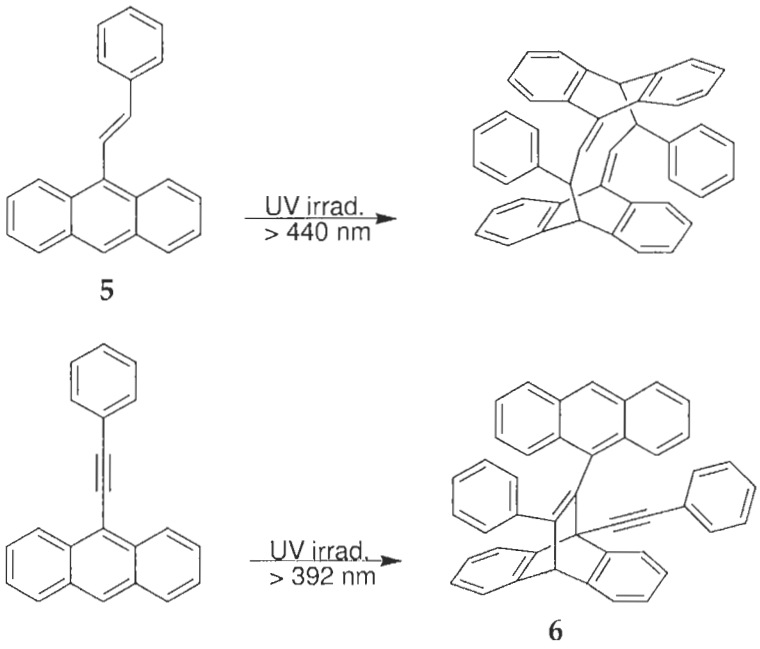
Scheme 1.12 The two modes of dimer formation of 2,6-didecyloxyanthracene

Another unusual mode of dimerisation was reported by Tobe *et al.*, who observed that the anthracenophane **4** preferred to undergo a [2+2] cycloaddition rather than the regular [4+4] reaction (Scheme 113).[48] This was attributed to the strain-induced formation of a Dewar benzene-like intermediate.[49]



Scheme 1.13 Photodimerisation of [6] (1,4)-anthracenophane (only one of the five isomers of the dimer is shown)

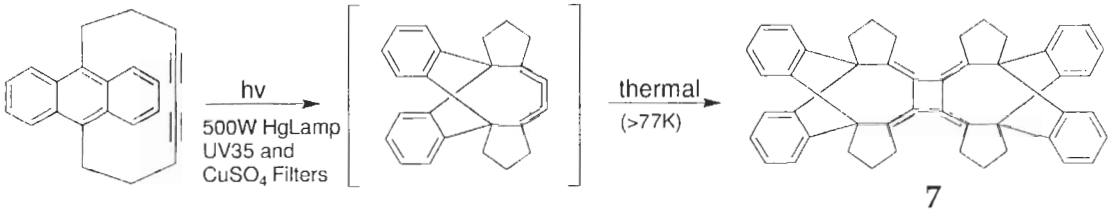
There have also been examples in which the pendant portions of a substituted anthracene are involved in the photochemistry. Following are three examples of such reactions (Schemes 1.14 and 1.15). The first two were reported by Becker and involve two similar phenyl-decorated anthracenes, yet yield very different results.[50,51] The first, **5,** undergoes a ($6\pi + 6\pi$) addition to yield a 12 member central ring. Changing the tether from an alkene to an alkyne promoted a ($4\pi + 2\pi$) reaction resulting in **6**.



Scheme 1.14 A [6+6] and a [4+2] photo-cycloaddition of two similarly 9-substituted anthracene structures

The final example is the impressive behaviour of 9,10-anthracenopha-4,6-diyne that rearranges and dimerises to form **7**. This process begins with the

photochemical rearrangement to the strained cumulene, which then reacts thermally to form the final dimeric structure.[52]



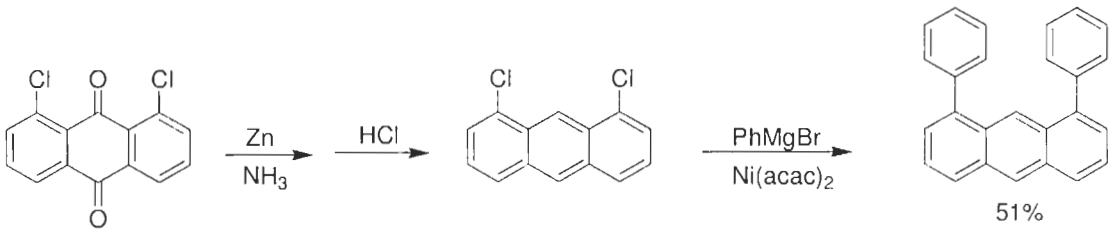
Scheme 1.15 The remarkable transformation of 9,10-anthracenopha-4,6-diyne

1.4.4 Synthetic Routes to Substituted Anthracenes

Studies aimed at investigating and/or controlling substituted anthracene photochemistry require, by definition, the production of substituted anthracenes. In the case of the majority of the studies described in this thesis, it was peripherally substituted anthracenes that were particularily desired. Even though examples of peripherally substituted anthracenes are uncommon, some work in this area has been done. Unfortunately, a systematic and flexible route to anthracenes with peripheral substitutions does not appear to have been developed. In this and the following section (1.4.4 and 1.4.4.1) is a brief summary of some of the methods that have been used to produce modified anthracenes. While many of the synthetic routes listed below are quite elegant and efficient, none of them completely satisfied all of the following requirements:

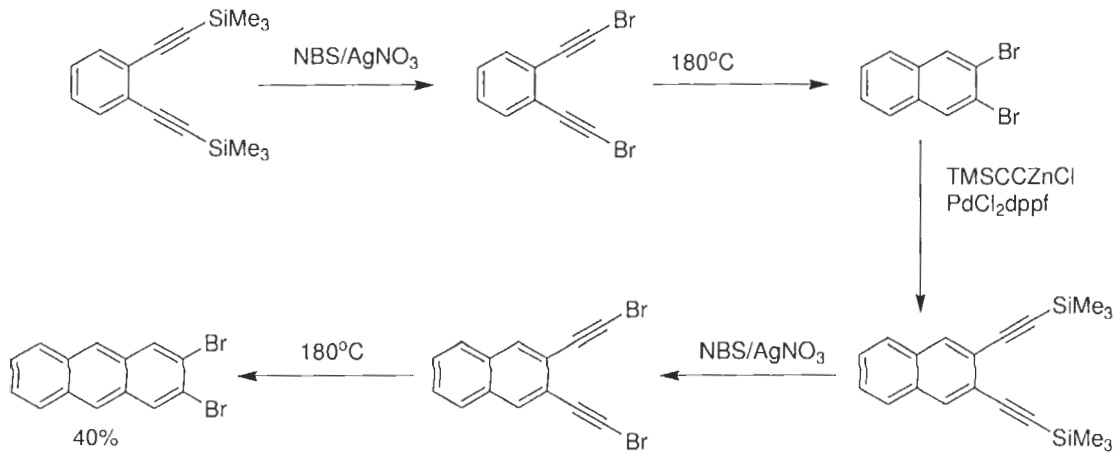
a) it must allow four peripheral groups (including aromatic rings) to be placed at the 2-,3-,6-, and 7- positions of the anthracene skeleton, b) it should also permit unsymmetrical anthracenes to be produced, and c) it would use synthetic precursors that could be stored for extended periods (months) without degradation and that are relatively easy to use.

Existing methods fall into two broad categories: ones in which the substituent groups are already in place before the skeleton is assembled (often through a Diels-Alder condensation), and ones in which the substitutions are made after the skeleton is constructed, usually *via* a metal-catalysed cross-coupling reaction using suitable halides or pseudo-halides in the appropriate positions. In many of the routes discussed, the targeted compounds were either anthrones or anthraquinones. These generally can then be reduced to the corresponding anthracenes.



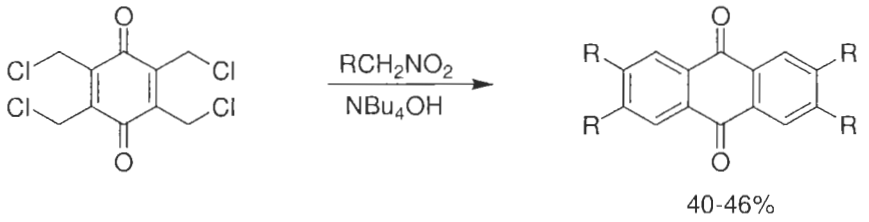
Scheme 1.16 A technique for attaching pendant phenyl groups to anthracene

The route shown in Scheme 1.16 was developed by House and is one of a very few that has been employed to incorporate phenyl groups onto the outer rings of an anthracene, in this case at the 1- and 8-positions.[53] This was accomplished *via* a Kumada reaction between 1-,8-dichloro anthracene and phenylmagnesium bromide. While this is a straightforward way of obtaining substituted anthracenes, it is limited by the necessity of having halides at the appropriate positions. Unfortunately, commercially available anthraquinones only possess halogens at the 1-,4-,5-, and/or 8- positions and cannot be employed to produce the desired **TPA**. Anthraquinone derivaties with halogens at the 2-, 3-, 6-, and 7-positions are not readily available. In Chapter 2 the synthesis of 2,3,6,7-tetrabromoanthraquinone will be described, which could potentially be employed as a precursor for this route to place the desired aryl substituents at peripheral positions.



Scheme 1.17 A reiterative approach to substituted PAHs

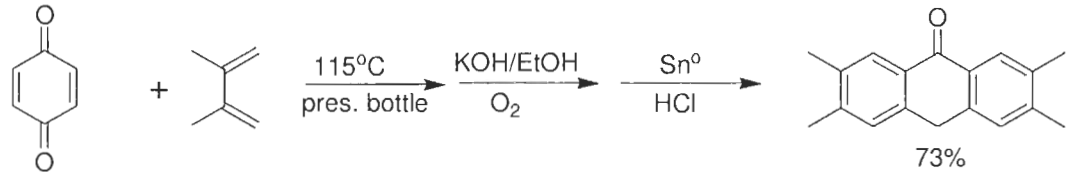
Anthony and Bowles have described a method for preparing 2,3-disubstituted anthracene derivatives using the Bergmann cyclisation (Scheme 1.17).[54] This iterative approach is particularly suited to constructing polycyclic aromatic hydrocarbons (PAHs) with a variety of core sizes, and Anthony has employed this methodology to produce PAHs from naphthalene to pentacene derivatives.[55] While only molecules substituted at the 2- and 3- positions were prepared, it may be possible to extend this methodology to produce compounds also substituted at the 6- and 7- positions from the appropriate tetra-substituted benzene. Preliminary efforts carried out in our laboratory (by K. Lau) to use this method in the assembly of substituted anthracenes were, however, unsuccessful.



Scheme 1.18 Using nitroalkanes in the production of anthraquinones[56]

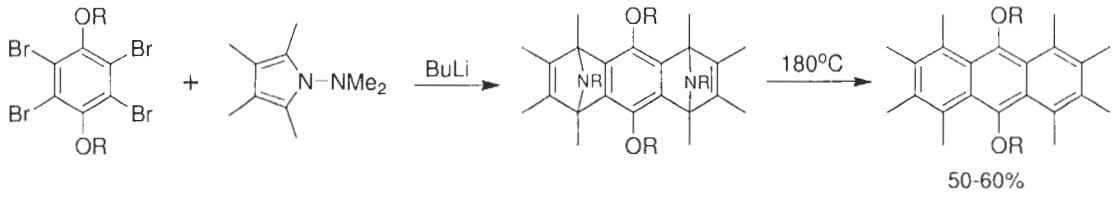
Scheme 1.18 shows the method that Crozet *et al.*[56] used to construct anthraquinones. This approach is similar to that of Anthony and Bowles, in that pendant chains are cyclised to form the aromatic core. In the Crozet approach, the final aromatic structure is formed by an addition/condensation with another synthetic precursor, a feature common to many of the following routes (Section 1.4.4.1). Unfortunately, this technique only allows for the formation of symmetrical structures.

1.4.4.1 Routes to Substituted Anthracenes Based on the Diels-Alder Reaction



Scheme 1.19 Diels-Alder addition to benzoquinone forming an anthrone

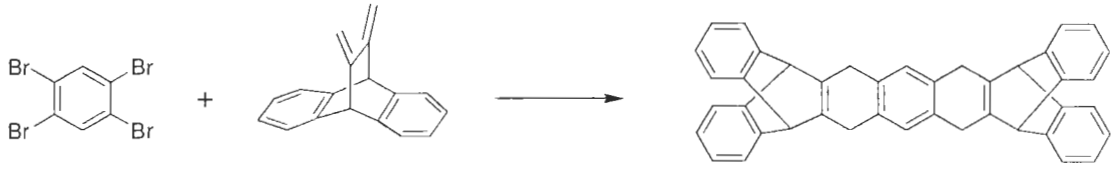
The method used by Godinez, shown in Scheme 1.19, centers around a Diels-Alder reaction between benzoquinone and 2,3-dimethylbutadiene. While this technique places groups at the desired 2-, 3-, 6-, and 7-positions, it was only used to obtain the methyl substituted anthrone. While 2,3-diphenylbutadiene is a known compound, it is anticipated that the steric bulk of phenyl groups would force the double bonds into a non-reactive *s-trans* conformation. In a cyclic diene, the *s-cis* conformation could be enforced, ensuring maximum reactivity. Accordingly, the two synthetic routes that were finally used (described in the following two chapters) employ cyclic dienes in a Diels-Alder synthesis, and as such, share similarities with the approach described above.[57]



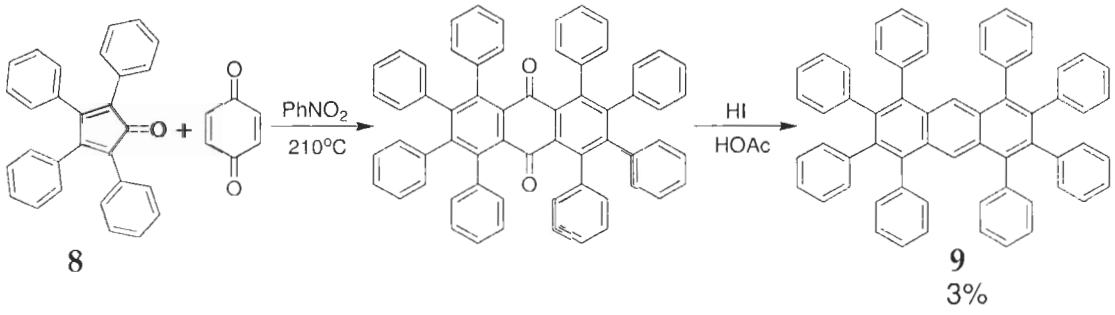
Scheme 1.20 Coupling of a benzyne derivative with a highly substituted pyrole

Hart *et al.* reported the synthesis of 1-,2-,3-,6-,7-,8- substituted anthracenes from the reaction of a pyrole and benzyne (Scheme 1.20).[58] Hart *et al.* has also reacted *in situ*-generated benzynes with substituted dienes to form tetrahydroanthracenes, as shown in Scheme 1.21. These compounds were then oxidised to create an anthracene core.[59] While benzynes are synthetically useful,

they must be generated *in situ* and, once formed, are very reactive and therefore can lead to unwanted side reactions. One of the aims of this project was to develop a synthetic route that was adaptable, modular and used synthetic intermediates that were both amenable to storage without degradation and easy to use. Some preliminary work (on another project) was done using benzynes; unfortunately, in our laboratory these reagents were found to be impractical, yielding unpredictable and variable results.



Scheme 1.21 Coupling of a phenyl-decorated diene with a benzyne



Scheme 1.22 A coupling of a cyclopentadienone with benzoquinone

By using a cyclopentadienone, Pascal *was* able to place phenyl groups at the peripheral positions *via* a Diels-Alder reaction between

tetraphenylcyclopentadienone **8** and benzoquinone (Scheme 1.22).[60] The yield of this reaction was quite low, producing the quinone in only 8% yield. This product was then converted to the corresponding anthracene product **9**, which was obtained in only a 3% overall yield. Unfortunately, cyclopentadienones are unstable without bulky substituents at the 2- and 5-positions. Therefore, this route has only been used to afford anthraquinones that are substituted at the 1-, 4-, 5-, and 8-positions. Despite these problems, Pascal's method did show great promise in producing anthracenes and in Chapter 3 a similar method to create anthraquinones from *in situ*-generated cyclopentadienones will be described.

1.5 Research Described in this Thesis

In this thesis, the synthesis and reactivity of an assortment of substituted anthracenes will be described. Special attention will be paid to anthracenes with peripheral substitutions, as these molecules have been historically neglected and only a few have been previously synthesised. In Chapters 2 and 3 are described two different yet complementary routes to produce anthraquinone forerunners to these anthracenes. In Chapter 4 the reduction of these anthraquinones to anthracenes and the photochemical reactions and studies undertaken on these compounds will be discussed.

CHAPTER 2: THIOPHENE-1,1- DIOXIDES AS PRECURSORS TO PERIPHERALLY SUBSTITUTED NAPHTHOQUINONES AND ANTHRAQUINONES

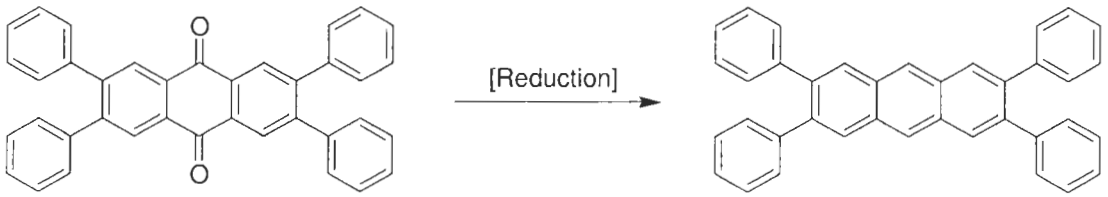
2.1 Introduction

In this chapter the synthesis of 2,3,6,7-tetraphenylanthraquinone **10** (Scheme 2.1) and related molecules will be described through a new and adaptable synthetic route that provides access to a broad array of substituted anthraquinones and naphthoquinones.[i]

In order to develop new strategies for controlling the selectivity of [4+4] cycloaddition reactions of anthracene and its derivatives, it was first necessary to prepare chromophores with a variety of substituents at various positions (see Chapter 1). Specifically targeted were peripherally substituted species such as 2,3,6,7-tetraphenylanthracene (**TPA**). In Chapter 4 a detailed description of the use of orthogonal steric demands in controlling the photochemistry of anthracenes will be described. Substituted anthraquinones were targeted as potential precursors that could be readily reduced to the corresponding

[i] Many of the results discussed in this chapter were first reported in: Bailey, D. & Williams, V. E. (2004). Tetrahedron Lett. 45, 2511-2513.

anthracene derivatives. Surprisingly, despite the apparent simplicity of the two structures in Scheme 2.1, neither had been previously prepared.



10 **TPA**

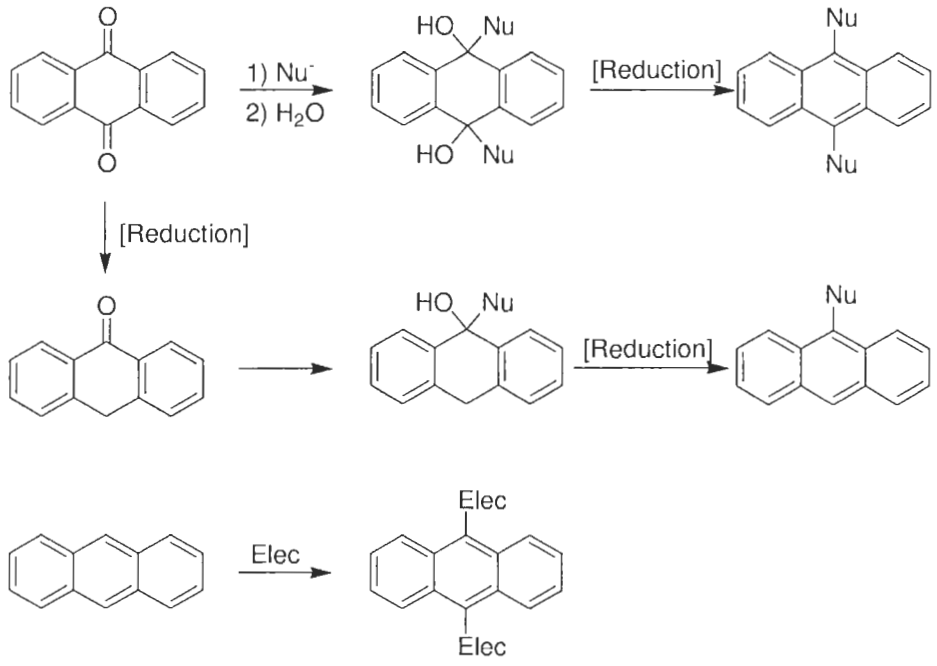
Scheme 2.1 Primary synthetic target 2,3,6,7-tetraphenylanthraquinone **10** and its derivative 2,3,6,7-tetraphenylanthracene **TPA**

2.1.1 Previous Synthetic Approaches to Substituted Anthracenes

The vast majority of modified anthracenes are substituted at the 9- and/or 10-positions. Substitution at these sites permits only limited control over the photochemical properties of anthracene. The prevalence of such centrally substituted anthracenes in studies can be ascribed to their ease of construction. Other substitution patterns have rarely been studied, as few efficient synthetic techniques allow functional groups to be placed at other positions.

The most common precursors to substituted anthracenes are 9,10-anthraquinones, anthrone, or anthracene itself. The reactive sites of all these species are at the 9- and 10-positions. A variety of electrophiles react at these positions on anthracene, while both anthraquinone and anthrone derivatives are

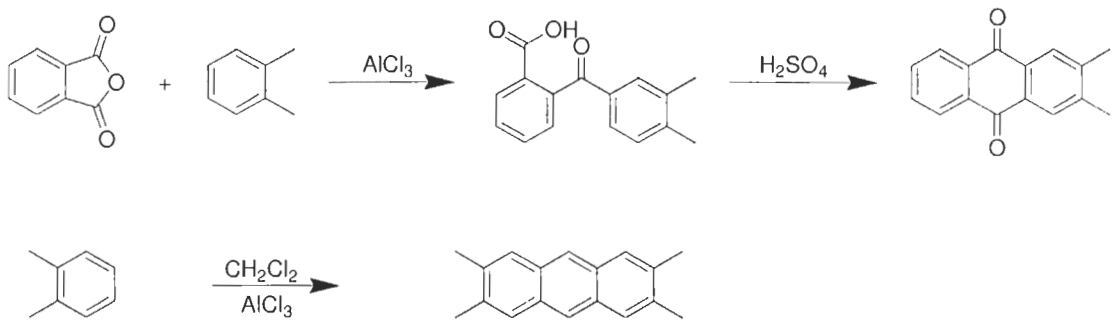
susceptible to nucleophilic attack at these positions. The relative ease with which these sites can be modified has biased research towards anthracenes modified only at these positions.



Scheme 2.2 Synthesis of centrally substituted anthracenes from anthraquinone, anthrone, and anthracene

If substitution at other positions is desired, then the anthracene skeleton typically must be formed with the functional groups already in place. The preparation of polyaromatic hydrocarbons (PAHs), as well as anthraquinones and anthrones, has historically been dominated by syntheses based on Friedel-Crafts techniques, such as those shown in Scheme 2.3.[61] However, this method has limitations regarding both the nature and pattern of substitution. For

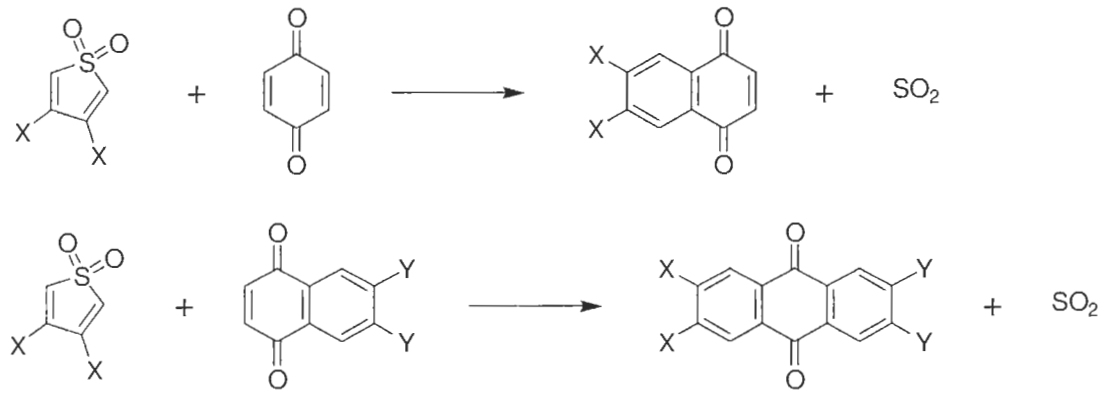
example, the standard technique of condensing phthalic anhydride and an aromatic ring to result in an anthraquinone (Scheme 2.3) is not compatible with placing aromatic groups at the 2-, 3-, 6- or 7-positions, since these groups would also be susceptible to Friedel-Crafts reactions.



Scheme 2.3 Classical approaches to PAH synthesis (bottom reaction[62])

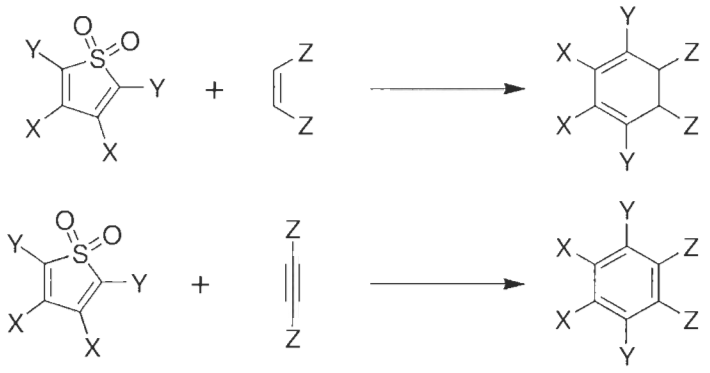
The goal of the work described in this chapter was to develop a synthetic route to peripherally substituted anthraquinones bearing a variety of substituents *via* a modular approach. Some of these compounds were targeted as precursors for the photochemical studies described in Chapter 4, while others were included in this study to demonstrate the synthetic versatility of the method and, indeed, could be useful for future photochemical studies. Thiophene dioxides were chosen because they exhibited the necessary reactivity and tolerated a variety of substituent groups to achieve this goal.

2.1.2 Reactivity and Properties of Thiophene Dioxides



Scheme 2.4 Generalised reaction of sulfones with 1,4-quinones under the conditions described in Section 2.3

Thiophene-1,1-dioxides (sulfones) share similarities in both their structure and their reactivity with cyclopentadienones described in Chapter 1. This allows a similar approach to that of Pascal (Scheme 1.22) for the construction of substituted anthraquinones and anthracenes. Sulfones have been shown to condense with a variety of dienophiles; alkenes, alkynes, and in a few instances quinones (see Schemes 2.5, 2.6 and 2.8).[63,64,65,66] They have also shown an affinity for acting as both the diene and dienophile while undergoing self-condensations.[67,68]



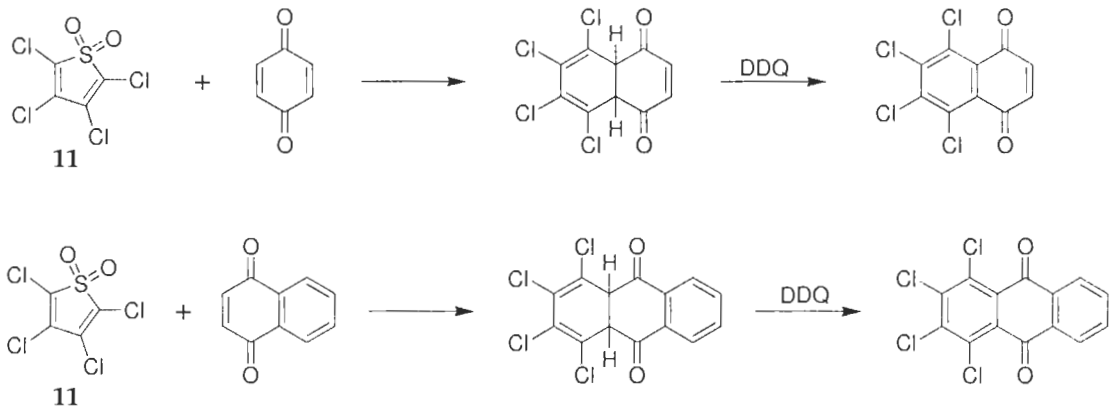
Scheme 2.5 Representative reactions of thiophene-1,1-dioxides with alkenes and alkynes

The following sections of this chapter discuss the construction of peripherally substituted naphthoquinones and anthraquinones *via* the Diels-Alder coupling of benzoquinone and naphthoquinones with thiophene 1,1-dioxides (Scheme 2.4). Thiophene dioxides have three primary properties that make them excellent candidates for use as synthetic intermediates: they have proven to be reactive with a variety of dienophiles, can be stored for prolonged periods without any special precautions, and can be constructed with relative ease with a variety of useful substituents.[69]

A feature common to many of the approaches described in Sections 1.4.4 and 1.4.4.1 was the utilisation of [4+2] cycloaddition reactions. Thiophene dioxides most commonly react *via* this pathway as well, and as such can be readily employed to create the carbon skeleton of anthracenes. Although

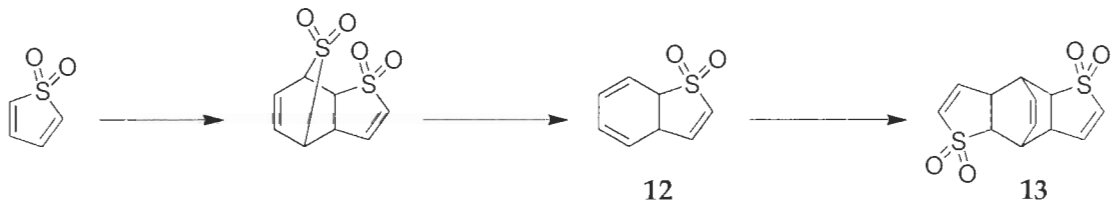
thiophene dioxides have been produced since 1931, their use in the assembly of anthraquinones has been limited.[64] In particular, disubstituted sulfones have received much less attention than their tetrasubstituted analogues, and the vast majority of synthetic studies that have used sulfones have focussed on one derivative, 2,3,4,5-tetrachlorothiophene-1,1-dioxide **11** (Scheme 2.6).

The studies of Raasch (Schemes 2.5 and 2.6), which are perhaps the most extensive on the use of **11**, explored its reactivity with alkynes, alkenes, and quinones, such as benzoquinone and naphthoquinone.[64] Of particular interest with respect to this thesis were his observations of reactions with quinones, which he noted formed a non-aromatic species (Scheme 2.6), which was then converted to the final aromatic product by an oxidation.



Scheme 2.6 Raasch's annulations of tetrachlorothiophene-1,1-dioxide with quinones

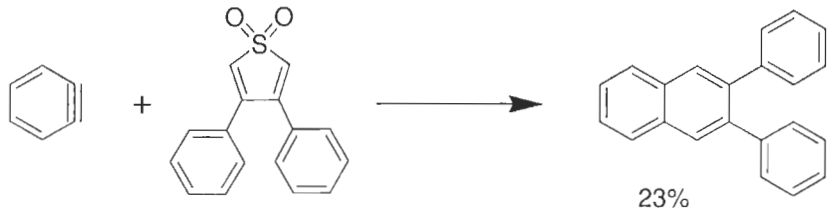
The stability of thiophene dioxides can be a significant concern in their production and use. For instance, unsubstituted thiophene dioxide will rapidly undergo a dimerisation at room temperature. This dimer then decomposes to **12** (Scheme 2.7), which can then react further to form **13**. These reactions happen very quickly; in a study by Nakayama, a neat solution of thiophene dioxide was completely converted into these two products within 10 minutes.[67] This dimerisation can also occur with substituted sulfones, as was observed by Dmowski in his study of 3-chloro-4-fluoro-sulfones.[64]



Scheme 2.7 Products formed by thiophene dioxide self-condensation

There have been only a few reports of phenyl-substituted sulfones as either products or reagents. One notable exception is the reaction reported by Nakayama in which benzynes were condensed with thiophene dioxides to produce substituted naphthalenes.[68] However, the reaction of greatest interest in which 3,4-diphenylthiophene-1,1-dioxide **14** was reacted with benzyne to produce 2,3-diphenylnaphthalene proceeded in low yields (23%) and required a

3-fold excess of benzyne (Scheme 2.8). These conditions and results suggest this route would not be useful for production of tetra-substituted anthracenes from the reaction of two equivalents thiophene dioxide with a 1,4-dibenzyne. However, this study does demonstrate that **14** can react in a [4+2] manner with a dienophile.

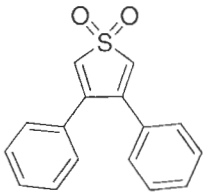


14

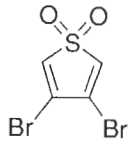
Scheme 2.8 Condensation of 3,4-diphenylthiophene-1,1-dioxide with benzyne

In addition, the results of Raasch (Schemes 2.5 & 2.6) suggested that sulfones could efficiently react with quinones to produce anthraquinones that could be easily transformed into anthracenes. For this reason, it was decided to begin the synthetic studies with an exploration of the reactions between 3,4-disubstituted sulfones and *p*-quinones.

2.1.2.1 Thiophene Dioxides used as Synthetic Precursors



14



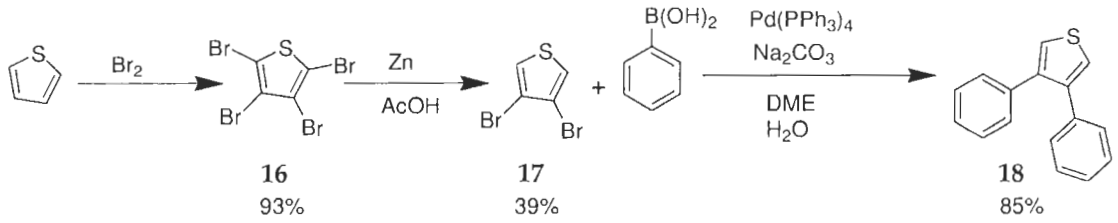
15

Scheme 2.9 The two sulfones that are to be discussed in this chapter

The two thiophene dioxides chosen for investigation were 3,4-dibromothiophene 1,1-dioxide **15** and 3,4-diphenylthiophene 1,1-dioxide **14**. These synthetic intermediates were chosen both to investigate the versatility of the proposed route, and for their synthetic utility. Aryl bromides can be used in palladium-catalysed cross-coupling reactions to install a wide variety of functional groups and undergo metal-halogen exchange to form Grignard reagents or aryllithiums. This synthetic versatility makes **15** an excellent candidate for further derivatisation to other anthracene structures. Compound **14** has a more immediate use in the planned photochemical studies as a precursor to a peripherally-substituted anthracene derivative with sterically-demanding groups.

2.2 Synthesis of Substituted Thiophene Dioxides

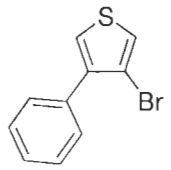
2.2.1 Construction of 3,4-Disubstituted Thiophenes



Scheme 2.10 Synthesis of 3,4-disubstituted thiophenes

The thiophene dioxides **14** and **15** both were synthesised from 3,4-dibromothiophene **17**. 2,3,4,5-Tetrabromothiophene **16** was first prepared in 93% yield following a modified literature procedure in which thiophene was treated with a large excess of bromine in refluxing acetic acid.[70] The bromines at the 2- and 5- positions were then selectively removed by zinc reduction to yield the desired **17** (39%).[71]

Phenyl-substituted thiophenes have been produced previously *via* one of two routes: 1) a metal-catalysed (Grignard, Suzuki) coupling of the aromatic group(s) to the thiophene, [72] or 2) formation of the thiophene skeleton with the substitutions already in place.[73,74,75] It was decided to follow the former strategy as it would easily allow the construction of **18** from **17**.



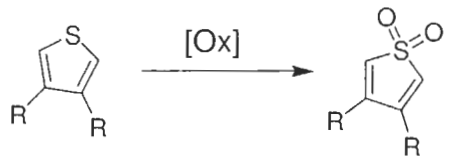
19

Thiophene **17** was reacted with phenylboronic acid under standard Suzuki conditions to produce compound **18** in 85% yield (Scheme 2.10). As to be expected, the replacement of the first bromine is much more rapid than the replacement of the second halide. After 16 h, there was observed only a 33% conversion of **17** to the diphenyl **18**, with the majority of the remaining material being monosubstituted product **19**. Much longer reaction times (160 h) were required for the conversion to **18** to reach an acceptable yield of 85%. While the slow conversion of the monosubstituted to disubstituted product was not examined closely, it should be possible to isolate this monosubstituted product and use it in the production of unsymmetrical 3,4-diarylthiophenes. As will be shown in the following chapter, an alternative technique that arrives at synthetic equivalents to these unsymmetric thiophene dioxides was developed.

2.2.2 Oxidation of Thiophenes to Thiophene-1,1-Dioxides

A variety of oxidation methods have been used to convert thiophenes to the 1,1-dioxides. The most commonly used oxidant used is *m*-chloroperoxybenzoic acid (*m*-CPBA),[76,77,78,79] although, peracetic acid,[80]

$HOF{\cdot}CH_3CN$,[81] sodium perborate,[82] hydrogen peroxide,[83] dimethyldioxirane (DMDO),[84,85,86] or a mixture of trifluoroacetic anhydride and hydrogen peroxide[87] have also been employed. The mono-oxide (sulfoxide) has also been formed using *m*-CPBA either alone or in concert with $BF_3{\cdot}Et_2O$.[88,89]



17 R=Br
18 R=Ph

15 R=Br
14 R=Ph

Scheme 2.11 Oxidation of thiophenes to their 1,1-dioxides

The first set of oxidation conditions investigated followed the method of Lu, Lemal, and Jasinski,[87] in which a mixture of 30% hydrogen peroxide and trifluoroacetic anhydride was used to oxidise the thiophene. Under these conditions, moderate yields (average ~55%) of the desired products were obtained. Unfortunately, these yields were not obtained consistently; the dibromothiophene was generally oxidised in yields that ranged from 32–70%, while those for the oxidation of diphenylthiophene were consistently higher and ranged from 50–91%.

The source of the inconsistent yields was never fully elucidated, but may have been due in part to the purity of both the hydrogen peroxide and the

trifluoroacetic anhydride. The hydrogen peroxide converts trifluoroacetic anhydride into trifluoroacetic peracid, which then oxidises the thiophene.[87] However, if the anhydride is first exposed to water in the absence of peroxide, it is hydrolysed to trifluoroacetic acid, which is not converted to the peracid. Hydrogen peroxide alone is also not sufficiently reactive to affect the oxidation of **17** and **18** to their dioxides. When an examination of the oxidation was performed using hydrogen peroxide and trifluoracetic acid (instead of the peracid), the reaction did not proceed to any measurable extent. It was also noted that the diminished yields were observed soon after a particularly humid stretch (>85% humidity) during the summer. Attempts to limit the exposure of the anhydride to moisture during storage proved only marginally successful in increasing the reaction yields. This oxidation method also proved to be very sensitive to the purity of the starting materials. If substrate of less than ~90% purity was used, the reaction mixture would include many additional products that proved very difficult to separate and characterise.

To circumvent this problem, an alternate means of oxidation was examined. The first alternative reagent examined was *m*-CPBA, but these reactions suffered similar problems as with the previous method.

The oxidation was also attempted utilising DMDO (dimethyldioxirane), which has been found by others to be a mild, yet quite effective oxidant of sulphur atoms, even those in hindered positions.[68,84,85] Dimethyldioxirane was prepared through the oxidation of acetone using the oxidising agent Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$). A mixture of Oxone®, $NaHCO_3$, and acetone yields dimethyldioxirane in approximately 15 minutes. The maximum concentration of DMDO produced by this method is typically only about 0.1 M. The resultant solution (acetone/DMDO) was then either used immediately to oxidise the desired thiophene or, if necessary, stored at -40°C overnight and then used the following day. Using a solution of DMDO allows the oxidation of the thiophenes to be accomplished simply by dissolving the desired thiophene in a minimum volume of CH_2Cl_2 and then adding it to the acetone/DMDO solution and stirring for 30 min. The remaining acetone and CH_2Cl_2 was then removed *in vacuo*.

While this method was found to oxidise the thiophenes very cleanly and efficiently, the reaction could only be done on a relatively small scale (≤ 250 mg, 1.3 mmol). Unfortunately, the apparatus required to produce the dimethyldioxirane limits the scale at which this reaction can be performed. During the production of DMDO, large amounts of gas are evolved, leading to a very vigorous reaction mixture that must be concomitantly distilled. This limitation, along with the large excesses of Oxone® and acetone that are required,

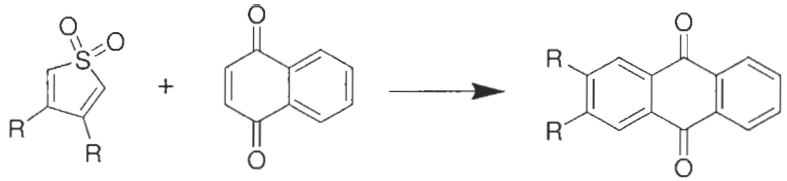
results in a very large and cumbersome apparatus being required. For instance, at the 250 mg scale, a 2 L round bottom flask with the associated 24-gauge distillation equipment is required, monopolising the bulk of a 4-foot fumehood. As the product is a starting material for further reactions, this procedure must be repeated numerous times to obtain sufficient quantities for continued synthesis. That being said, the short preparation time allowed many DMDO oxidations to be carried out in a single day. In the next chapter an alternative method that addresses some of these issues of scale will be discussed.

Unlike the DMDO that is used to oxidise the thiophenes, the thiophene dioxides themselves are stable enough to not require any special precautions in their storage. Both the dibromosulfone **15** and diphenylsulfone **14** have been stored for many months without any degradation or loss of reactivity.

2.3 Preparation of Substituted Naphthoquinones and Anthraquinones

2.3.1 Reactions of 1,1-Thiophene Dioxides with Naphthoquinone

In order to demonstrate the feasibility of preparing anthraquinones from these starting materials, the reaction of both sulfones with 1,4-naphthoquinone were examined first.

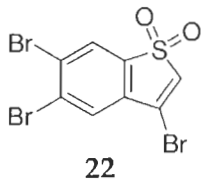


14 R=Ph
15 R=Br

21 R=Ph
20 R=Br

Scheme 2.12 Condensation of substituted thiophene dioxides with naphthoquinone

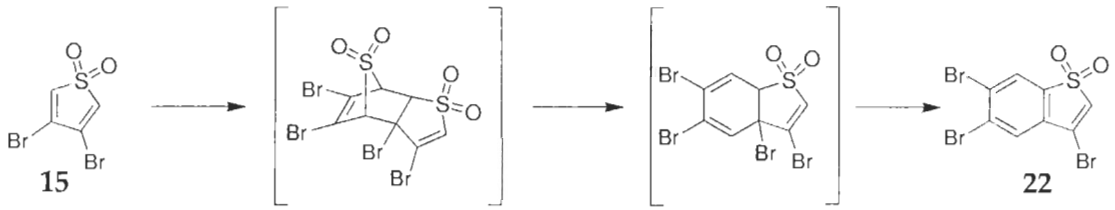
Initial studies focused on the reaction of a 1:1 mixture of the sulfone **15** with naphthoquinone in refluxing toluene for 24 h. Under these conditions, the quinone **20** was obtained, albeit in low yields (~30% by ^{1}H-NMR analysis). Despite the low yields, no side products were formed to any measurable extent, nor were any dihydro intermediates observed, in contrast with the results obtained by Raasch (see Scheme 2.6). Increasing the temperature by changing the solvent to refluxing xylenes had a negligible effect on the product yield.



22

When the solvent was changed to acetic acid and the reaction time increased to 48 h, substantially improved conversions of the sulfone were obtained. However, the major product (72%) was found to be an unwanted

species that was identified as the sulfone **22**. This sulfone forms as the exclusive product when the dibromothiophene dioxide **15** is heated in the absence of quinone, and presumably arises from the dimerisation of **15** (Scheme 2.11).[63] The tendency for sulfone **15** to undergo this reaction in solution is quite pronounced. Even during the room temperature oxidation of this thiophene, small amounts (< 5%) of **22** were formed. This reaction was found to be more pronounced when the $(CF_3CO)_2O/H_2O_2$ oxidation method was employed rather than when the DMDO-based oxidation was used.

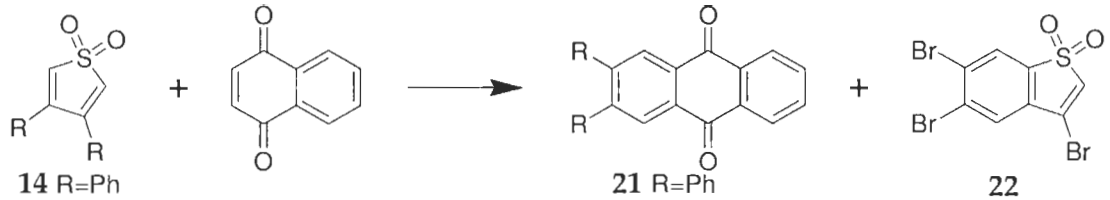


Scheme 2.13 Proposed mechanism for formation of **22**

In an attempt to suppress the formation of this side product, the ratio of naphthoquinone to sulfone was increased to 2:1. This afforded the unsymmetrical anthraquinone derivative **20** in 28% yield. Again, the major product for this reaction was identified as the sulfone **22**, which was isolated in 49% yield (Table 2.1). To fully eliminate this problem, a ratio of 10:1

naphthoquinone : sulfone was employed, which led to the anthraquinone **20** being isolated in 76% yield.

Interestingly, the diphenylsulfone analogue **14** does not undergo homodimerisation to an appreciable extent and reacts with 2 equivalents of naphthoquinone to afford the 3,4-diphenylanthraquinone **21** in 70% yield. While no studies were undertaken to determine the source of the differing reactivities of **14** and **15**, it may be reasonably assumed that it is due either to the difference in size between the two types of substituents, or the differences in leaving group ability during the elimination step. The bulk of the phenyl groups may prevent the sulfone from dimerising, or if once dimerised would be less likely to act as a leaving group, preventing the elimination step that permits aromatisation.



Sulfone (equiv)	Naphthoquinone (equiv)	Product(s) (equiv)	
15 (1.00)	(1.00)	**20** (0.03)	**22** (0.36)
15 (1.00)	(2.00)	**20** (0.28)	**22** (0.25)
15 (1.00)	(3.00)	**20** (0.58)	**22** (0.10)
15 (1.00)	(10.00)	**20** (0.76)	**22** (0.00)
14 (1.00)	(1.00)	**21** (0.61)	
14 (1.00)	(2.00)	**21** (0.70)	

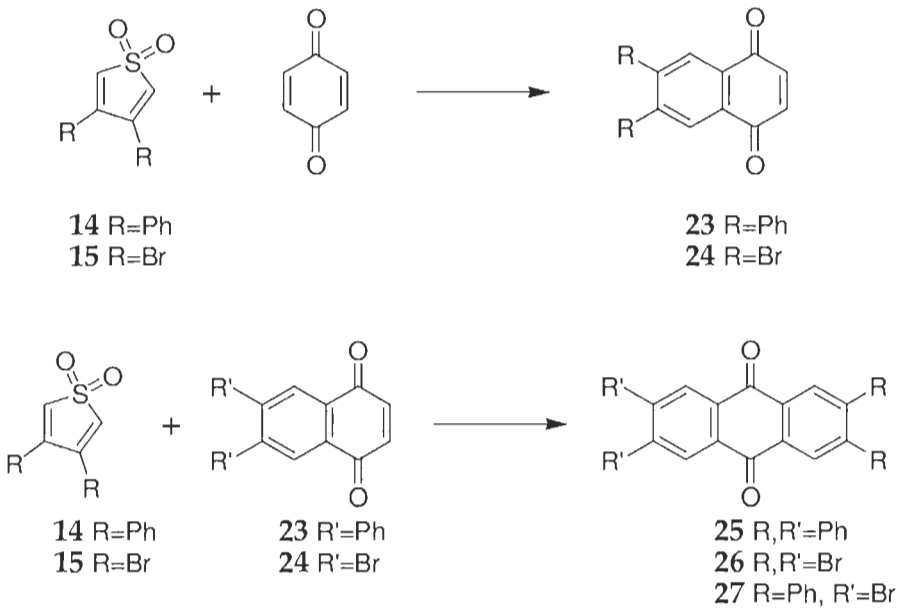
Table 2.1 Summary of Representative Reactions Between Sulfones and Naphthoquinone

It should be noted that, in contrast with the findings of Raasch, (Section 2.1.2) *all* reactions that were undertaken involving thiophene-dioxides resulted in aromatic species, without any dihydro intermediates being observed.

2.3.2 Reactions of 1,1-Thiophene Dioxides with Benzoquinone

While using 1,4-naphthoquinone as the dienophile allows for the construction of disubstituted anthraquinones, substituted naphthoquinones were needed for the construction of tetrasubstituted anthraquinones. Therefore,

attention was turned towards the construction of substituted naphthoquinones *via* the reaction of the substituted thiophene dioxides with 1,4-benzoquinone (Scheme 2.14).

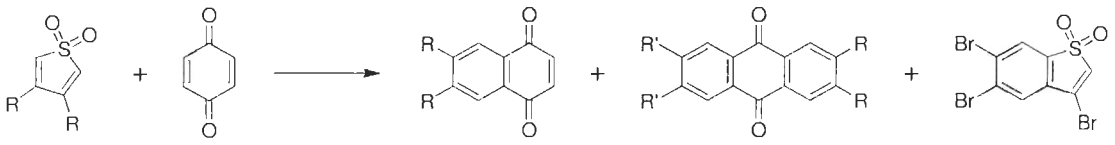


Scheme 2.14 Construction of tetrasubstituted anthraquinones

Preliminary experiments focused on the reaction of the diphenyl derivative **14** with benzoquinone, in an attempt to prepare the diphenylnaphthoquinone **23**, which could then in turn be reacted with a second equivalent of sulfone to afford the anthraquinones **25** and **27**.

Surprisingly, the condensation of diphenylthiophene dioxide **14** with 2 equivalents of benzoquinone in refluxing acetic acid directly produced the

double condensation product 2,3,6,7-tetraphenyl-9,10-anthraquinone, **25**, in 52% yield. Only when a very large excess of benzoquinone (10 equivalents) was used was the naphthoquinone product **23** formed as the major product. Even under these conditions, appreciable quantities of the anthraquinone **25** were formed (see Table 2.2). These results differ significantly from those obtained for the dibromo equivalent **15**. Unlike synthetic intermediate **15,** no homocoupled product was observed under any conditions, and the reaction of this phenyl substituted thiophene dioxide **14** with benzoquinone preferentially formed the double condensation product **25** over the singly condensed naphthoquinone **23**.



14 R=Ph
15 R=Br

23 R=Ph
24 R=Br

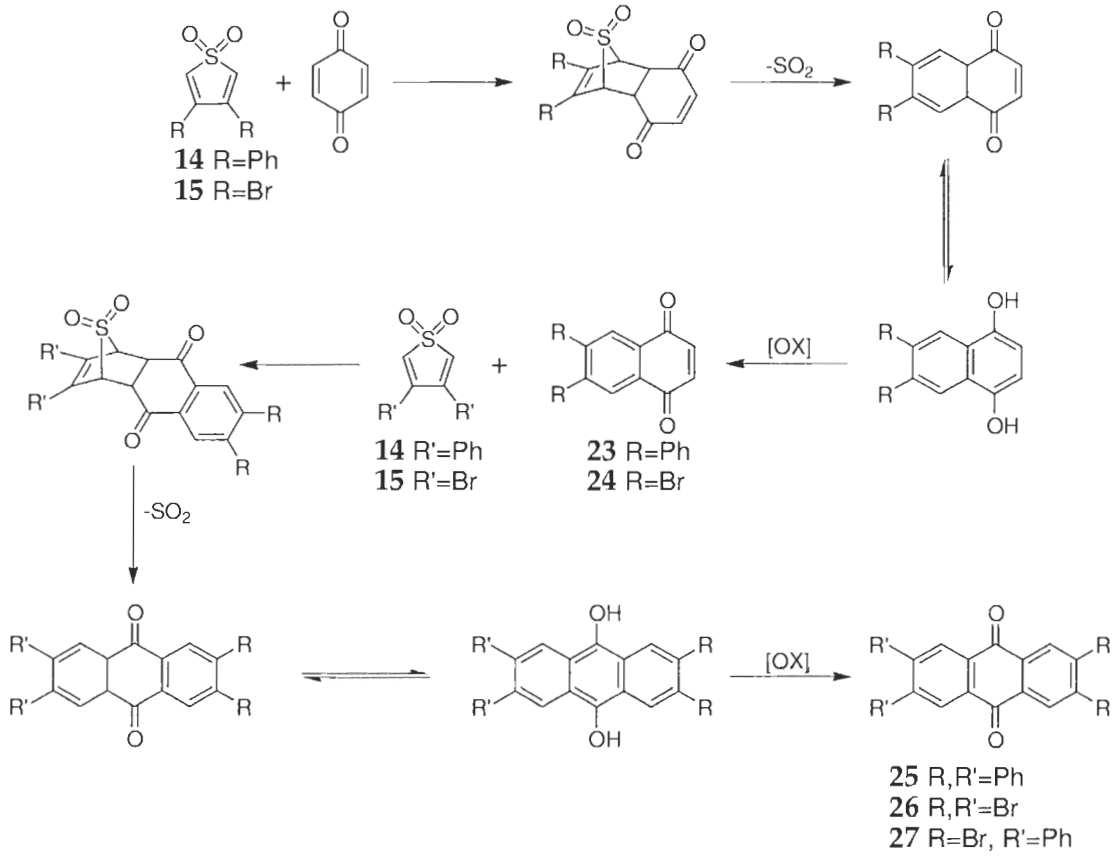
25 R,R'=Ph

22

Sulfone (equiv)	Benzoquinone (equiv)	Solvent	Products (equiv)	
15 (1.00)	(1.00)	AcOH	**24** (0.03)	**22** (0.36)
15 (1.00)	(2.00)	AcOH	**24** (0.12)	**22** (0.30)
15 (1.00)	(10.00)	AcOH	**24** (0.56)	**22** (0.00)
14 (1.00)	(2.00)	AcOH	**23** (0.00)	**25** (0.26)
14 (1.00)	(3.45)	AcOH	**23** (0.30)	**25** (0.17)
14 (1.00)	(10.00)	AcOH	**23** (0.35)	**25** (0.10)
14 (1.00)	(2.00)	Toluene	**23** (0.39)	**25** (0.16)

Table 2.2 Summary of representative reactions between sulfones and benzoquinone

The outcome of this condensation was strongly dependent upon the solvent employed. For example, when the reaction was carried out in toluene rather than acetic acid, the naphthoquinone product was formed in a much higher ratio (Table 2.2). The reason for this difference is unclear at this time, although a similar solvent effect has been observed for the Diels–Alder reaction of benzoquinone with anthracene.[90]



Scheme 2.15 Proposed reaction scheme of sulfone addition to benzoquinone and naphthoquinone showing tautomerisations[91]

Scheme 2.15 shows a proposed mechanism, suggested by Bluestone, of the reactions of sulfones such as **14** and **15** with benzoquinone.[91] Acetic acid may promote this reactivity through two mechanisms: protonation of the quinone, and promotion of the quinone-hydroquinone tautomerisation. The tautomerisation between *p*-quinones and their respective hydroquinones is quite facile in acid,[92] suggesting that promotion of the hydroquinone tautomer by acetic acid seems quite reasonable. The subsequent oxidation of the

hydroquinone to its quinone could then be carried out by either unreacted benzoquinone in the reaction mixture or by atmospheric oxygen.

Another role of the acetic acid could be to protonate the quinone in solution. The resulting cationic species should behave as stronger dienophiles by lowering the energy level of the LUMO, thereby decreasing the energy difference between the LUMO of the dienophile and HOMO of the diene, thus increasing the reaction rate.

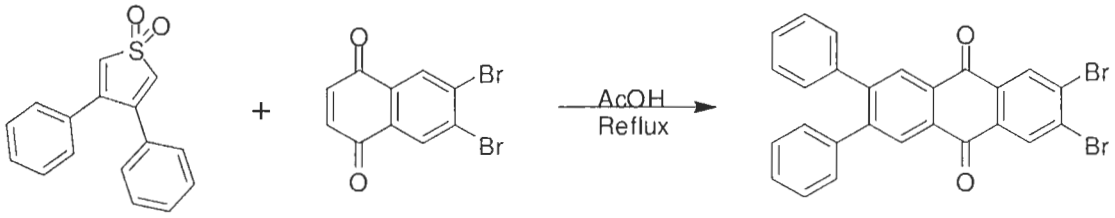
The predilection of the sulfone **14** to form the doubly condensed tetrasubstituted anthraquinone suggests that one of the intermediates *en route* to **25** may be a much better dienophile than benzoquinone itself. Another possible explanation for this reactivity may be found in the oxidative steps of this reaction. As mentioned earlier, the oxidation of these hydroquinones may be facilitated by quinone species left in solution. If this were the case, then during the reaction the benzoquinone in solution would be converted to its hydroquinone, reducing the amount of benzoquinone left to react with the sulfone, and thereby promoting the double-condensation. However, this second possibility appears remote, since anthraquinone is formed even when a very large excess of benzoquinone was used.

In contrast with the diphenyl sulfone, the reaction of the dibromosulfone **15** with 1 equivalent of benzoquinone yielded no observable 2,3,6,7-tetrabromoanthraquinone. The naphthoquinone **24** was formed in only trace quantities, while the self-condensed product **22** was again obtained as the major product. Using 2 equivalents of benzoquinone gave only slightly better results; it was only when a large excess (10x) of this dienophile was employed that the naphthoquinone **24** formed as the major product.

In order to prepare the tetrabromoanthraquinone **26**, dibromonaphthoquinone **24** was isolated first and then condensed with excess of **15** to obtain the desired product **26,** albeit in poor (< 20%) yields. Isolation and purification of this compound was difficult owing to its low solubility in most organic solvents.

Despite the differences in reactivity, all of the systems mentioned undergo a remarkable series of transformations in a single pot reaction, as shown in Scheme 2.15. In the case of the double addition of the diphenylsulfone **14** with the benzoquinone to form tetraphenylanthraquinone **25**, this constitutes a formal eight-step transformation occurring in a one-pot synthesis.

2.3.3 Construction of an Unsymmetrical Anthraquinone



14 **24** **27**

76%

Scheme 2.16 Construction of 2,3-dibromo-6,7-diphenylanthraquinone **27**

The iterative approach described above could, in principle, be used to produce the unsymmetrical 2,3-dibromo-5,6-diphenylanthraquinone **27.** Two possible routes could be followed; reaction of diphenylnaphthoquinone **23** with the dibromothiophene dioxide **15**, or the complementary reaction of **14** with **24** (see Scheme 2.16). The first step of either route entails the reaction of inexpensive benzoquinone with one of the sulfones, while the second step of both routes uses a more difficult to obtain reactant, the substituted naphthoquinone. For this reason, the efficiency of the second step is more vital than that of the first. If the sulfone **15** is utilised, a large excess of quinone **23** is required to prevent formation of **22.** As this quinone is not as expendable as simple unsubstituted benzoquinone or naphthoquinone, this route was not followed. This left the reaction of the phenyl-substituted sulfone **14** with

dibromonaphthoquinone **24** as the preferred route. Using this approach, the unsymmetrical **27** was obtained in 76% yield.

2.4 Conclusions

In the present chapter an efficient synthesis of both peripherally substituted naphthoquinones and anthraquinones from 3,4-disubstituted 1,1-thiophenedioxides was described. This approach allows both aromatic and non-aromatic substituents to be easily incorporated onto the framework of anthraquinones and naphthoquinones. This synthetic route also led to the construction of the novel anthraquinones 2,3,6,7-tetraphenylanthraquinone **25** and 2,3-dibromo-6,7-diphenylanthraquinone **27**.

Of particular interest were the differing reactivities of the two sulfones **14** and **15** that were used in the construction of the substituted naphthoquinones and anthraquinones. The bromo-substituted thiophene dioxide **15** showed a predilection to homodimerise that its phenyl-substituted cohort **14** did not. This difference in reactivity was also evident in the reactions of these compounds with benzoquinone. Compound **15** was apt to condense twice with benzoquinone, resulting in a tetra-substituted anthraquinone. The single addition of sulfone **14** to benzoquinone to form the naphthoquinone could be

biased either through the use of a large excess of benzoquinone or by changing the solvent from acetic acid to toluene.

The bromine-substituted derivative **15** would only add once to benzoquinone to form the dibromonaphthoquinone. The one-pot double addition could not be induced for this compound, since a significant excess of benzoquinone was required in order to suppress the formation of **22**. The difference in reactivity can be most likely traced to the steric requirements of the phenyl groups versus that of the bromine substituents. The steric bulk of the phenyl groups prevent the homocoupling that dominates the chemistry of compound **15**, thus enabling the phenyl-decorated sulfone **14** to react more readily with benzoquinone and naphthoquinone.

In Chapter 4 the reduction of the anthraquinones to anthracenes will be discussed, along with the photochemistry of these substituted anthracenes. In the following chapter an alternative, complementary method for naphthoquinone and anthraquinone construction that allows the introduction of greater dissymmetry in the product than the method described above will be discussed.

2.5 Future Work

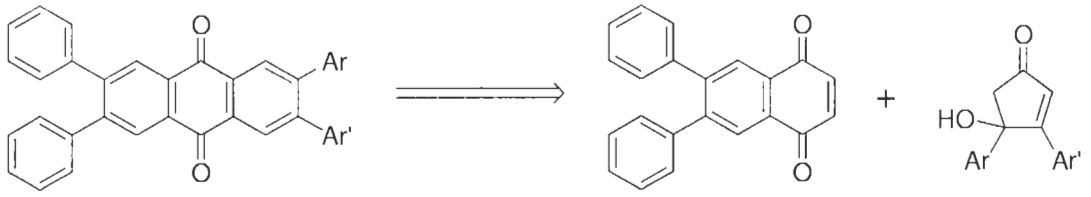
This synthetic method has demonstrated its efficiency in producing both symmetrical and unsymmetrical anthraquinones and naphthoquinones. However, only two different groups (phenyl- and bromo-) were used in these preliminary studies. The most obvious direction in which this research can progress is through an exploration of different substituted thiophene dioxides as synthetic intermediates. There are many boronic acids available for purchase or that may be synthesised relatively easily; coupling these with 3,4-dibromothiophene **17** and converting the resulting product into their dioxide equivalents would greatly expand the stable of compounds available for this chemistry. Also, attempting to produce unsymmetrical sulfones with two different functional groups would open a new pattern of substitution similar to those discussed in the next chapter.

Further investigations into the differences of reactivity between the sulfones **14** and **15** with quinones may also prove fruitful. While many of the differences in reactivity are likely due to the differences in steric demands, it is possible that there are other factors at play. Specifically, and most likely, differences in the electronegativity between these groups, as well as differences in the HOMO and LUMO of these compounds may contribute to their different reactivities. A more systematic study with a variety of different sulfones varying

in both their steric demands and electronegativity may shed some light on the sources of the differing reactivity.

CHAPTER 3: 4-HYDROXYCYCLOPENT-2-ENONES AS PRECURSORS TO PERIPHERALLY SUBSTITUTED NAPHTHOQUINONES AND ANTHRAQUINONES

3.1 Introduction



Ar = Aromatic Group
Ar = Ar' or Ar ≠ Ar'

Scheme 3.1 Retro-synthetic overview of the route employed to create low symmetry peripherally substituted anthracenes

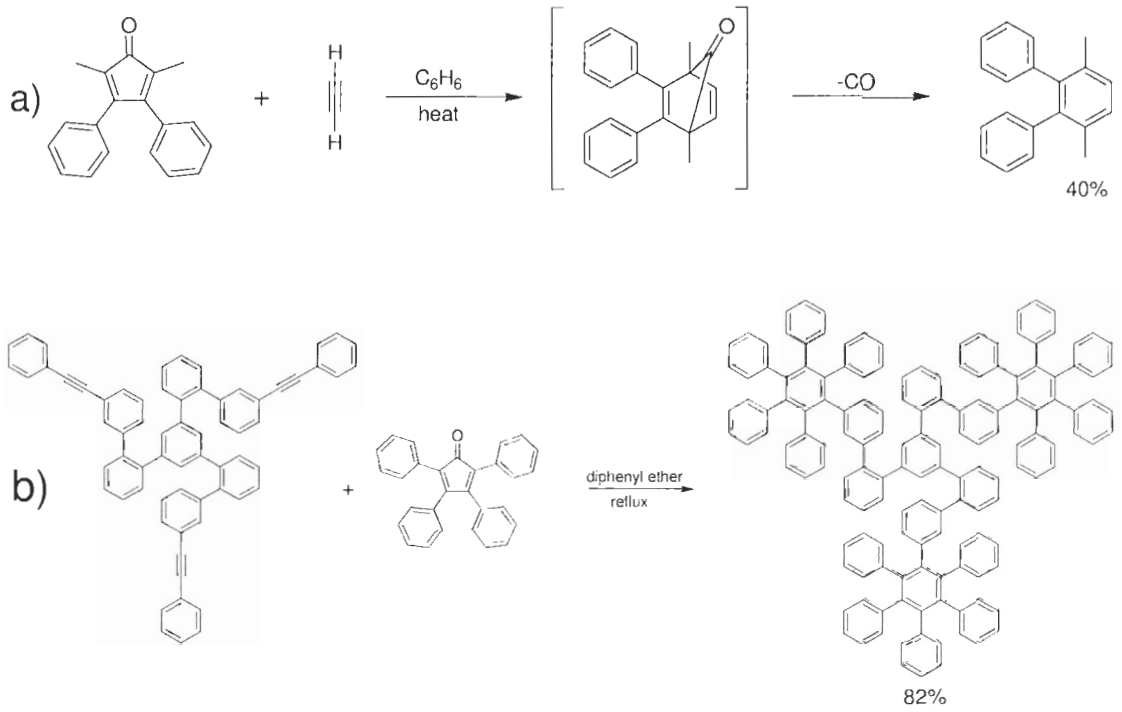
In the previous chapter, a synthetic route to peripherally substituted anthraquinones was described. This route, while useful, does have some shortcomings. Oxidation of the thiophene to its dioxide can only be accomplished on a small scale (~250 mg), thus limiting the quantities of the anthraquinone derivatives that can be prepared. Preparation of the phenyl-substituted sulfones also required high loadings of an expensive Pd(0) catalyst for efficient preparation. As well, the use of palladium catalysed cross-coupling

reactions does not easily lend itself to placing two *different* aromatic groups on the thiophene ring, since the reaction would have to be halted before completion and a mixture of products would have to be separated (see Chapter 2, Section 2.2.1). Finally, the route from the starting material to the reactive phenyl-substituted synthetic intermediate **14** is a somewhat cumbersome 4-step synthesis (see Chapter 2 Schemes 2.10 and 2.11), with an overall yield of 22%.

These aforementioned limitations and the desire to synthesise phenyl-substituted anthracenes led to an exploration of alternate and potentially more efficient synthetic routes to arrive at these structures. In the present chapter a complementary method based on cyclopentadienones that addresses and overcomes some of the shortcomings inherent to the thiophene dioxide-based route will be discussed.[ii]

[ii] Many of the results discussed in this chapter were first reported in the following journal article. Bailey, D., Murphy, J. N. & Williams, V. E. (2006). Canadian Journal Of Chemistry-Revue Canadienne De Chimie 84, 659-666.
The synthesis and characterisation of **37a** and **37b** *via* a Hagihara-Sonogashira were partially performed by J.N. Murphy.

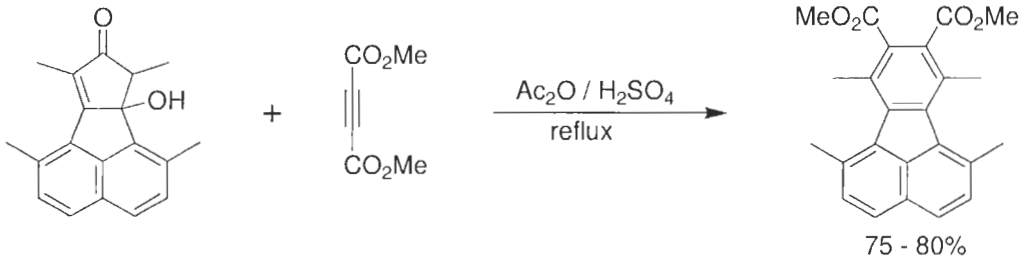
3.1.1 Use of Cyclopentadienones in Synthesis



Scheme 3.2 Reactions of cyclones with alkynes [94,95]

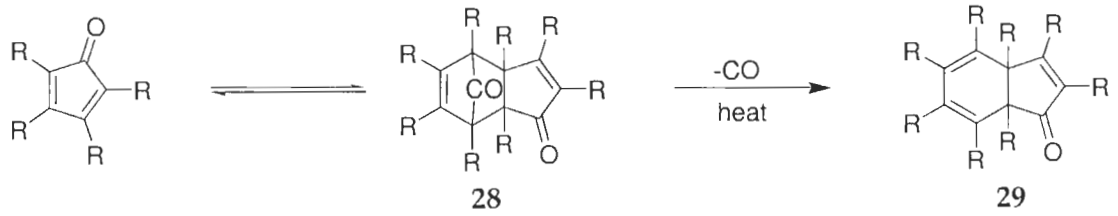
Cyclopentadienones, commonly termed "cyclones", are known to condense with alkynes to form Diels-Alder adducts that, upon loss of carbon monoxide, afford highly substituted benzene derivatives (Schemes 3.2-3.5). [93,94,95] These compounds can be regarded as synthetic equivalents to thiophene-1,1-dioxides, although cyclopentadienones tend to be more reactive than the sulfones. Similar to the sulfones studied in the previous chapter (albeit to a much greater extent) cyclopentadienones are often unstable, especially when they lack substitutions at the 2- and 5-positions. Derivatives that lack bulky

groups at these sites generally must be generated *in situ* from precursors such as the corresponding hydroxy-cyclopent-2-enones.[93,96,97,98] (Scheme 3.3)



Scheme 3.3 Acid-catalysed dehydration of a hydroxyl-cyclopent-2-enone and its use in synthesis [94]

Cyclones without bulky groups at the 2- and 5-positions tend to form dimers of the type shown below (**28** Scheme 3.4). These dimers are often in equilibrium with the monomeric structure, with the position of the equilibrium dependent on the size of the substituents. Generally, if the groups at the 2- and 5- positions are larger than a methyl substituent, the monomer form will be preferred.[93] Once the dimer **28** is formed, it is capable of losing carbon monoxide yielding compound **29**. Cyclopentadienones that follow this route of decarbonylation instead of reverting to the monomer only tend to do so at high temperatures (>200°C).

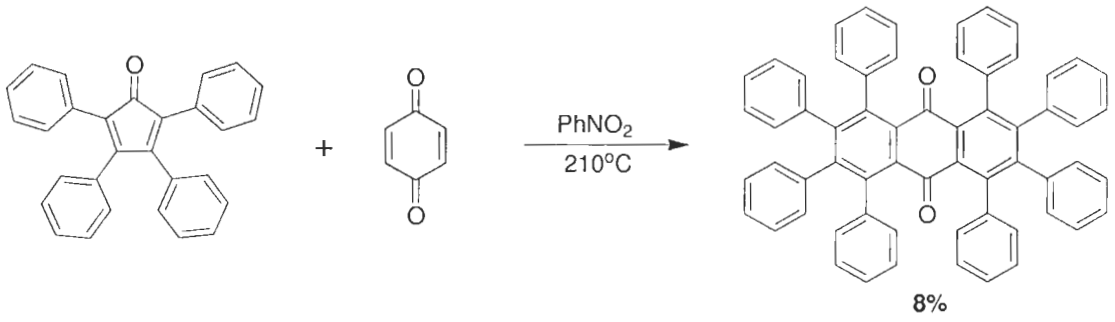


28 29

Scheme 3.4 Dimer form of cyclopentadienones and its loss of CO

Although hydroxycyclopentenones (Scheme 3.3) are relatively stable molecules, they can be induced to dehydrate to form the diene if exposed to strong acids.[93] If the cyclopentadienone is generated in the presence of a dienophile, it can then react with this dienophile to the exclusion of any dimer formation.[99]

Cyclopentadienones react not only with alkynes, but can also undergo Diels-Alder condensations with other dienophiles such as quinones. Despite this, cyclones have rarely been employed in the synthesis of anthraquinones.[100,101] Scheme 3.5 shows one of the few examples of such reactions. Furthermore, while there is some precedent for *in situ*-generated cyclones being used in Diels-Alder reactions with alkynes, (Scheme 3.3) there are no examples of these *in situ*-generated species being trapped with quinone dienophiles to afford either anthraquinones or naphthoquinones.[93,100]



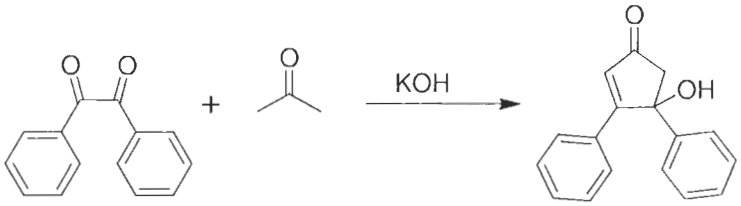
Scheme 3.5 Construction of a substituted anthraquinone using tetracyclone[101]

In this chapter the preparation of substituted naphthoquinones and anthraquinones from *in situ*-generated cyclopentadienones will be discussed. It was anticipated that this methodology would address some of the limitations of the sulfone-based route of Chapter 2, while also allowing new substituent groups to be incorporated onto the anthraquinone skeleton. Since electronic and steric effects both play important roles in the photochemistry of anthracene derivatives, a range of anthraquinones with different pendant aromatic rings were targeted.[7,102] The preparation of a variety of these synthetic intermediates and their use in the construction of substituted anthraquinones will be described in the following sections.

3.2 Preparation of Substituted Naphthoquinones and Anthraquinones

3.2.1 Reactions of 4-Hydroxy-3,4-diphenylcyclopent-2-enone with Naphthoquinone

In a test of the general principle, the first synthesis that was attempted used the simple 4-hydroxy-3,4-diphenylcyclopent-2-enone **30** (Scheme 3.6). This compound is easily and efficiently (96%) synthesised from commercially available benzil and acetone, in an aldol-style base-catalysed reaction. This product can be synthesised on quite a large scale (25 g), which potentially allows significant amounts of the naphtho- and anthraquinones to be quickly prepared from this synthetic intermediate.



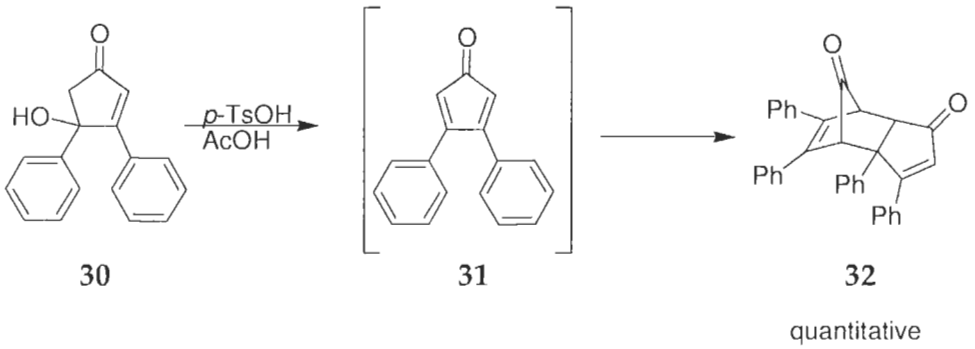
30

96%

Scheme 3.6 Preparation of 4-hydroxy-3,4-diphenylcyclopent-2-enone

Heating **30** in refluxing acetic acid for 48 hours caused no appreciable decomposition of this compound, presumably because acetic acid was not sufficiently acidic to promote the desired elimination to the cyclone. However,

when this reaction was carried out in the presence of catalytic *p*-TsOH, compound **32** was obtained quantitatively. Decarbonylation of this compound was not observed and has been reported as only occurring at temperatures greater than 200°C (Scheme 3.7).[93] This compound is generated by the Diels-Alder dimerisation of two diphenyl-cyclopentadienone molecules **31**, demonstrating that *p*-TsOH was sufficiently acidic to affect the dehydration, producing the reactive cyclopentadienone **31**.



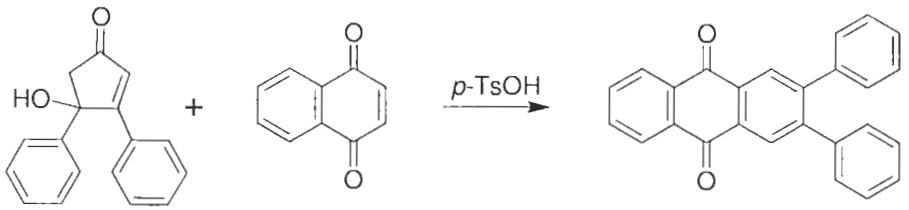
30 **31** **32**

quantitative

Scheme 3.7 Reaction of **31** to form dimer **32**

It is interesting to note that the phenyl groups of **31** do not prevent this molecule from dimerising, while the related sulfone **14** is stable towards dimerisation. This difference in reactivities is most likely due to differences in electronics, as these species have similar steric demands. Moreover, unlike the analogous sulfones, the cyclone species may have some anti-aromatic character and, as such, are expected to be more reactive. Cyclones also lack the tetrahedral

sulphur centre of the sulfones. The tetrahedral centres place the sigma-bonding electrons of the sulphur oxygen bonds into an orientation that may allow these electrons to have positive interactions with the pi-system electrons of the thiophene ring. This phenomenon is termed spiroconjugation,[103] and while more common for tetrahedral carbon atoms at the junction point of two rings, may also be occurring here as well.



30 **21**

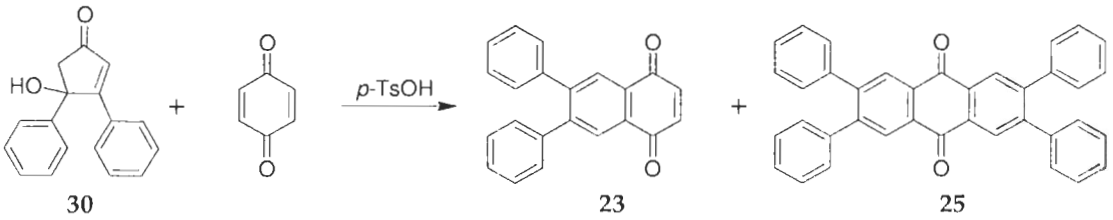
Scheme 3.8 Condensation of **30** with naphthoquinone

With evidence that the desired reactive species **31** did form, the next step was to attempt its condensation with 1,4-naphthoquinone. When a mixture of the hydroxy-cyclopentenone **30** and naphthoquinone were heated in refluxing acetic acid in the presence of catalytic *p*-TsOH, the desired anthraquinone **21** was formed as the major product in 42% yield. Significantly, only a trace quantity (<5%) of the dimer **32** was observed under these conditions. More generally, this side product (**32**) did not form in any appreciable amount in subsequent reactions of **30** with any quinone. Unlike the dibromosulfone **15** discussed in

Chapter 2, the dimerisation of **30** does not pose a significant problem in synthesis.

3.2.2 Reactions of 4-Hydroxy-3,4-Diphenylcyclopent-2-enone with Benzoquinone

The condensation of **30** with 2 equivalents of 1,4-benzoquinone was next investigated. Underlining the similar reactivity of cyclopentadienones and sulfones, this reaction followed the same two major reaction pathways: the double condensation leading to the anthraquinone **25,** and the formation of the mono-adduct naphthoquinone **23**. These quinones formed in approximately a 1:1 ratio (Scheme 3.9). As with the corresponding reactions of the sulfones, significant quantities of the anthraquinone were formed, even in the presence of a 2-fold excess of benzoquinone, conditions that should strongly promote formation of the naphthoquinone. The tendency to undergo double condensation is not as pronounced with species **30** as it is for the diphenylsulfone **14**. Recall that when sulfone **14** was reacted with 2 equivalents of benzoquinone, only the anthraquinone **25** was formed. Despite the effect not being as pronounced, it still suggests that compound **23** or one of the other precursors of **25** may be a much more reactive dienophile than benzoquinone itself (see Chapter 2 Section 2.3.2 for a more detailed discussion). It should also be noted that as with the sulfone-based reactions, no intermediate species were observed.



30 23 25

Scheme 3.9 Condensation of **30** with benzoquinone

As noted in Chapter 2, the formation of a naphthoquinone is useful in the preparation of lower symmetry anthraquinones. In an attempt to bias the reaction towards the formation of compound **23**, the condensation of **30** with benzoquinone was carried out in refluxing toluene, since the use of this solvent was previously shown to favour formation of the monoadduct.[104,105] However, in contrast with the sulfone **14**, hydroxycyclopentenone **30** requires an acidic environment (in this case, catalytic *p*-toluenesulfonic acid) to form its reactive species, the cyclopentadienone. Unfortunately, when toluene was used as the solvent, the formation of the cyclopentadienone intermediate **31** was considerably slower than when the reaction was carried out in acetic acid. After 2 days, no appreciable reaction of the starting materials was observed (as monitored by ^{1}H-NMR). Allowing this reaction to proceed for 6 days led to only

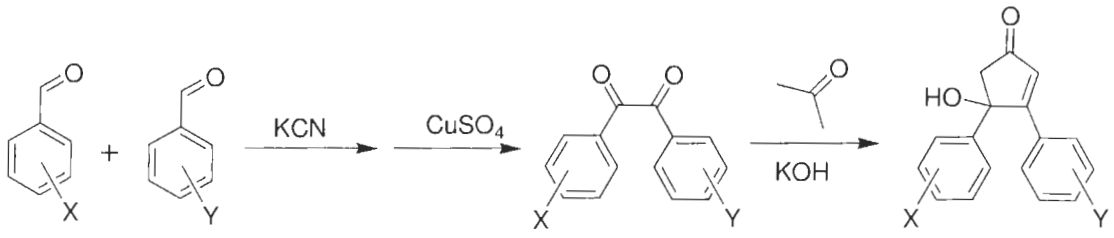
25% of compound **30** being consumed; although the ratio of naphthoquinone **23** to anthraquinone **25** did increase to 20:1.

If the cyclopentadieneone condensation with quinones follows a similar mechanism as the sulfone condensation with quinones then the tautomerisation to the hydroquinone (Scheme 2.15) may be catalysed by the presence of acid. So, in order to increase the rate of reaction in toluene a small amount of acetic acid (5 drops) was added to the reaction mixture. Under these conditions, 40% of the hydroxycyclopentenone reacted after 2 days. Unfortunately, the ratio of naphthoquinone **23** to anthraquinone **25** dropped to 5:1. Alternatively, the reaction could also be biased towards the formation of the naphthoquinone product by adding the catalytic *p*-TsOH in two equal portions over two days and allowing the reaction to proceed for 72 hours instead of the usual 48. Under these conditions the proportion of naphthoquinone product **23** to anthraquinone **25** could be increased to 5:1. This method had the advantage of allowing the reaction to proceed at an acceptable rate, and under these conditions, the entire cyclone starting material was consumed.

3.2.3 Preparation of 4-Hydroxycyclopent-2-enones with Differing Substituents

While it was not possible to control the product mixture through solvent choice to the same extent as it was in the case of the sulfones (Chapter 2), using cyclones did show enough promise to warrant further investigation. As mentioned earlier, one of the primary goals of this synthetic route was to allow the incorporation of greater dissymmetry into anthracene structures.

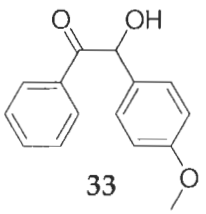
To this end, it was first necessary to prepare unsymmetrical benzil derivatives (Scheme 3.10). The primary method employed involved the cross-coupling of aromatic aldehydes to first produce benzoin derivatives and then oxidise these intermediates to the desired benzils, which could then be coupled with acetone.



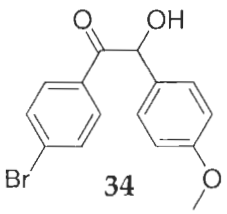
Scheme 3.10 Reaction scheme to produce unsymmetrical hydroxycyclopentenones

Coupling two substituted benzaldehydes (X and Y) *via* a benzoin condensation ostensibly can result in three products (XX, YY, and XY).

Fortunately, this reaction commonly favours the formation of the cross-benzoin product (XY), particularly when one aldehyde is electron deficient and the other electron rich.

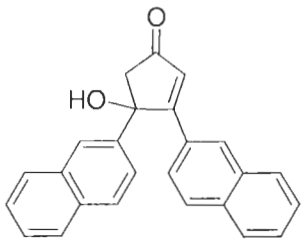


33

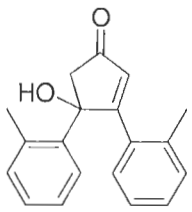


34

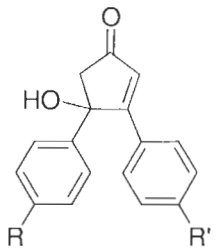
This trend was especially apparent in two of the studied cases: the coupling of 4-anisaldehyde with benzaldehyde, and the coupling of 4-anisaldehyde with 4-bromobenzaldehyde. Following a slightly modified literature preparation,[106] the coupling of anisaldehyde with benzaldehyde results in a mixture of two products in which the cross-benzoin compound was the favoured product **33**; the other compound formed was the product of two benzaldehydes. No homo-coupled anisaldehyde was observed. This mixture of benzoin products was treated with $CuSO_4$ to afford the respective diones, which were then seperated *via* silica gel chromatography. When anisaldehyde was reacted with bromobenzaldehyde, only the cross-benzoin **34** was formed. These procedures are described in detail in the experimental chapter.[107,108,109]



35



36



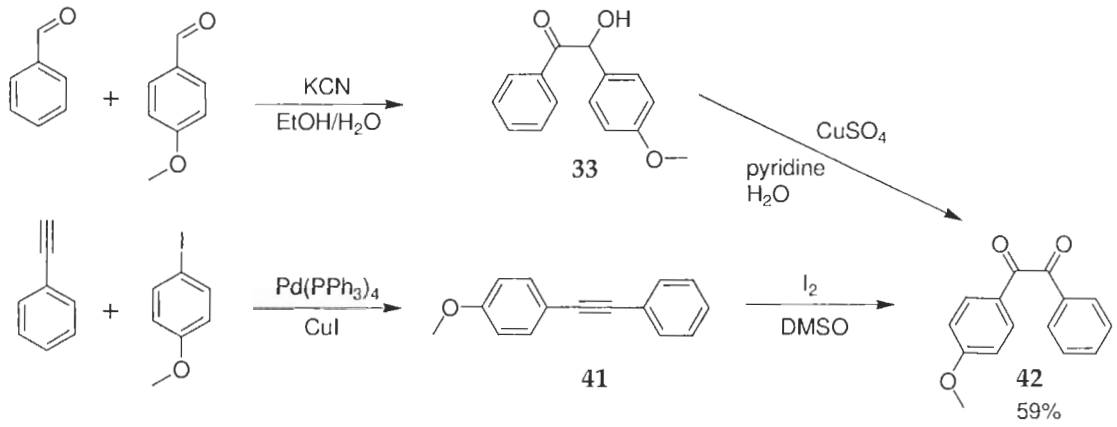
37 R = OCH_3, R' = H
38 R = OCH_3, R' = OCH_3
39 R = OCH_3, R' = Br
40 R = Br, R' = Br

Scheme 3.11 Additional synthetic intermediates used in substituted anthraquinone construction. Note: regioisomers of unsymmetrical derivatives are not shown.

The symmetrical 4-hydroxy-3,4-diaryl-2-cyclopentenones **35**, **36**, **38**, and **40** were synthesised from 2-naphthaldehyde, *o*-tolualdehyde, *p*-anisaldehyde, and *p*-bromoaldehyde, respectively. As with the reactions described above, the preparations employed slightly modified versions of literature procedures.[106] These synthetic intermediates were prepared to allow production of anthraquinones that fulfilled a variety of roles, as well as demonstrating the versatility of this synthetic technique in the construction of novel structures. Section 3.2.4 describes the potential applications of the structures that were produced from these synthetic intermediates.

3.2.3.1 Construction of the Regioisomeric Compound 37 *via* Two Routes

Compound **37** was a synthetic intermediate of interest, as the methoxy group provides a single easily accessible attachment point to the anthracene framework for eventual incorporation into other structures such as polymers.[110] Although the cross-benzoin route described above has the advantage of employing relatively inexpensive starting materials, it does yield the mixture of benzoin and compound **33** in an approximately 1:3 ratio, with the desired benzil **42** only being isolated in 22% yield. Due to these intrinsic limitations of this synthetic route, a more systematic approach to this compound was investigated.



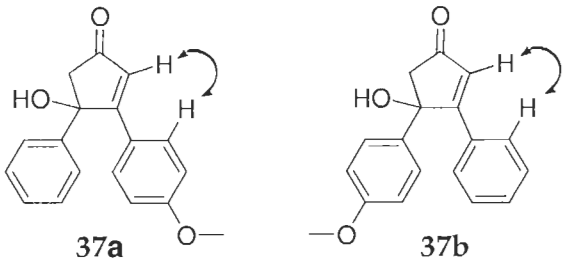
Scheme 3.12 Two routes to unsymmetrical diones

The method investigated (bottom Scheme 3.12) proceeded *via* the oxidation of the diphenylacetylene derivative **41,** which was readily prepared from phenylacetylene and *p*-iodoanisole using standard Hagihara-Sonogashira

conditions. Conversion of this compound to **42** has previously been reported using catalytic palladium chloride in DMSO.[111] It was found that, contrary to this previous report, **41** could also be cleanly oxidised to **42** in the presence of I_2/DMSO. This oxidation has the advantage of using less expensive reagents, while still proceeding cleanly and in high yields. The overall yields for this palladium catalysed route are considerably higher (59% versus 22%) than for the cross-benzoin method, although the use of more costly reagents is required.

3.2.3.2 Regioisomers of Compound 37

Condensation of the unsymmetrical 1-(4-methoxyphenyl)-2-phenylethane-1,2-dione (**42**) with acetone yields two products that were formed in a 5:2 ratio. These products were readily separated by column chromatography (silica gel) and were identified as the two regioisomers of the hydroxy-cyclopent-2-enone **37**:**37a** and **37b** (Scheme 3.13). In order to positively identify the two isomers, NOESY spectra were obtained for both compounds.

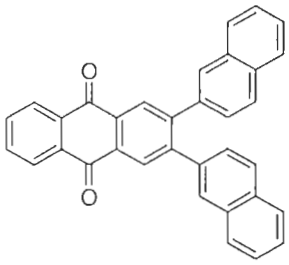


Scheme 3.13 Regioisomers formed during condensation of acetone with an unsymetrical dione (NOE correlations shown by arrows)

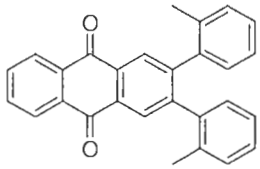
The spectrum of the major product showed a strong nuclear Overhauser effect between protons on the anisole ring and the vinylic proton on the cyclopentene ring, which led to the identification of this compound as **37a**. Conversely, a significant cross peak was observed between the phenyl ring and the vinylic proton in the NOESY spectrum of the minor product, confirming the identity of this compound as the second regioisomer **37b**. The formation of **37a** as the major product is consistent with the stabilisation of the incipient positive charge on the cyclopentane ring by the electron-donating *p*-methoxy group during the elimination of water. From a practical standpoint, the formation of two isomers is not problematic, since both **37a** and **37b** yield the same cyclopentiadienone upon loss of water.

3.2.4 Preparation of Anthraquinones with Varied Aryl Substituents

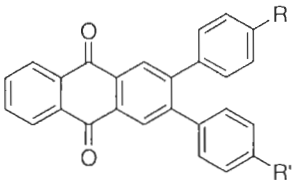
Having constructed a variety of cyclone precursors, the next step was to use these in the construction of anthraquinones. Each compound was targeted for a specific reason. The naphthyl- and *o*-tolyl-substituted derivatives **43** and **44** (Scheme 3.14) were targeted as more sterically congested analogs of **21**. On the other hand, the introduction of *para*-substituents onto the peripheral aromatic rings in compounds **45-49** should not appreciably alter the lateral bulk of the phenyl rings, but will change the electronic properties of these molecules. The methoxy- and bromo-substituents were also chosen as they provide useful points of attachment for the eventual incorporation of these compounds into polymers or other structures.



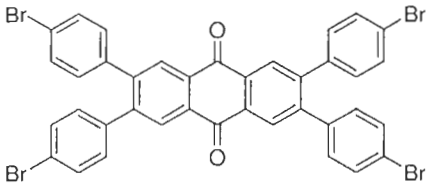
43
18%



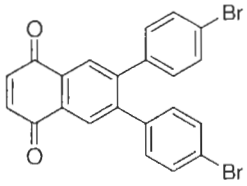
44
17%



45 R = OCH_3, R' = H 18%
46 R = OCH_3, R' = OCH_3 8%
47 R = OCH_3, R' = Br 21%



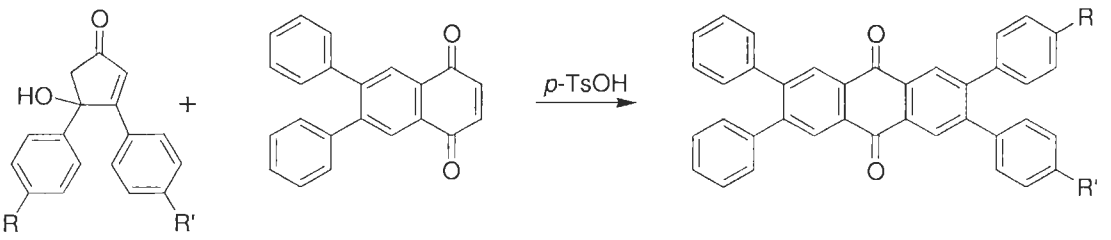
48
9%



49
3%

Scheme 3.14 A selection of quinones with novel aryl substituents. Yields shown are the isolated yields from the condensation of the hydroxycyclone precursor with the appropriate quinone.

It is also possible to use the hydroxycyclopent-2-enone intermediates **35**-**40** in the synthesis of 2,3,6,7-tetraarylanthraquinones bearing different aromatic rings at one or more of the sites. For this reason, 2-(*p*-methoxyphenyl)-3,6,7-triphenylanthraquinone **50** (Scheme 3.15) was targeted. It was possible to prepare both the mono- and dimethoxy-tetraphenylanthracene compounds **50** and **51** in modest yields (13% and 23%, respectively) from compounds **37** and **38**.



37 R=OCH_3, R'=H
38 R=OCH_3, R'=OCH_3

23

50 R=OCH_3, R'=H 26%
51 R=OCH_3, R'=OCH_3 13%

Scheme 3.15 Construction of anthraquinones bearing two types of aromatic rings *via* a 2-stage addition

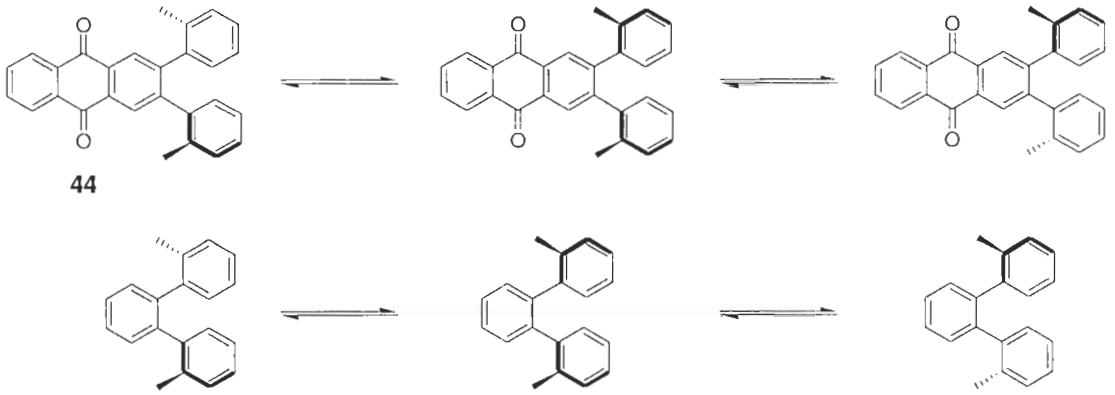
Condensation of these compounds (**35–40**) with 1,4-naphthoquinone (or 1,4-benzoquinone in the case of **48**) afforded the desired products **43-48** in isolated yields that varied from 7-21% (Scheme 3.14). It is not entirely clear at this time why the reactions involving these substituted derivatives were much lower than for the unsubstituted parent compound (Table 3.1). Part of the reason for the lower yields may be attributed to lower reactivity of these cyclones, although, it should be kept in mind that the conditions of both the reaction and separation of these compounds did not go through the same refinement process as for the reactions of parent **30**. Specifically, the optimal conditions for the purification of the final compounds have definite room for improvement. The only exception was the dianisole **38**, which did appear to be a problematic reactant that always led to the creation of significant amounts of unidentified side products. This synthetic intermediate was also significantly more difficult to

purify than others, often being accompanied by unidentified contaminants, which were apparent in the ^{1}H-NMR spectra. Unfortunately, these impurities proved quite difficult to remove.

Quinone **(equiv)**	Hydroxycyclopentanone **(equiv)**	Product(s) **(equiv)**	
Benzoquinone (2.00)	**40** (1.00)	**49** (0.13)	**48** (0.07)
Naphthoquinone (2.00)	**30** (1.00)	**21** (0.38)	
Naphthoquinone (2.00)	**35** (1.00)	**43** (0.18)	
Naphthoquinone (2.00)	**32** (1.00)	**44** (0.17)	
Naphthoquinone (2.00)	**37** (1.00)	**45** (0.18)	
Naphthoquinone (2.00)	**38** (1.00)	**46** (0.08)	
Naphthoquinone (2.00)	**39** (1.00)	**47** (0.21)	
23 (1.60)	**37** (1.00)	**50** (0.23)	
23 (0.85)	**38** (1.00)	**51** (0.14)	

Table 3.1 Summary of reactions between quinones and various hydroxycyclopentanones

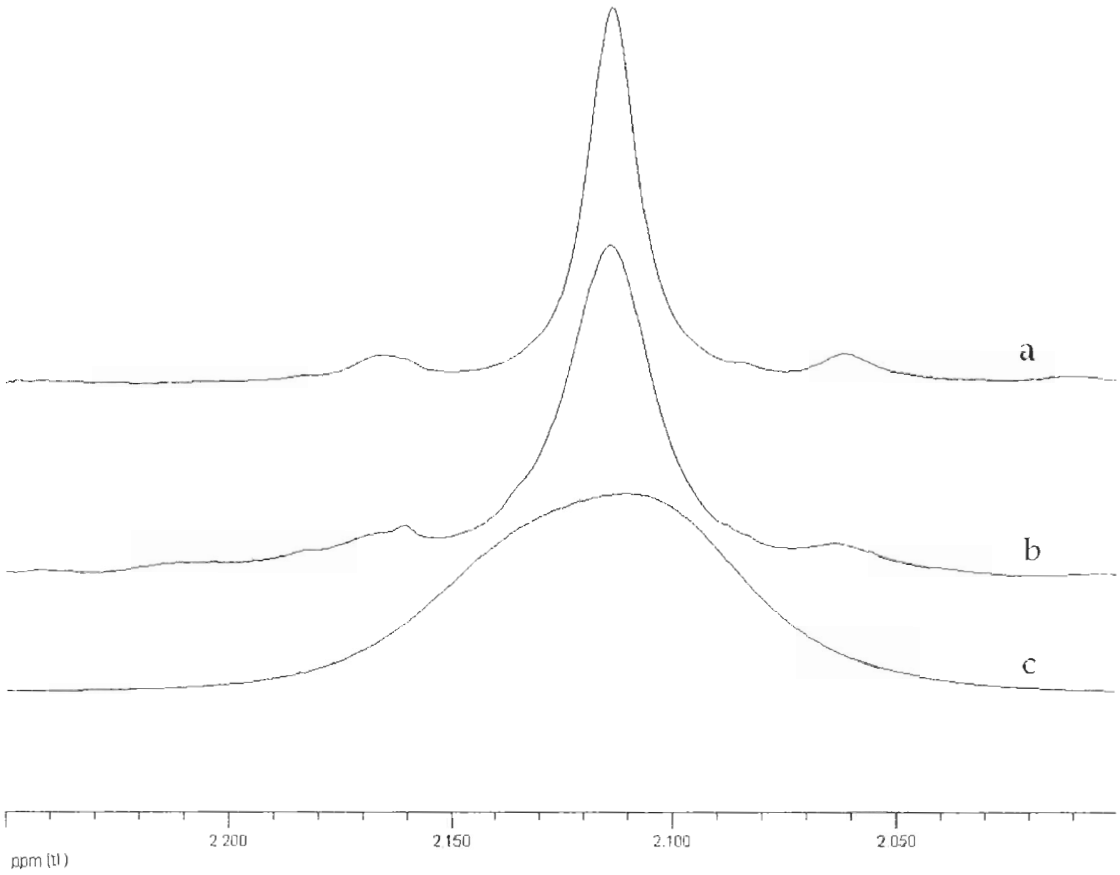
3.2.4.1 Dynamic Behaviour of 2,3-di*o*-tolylanthraquinone (44)



44

Scheme 3.16 Syn-anti isomerisation in 2,3-di*o*-tolylanthraquinone **44** and 2,2′-dimethyl-*o*-terphenyl

In the course of characterising the tolyl derivative **44**, it was noted that several peaks in both the ^{1}H- and ^{13}C-NMR spectra of this compound were appreciably broadened. The affected peaks were identified as those associated with the pendant tolyl groups, suggesting that these rings are undergoing conformational syn/anti-isomerism on the NMR timescale. This is consistent with the observation that a similar molecule, 2,2′-dimethyl-*o*-terphenyl, has a barrier to isomerisation of 62 kJ/mol, with an NMR coalescence temperature of 9°C (Scheme 3.16).[112] Although quantitative variable temperature NMR experiments were not carried out on **44**, the tolyl peaks were observed to sharpen at elevated temperatures, as expected (Scheme 3.17).



Scheme 3.17 ^{1}H-NMR Spectra of methyl groups of compound **44** at increasing temperatures, from top to bottom: 55°C (a), 40°C (b), and 23°C (c)

3.3 Conclusions

The cyclopentadienone-based synthetic route described above was shown to be complementary to the sulfone route discussed in Chapter 2 for the construction of both peripherally substituted naphthoquinones and anthraquinones. The primary concerns with the thiophene route were two-fold: inability to produce the required synthetic intermediate in large quantities, and

the limitations to the readily accessible substitution patterns. Both of these concerns were successfully addressed through the use of cyclopentadienones. It is possible to produce the hydroxycyclopentenone species in much greater quantities than it is for the sulfone equivalent. This makes the approach attractive, despite the lower yields obtained during the Diels-Alder reaction. In addition, the production of hydroxyclopentenones requires the use of less expensive reagents: acetone and potassium hydroxide versus the Pd^0 catalyst and phenylboronic acid required in the production of the sulfones of Chapter 2. For these reasons, after the development of the condensation route described in this chapter, sulfones were no longer employed in this research project for the production of synthetic intermediates that incorporate phenyl groups onto both the naphthoquinone and anthraquinone skeleton. Also, preparing precursors possessing two *different* aromatic groups is easily accomplished through this route, in contrast to the procedure using sulfones.

There are some intrinsic limits to this cyclopentadienone-based method in both the nature and positions of substitutions allowed. Specifically, a synthetic equivalent to the dibromosulfone **15** is not accessible. In addition, placing groups at the 2- and 5-positions requires a 1,3-disubstituted propanone that must either be purchased (limited options) or first created (time consuming). The propanones must also be used in significant excess of the benzil for the reaction

to proceed effectively (*vide supra*). In contrast, placing groups at these positions on a thiophene-dioxide is quite straightforward. Recall the bromination of thiophene preferentially occurs at the 2- and 5- positions over the 3,4-positions.

Despite the differences, the general mechanism of these reactions (sulfone and cyclone) is quite similar. They both begin with a Diels-Alder reaction followed by extrusion of a small gaseous molecule (SO_2 or CO). After this point, it is assumed that the reactions follow an analagous, if not identical, mechanism as the reactive species are identical and the reaction conditions are very similar. These similarities in mechanism result in similarities in reactivity. This was demonstrated by the reactions of the diphenyl derivatives of both synthetic intermediates. Both exhibited a tendency to undergo a double condensation with benzoquinone in preference to the single addition. However, the slight differences in conditions required to affect the additions (use of *p*-TsOH for the cyclopentadienone-route) meant that variations in solvent could not be used with equal effectiveness in controlling product distributions.

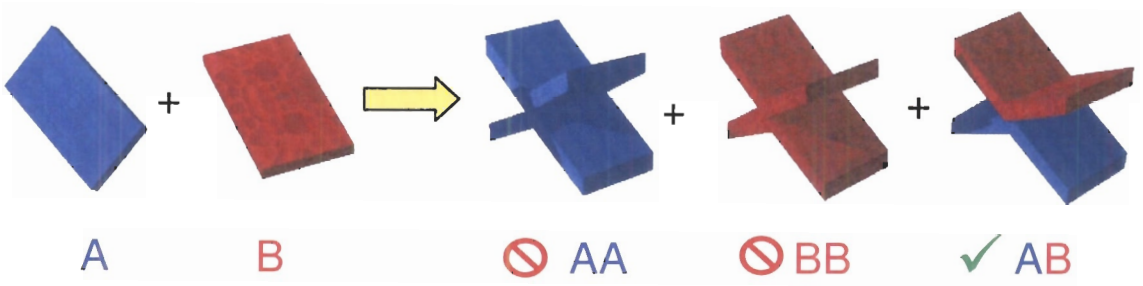
The synthetic routes described in this and the preceding Chapter are both capable of producing a variety of peripherally substituted naphthoquinones and anthraquinones. Both also have intrinsic deficiencies and strengths. Used in conjunction, an extensive array of substitution patterns are obtainable.

3.4 Future Work

Refinement of the synthetic procedure to increase the yields of many of the reactions described in this chapter would be desirable for their use in further syntheses. An extension of the methodology to include heterocycles as the pendent substituents could also prove interesting for both the photochemical properties of the final compounds made from these synthetic intermediates as well as for their possible interactions with metals. The construction of the 2,3,6,7-tetratolylanthraquinone and its anthracene derivative could also prove useful in further elucidating the effects of steric demands on the photochemistry of anthracenes (see Chapter 4 for more details). Given the stability of the dimer **32** (Scheme 3.7) it may be possible to use this species as the source of the reactive cyclone instead of the hydroxy-cyclopentenone **30**. This could allow the Diels-Alder reaction to be performed in a non-acidic environment.

CHAPTER 4: ANTHRACENE PHOTOCHEMISTRY

4.1 Introduction



Scheme 4.1 A representation of selective [4+4]-cycloaddition of anthracene derivatives

In this chapter, attempts to control the selectivity of the photocycloadditions of mixtures of anthracene derivatives are described. The objective was to develop a system in which irradiation of a mixture of two anthracene species (A and B) would result in the formation of only a single product AB (Scheme 4.1). It was anticipated that this could be accomplished

through judicious placement of sterically demanding groups on the anthracene skeleton.[iii]

As discussed in the introduction, it has been shown that symmetrical 9,10-disubstituted anthracene molecules generally do not dimerise, presumably due to the steric interactions that may both slow the rate of reaction and destabilise the resulting photodimers.[113] It was posited that sterically demanding groups placed at the peripheral 2-, 3-, 6-, and 7-positions of anthracene would have a similar effect, preventing homodimerisation, while still allowing cyclomer formation with anthracenes lacking substituents at these positions. Thus, a mixture of 9,10-dimethylanthracene (**DMA**) and 2,3,6,7-tetraphenylanthracene (**TPA**) should exclusively form the cross-cyclomer when irradiated with near UV light.

[iii] Many of the results discussed in this chapter were first reported in: Bailey, D. & Williams, V. E. (2005). Chem. Commun. 2569-2571. and Bailey, D. & Williams, V. E. (2006). J. Org. Chem. 71, 5778-5780.

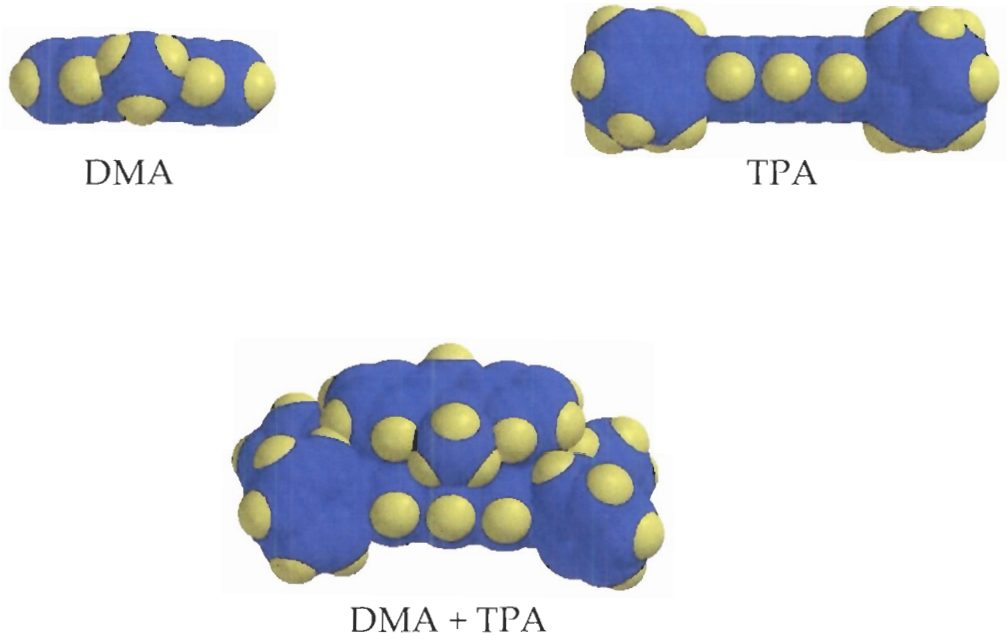


Figure 4.2 Space filling models of 9,10-dimethylanthracene (**DMA**) and 2,3,6,7-tetraphenylanthracene (**TPA**) demonstrating their orthogonal steric demands[iv]

The synthetic routes described in the previous chapters allowed the production of a series of peripherally substituted anthraquinones. In this chapter, the final steps in the preparation of substituted anthracenes, their photoreactivity, and the reversion of the resulting cyclomers back to their constituent anthracenes will be discussed. As well, a second approach to

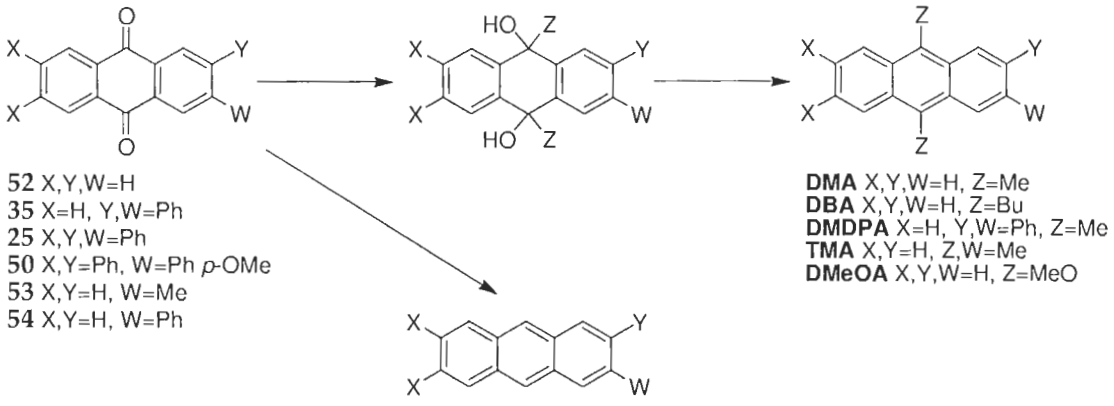
[iv] Space filling models of equilibrium geometry calculated *via* the Hartree-Fock method with the 3-21G* basis set using the molecular modelling program "Spartan '02" Copyright © 1991-2002 Wavefunction Inc.

controlling anthracene photochemistry through selective excitation of only one of the chromophores of a binary mixture will be described.

4.2 Preparation of Substituted Anthracenes

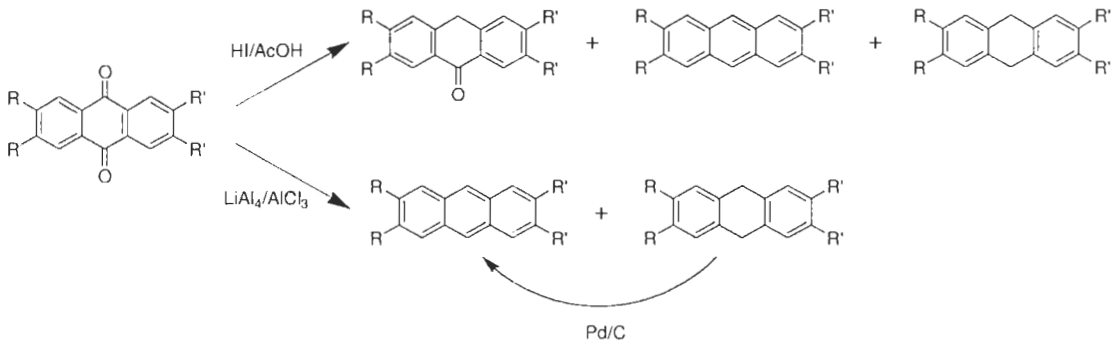
4.2.1 Introduction

In order to exploit the anthraquinones whose syntheses were described in the previous two chapters, it was first necessary to reduce them to the corresponding anthracenes. Scheme 4.3 shows the methods utilised to produce the novel anthracenes that were targeted. These routes will be discussed in greater detail in the following sections.



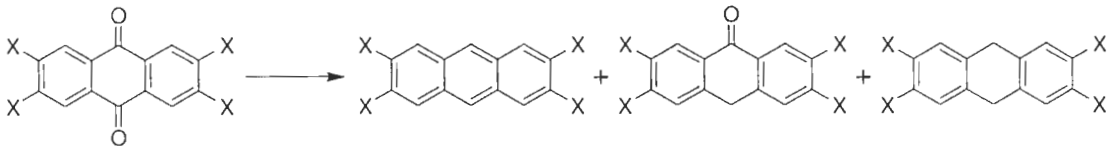
Scheme 4.3 Synthetic routes from anthraquinones to anthracenes

4.2.2 Reduction of Anthraquinones Using Hydride Sources



Scheme 4.4 Reduction of anthraquinones to anthracenes

Anthraquinones are commonly reduced to anthracenes using a mixture of HI and AcOH.[114] Unfortunately, this method proved inappropriate for reducing 2,3,6,7-tetraphenylanthraquinone **25** to **TPA**, even after many attempts and experimentation (Trial 1, Table 4.1). While some of the desired product was obtained, a significant amount of the reaction mixture was not reduced at all (usually 10-20%) while the remainder was either reduced to the anthrone (usually 20-30%) or over reduced to the dihydroanthracene (5-15%) (Scheme 4.4 top). Separation of these two products from the anthracene was not possible in many cases.



A **B** **C** **D**

52 X=H
25 X=Ph

Trial	Reagents	Conditions	Starting Material(s)	Products
1	HI / HOAc	reflux 15 – 114 h	**25** & **52**	A : B : C : D 2:7:4:1
2	Zn / AcOH	reflux 16 h	**52**	A : B 1:1
3	$NaBH_4$ / *i*-PrOH	reflux 15 h	**25**	A : B 1:2
4	$NaBH_4$ / BF_3Et_2O	stirred 30 min	**52**	B : C 1:3
5	$NaBH_4$ / H^+ / $NaBH_4$	stirred 19 h	**52**	A : C 3:4
6	$NaBH_4$ / $PhNHNH_2$	reflux 18 h	**25**	A : C : unknown products 1:5:?
7	$LiAlH_4$	reflux 28 h	**52**	B : C 5:1
8	$NaBH_4$ / MeOH, Diglyme	stirred 18 h	**25C** & **52C**	C
9	$LiAlH_4$ / $AlCl_3$	reflux 24 h	**25**	B : D 7:1

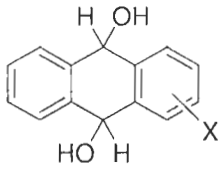
Table 4.1 Summary of conditions attempted in the reduction of anthraquinones

To achieve the desired reduction a myriad of conditions were attempted, the results of which are summarised in Table 4.1. The next technique examined consisted of using zinc with acetic acid. This method did not prove very

efficacious, yielding an equimolar mixture of quinone starting material and anthracene, even after prolonged heating in refluxing acetic acid.

The remaining methods examined all utilised an alkali-earth salt reducing agent, either sodium borohydride or lithium aluminium hydride. Treatment of the quinone with $NaBH_4$ in refluxing isopropanol resulted in a mixture of the anthraquinone and anthracene derivative (Trial 3). A Lewis acid ($BF_3{\cdot}Et_2O$) was added in an attempt to activate the quinone to hydride reduction,[115] which afforded slightly improved results, yielding a mixture of the anthrone and the anthracene products (Trial 4).

The next method followed the procedure of Klanderman *et al.* in which a variety of methyl-, methoxy-, and chloro-substituted anthraquinones were reduced by adding the hydride source in two portions, with the intermediate mixture being acidified and then neutralised before addition of the second portion of $NaBH_4$ (Trial 5).[116] It was suggested that the first addition of hydride would reduce the quinone to the diol **55** of the type shown below, while the acid would convert the intermediate to the anthrone, which would then be reduced to the anthracene by the second addition of $NaBH_4$.[116]



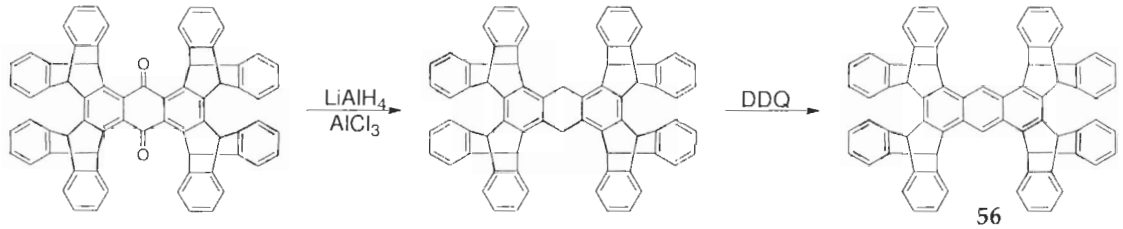
55

Unfortunately, this method did not provide any significant improvements over the other methods, yielding a mixture of the anthraquinone and anthrone. Using a method similar to that of Klanderman[116], phenylhydrazine was added after the addition of the hydride source to provoke the elimination of the resultant diol species (Trial 6). This method was reported by Norvez for the reduction of 1,4,5,8-tetramethoxyanthraquinones.[117] Unfortunately, this technique proved largely unsuccessful, yielding a mixture of anthrone and unknown aromatic side products. At this point, it was decided to move to a more powerful reducing agent. However, contrary to previous reports, application of $LiAlH_4$ alone did not prove satisfactory, only reducing the quinone to its corresponding anthrone, but no further (Trial 7).[118]

As many of these systems consistently provided the partially reduced anthrone as a product, a technique to reduce this species was sought. Marquardt and McCormick developed a method using $NaBH_4$ and diglyme in methanol to reduce methyl, methoxy, and halogen substituted anthrones to their respective

anthracenes (Trial 8).[119] Unfortunately, this method did not prove effective, returning only starting materials.

Eventually it was found that the most reliable method of reduction was by exposing the quinone to a mixture of lithium aluminum hydride and aluminum trichloride (Trial 9). Hart used a similar method in the production of the anthracene **56**.[120] The congested nature of Hart's anthracene structure was similar to that of the tetraphenyl derivative **25,** suggesting this reductive method might prove successful with the many sterically crowded anthracenes described in this thesis.

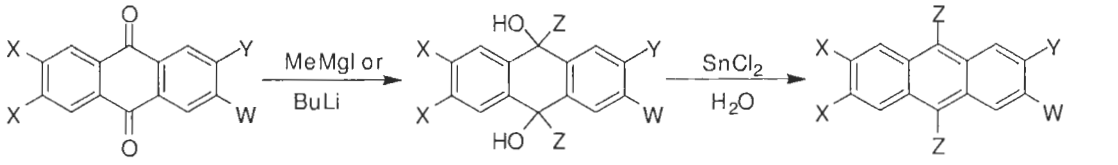


Scheme 4.5 Reduction method used by Hart to produce the congested anthracene **56**

This potent mixture of $LiAlH_4/AlCl_3$ consistently reduced the vast majority of quinones to the corresponding anthracene (>85% by ^{1}H-NMR). Unfortunately, a substantial amount (10-15%) of the compound was also over-reduced to the dihydroanthracene (bottom of Scheme 4.4). These products proved difficult to

separate by either chromatography or recrystallisation. Fortunately, this problem could be circumvented by exposing the entire product mixture to palladium on charcoal in refluxing xylenes, which cleanly reoxidised the dihydroanthracene to the anthracene. This final reaction mixture would then contain only the desired anthracene and a small quantity (<10%) of the related quinone. While separating the anthracenes from their related anthrones and dihydroanthracenes was not feasible, the anthraquinones were always easy to separate, irrespective of substituents. This separation was routinely accomplished through chromatography on silica gel followed by recrystallisation from acetone providing pure samples of the anthracene in an average yield of 76%.

4.2.3 Addition of Substituents at the 9 and 10 Positions

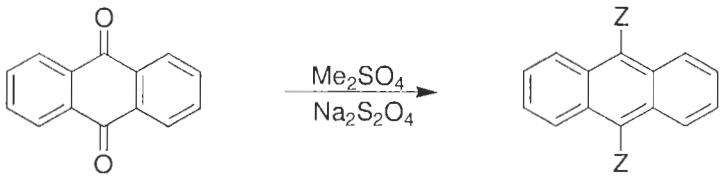


52 X,Y,W=H
21 X=H, Y,W=Ph
53 X,Y=H, W=Me

DMA X,Y,W=H, Z=Me
DBA X,Y,W=H, Z=Bu
DMDPA X=H, Y,W=Ph, Z=Me
TMA X,Y=H, Z,W=Me

Scheme 4.6 Preparation of 9,10-dialkyl anthracenes

While the majority of this research project is focussed on anthracenes decorated at their peripheral positions, 9,10-functionalised anthracenes were also investigated. Since bond formation during photodimerisation occurs at the central 9,10 positions, any effects that substituent groups may have should be at their greatest at these positions. Several of these 9,10-substituted compounds were also required to provide partners for the peripherally substituted anthracenes in sterically-controlled photoreactions.



52 **DMeOA** Z=MeO 72%

Scheme 4.7 Preparation of 9,10-dimethoxyanthracene **DMeOA**

Alkyl groups were installed at the 9- and 10-positions of the anthracene derivatives through reaction of the appropriate anthraquinone with either a Grignard reagent or an alkyllithium (Scheme 4.6). The alkoxy **DMeOA** was prepared by a methylation of anthraquinone by dimethylsulfate (Scheme 4.7). These synthetic procedures followed standard methods and are described in more detail in the experimental chapter. Using these methods it was possible to obtain 9,10-dimethylanthracene **DMA**, 9,10-dibutylanthracene **DBA**, 2,9,10-

trimethylanthracene **TMA**, 9,10-dimethoxyanthracene **DMeOA**, and 9,10-dimethyl-2,3-diphenylanthracene **DMDPA** in yields ranging from 23% to 72%.

4.3 Using Steric Complementarity to Control Anthracene Photochemistry

4.3.1 Introduction

The intention of this research project was to use sterically demanding substituent groups to enforce a strict regime of selective reactivity on binary anthracene mixtures in order to obtain cross-cyclomer products to the exclusion of the formation of the homodimers. This selectivity is represented in Scheme 4.1 in which the coloured anthracenes "A" and "B" represent anthracenes with two different substituent patterns and/or groups. Irradiation of this mixture only leads to the "AB" cross cyclomer without the accompanying formation of "AA" and "BB" products.

While 9,10-dimethylanthracene exhibits only a limited tendency to homodimerise, it reacts quite readily with anthracene derivatives that lack functional groups at the 9- and/or 10-positions. Unfortunately, since both unsubstituted anthracene and 9-substituted derivatives tend to dimerise, any reactions of these compounds with **DMA** exhibit limited selectivity. In an effort to design a suitable partner for **DMA**, an anthracene derivative that lacked

groups at the 9- and 10-positions but possessed bulky groups at the peripheral 2-, 3-, 6-, and 7-positions was targeted. It was reasoned that a substitution pattern of this type would inhibit homodimer formation while permitting reaction with 9,10-disubsituted derivatives such as 9,10-dimethylanthracene. It was also expected that the non-interacting orthogonal bulk of these pairs of anthracenes would not have a detrimental affect on the stability of the resulting cyclomer.

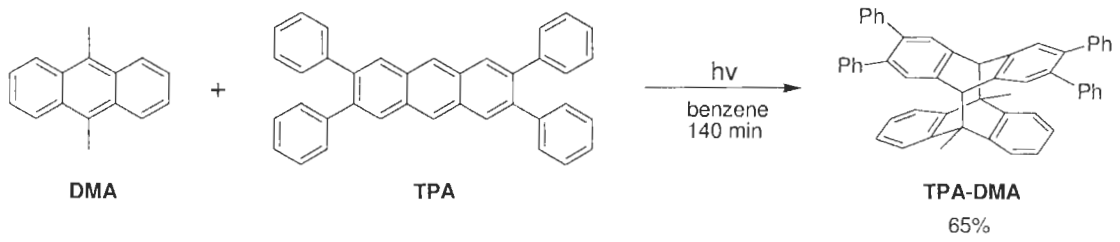
A similar strategy of using sterically bulky groups has been successfully employed to attenuate the deleterious effects of self-association on the photophysical properties of conjugated polymers while still allowing interactions with small molecule analytes.[100] Phenyl groups have also been used extensively as "insulation" for both reactive functionalities[121] and nanostructured materials[122,123,124,125] and it was expected that 2,3,6,7-tetraphenylanthracene would possess sufficient lateral bulk to inhibit homodimerisation (Figure 4.2).

4.3.2 Cyclomer formation

4.3.2.1 Cycloaddition of 2,3,6,7-Tetraphenylanthracene with 9,10-Dimethylanthracene

The initial studies focussed on the reactivities that the substituted anthracenes have when irradiated in the absence of any other reactive species. When 2,3,6,7-tetraphenylanthracene **TPA** was irradiated in the Rayonet

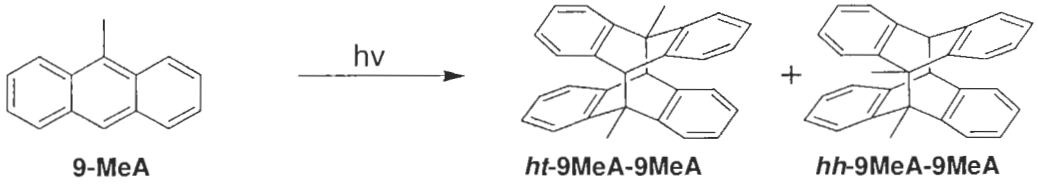
Photochemical Reactor© using lamps whose output is centred at 300 nm, no dimer formation nor any other reactivity was observed, regardless of the duration of irradiation (up to 26 h). In comparison, using the same 300 nm-centred lamps results in a 75% conversion of anthracene to dianthracene after 2 hours. This suggests that the peripheral phenyl groups were inhibiting the homodimer formation.



DMA + TPA → TPA-DMA (65%)

Scheme 4.8 Photoinduced coupling of 9,10-dimethylanthracene and 2,3,6,7-tetraphenylanthracene

Although compounds **DMA** and **TPA** show very limited reactivity in isolation, irradiation of an equimolar mixture of these compounds (4 mM each in benzene) over 140 min with lamps centred at 300 nm afforded a single product in 65% yield (Scheme 4.8). This product showed a high degree of stability and could be isolated from the starting materials by both column chromatography and through recrystallisation from heated solvents such as acetone and ethanol.



Scheme 4.9 Homodimerisation of 9-Methylanthracene

Both the ^{1}H and ^{13}C NMR spectra of this photoproduct are consistent with the cross-dimer **TPA-DMA**. Of particular note is the presence of two singlets in the ^{1}H NMR spectrum at 4.1 and 2.2 ppm, corresponding to the dimer's bridgehead protons and the methyl groups, respectively. These chemical shifts are almost identical to those of the head-to-tail dimer of 9-methylanthracene (ht-9MeA-9MeA) (Scheme 4.9) as one would expect given their similar chemical environments, *i.e.* a bridgehead proton adjacent to a methyl group.[126] The assignment was further confirmed by the observation of a nuclear Overhauser effect between these two sets of protons, indicating that they are, indeed, in close proximity to one another (Figure 4.10). This NOE difference spectrum also showed that one set of protons on the phenyl rings are quite close to the bridgehead protons. This was later confirmed through X-ray crystallography (*vide infra*), by which it was determined that H_a was approximately 2.4 Å from both the methyl groups and H_b (Figure 4.10).

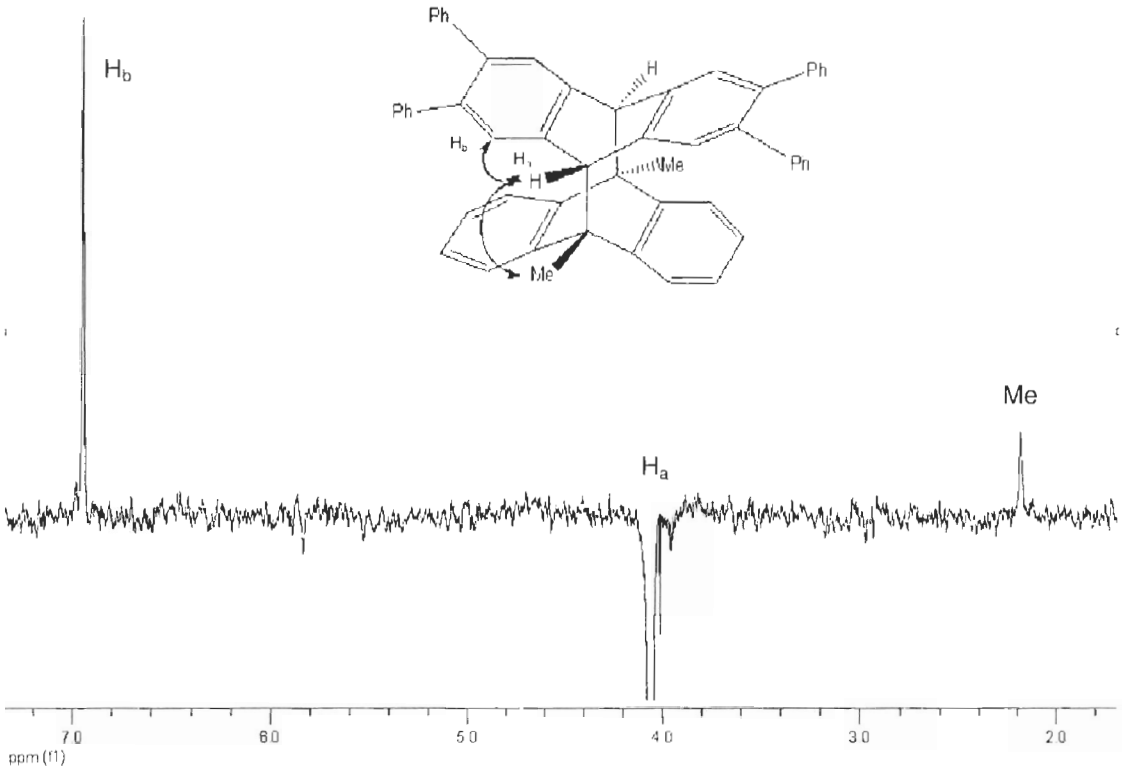


Figure 4.10 NOE difference spectrum and structure of the photodimer **TPA-DMA**, in this study proton "H_a" was saturated

Characterisation of this compound by mass spectrometry posed a greater challenge, since dianthracenes tend to fragment into their component monomers when ionized.[3] Thus, the MALDI–TOF spectrum of **TPA-DMA** exhibited only peaks corresponding to the two monomers, while the FAB-MS (Fast Atom Bombardment Mass Spectroscopy) spectrum showed a weak molecular ion peak for the dimer, in addition to a much more intense peak for **TPA**.

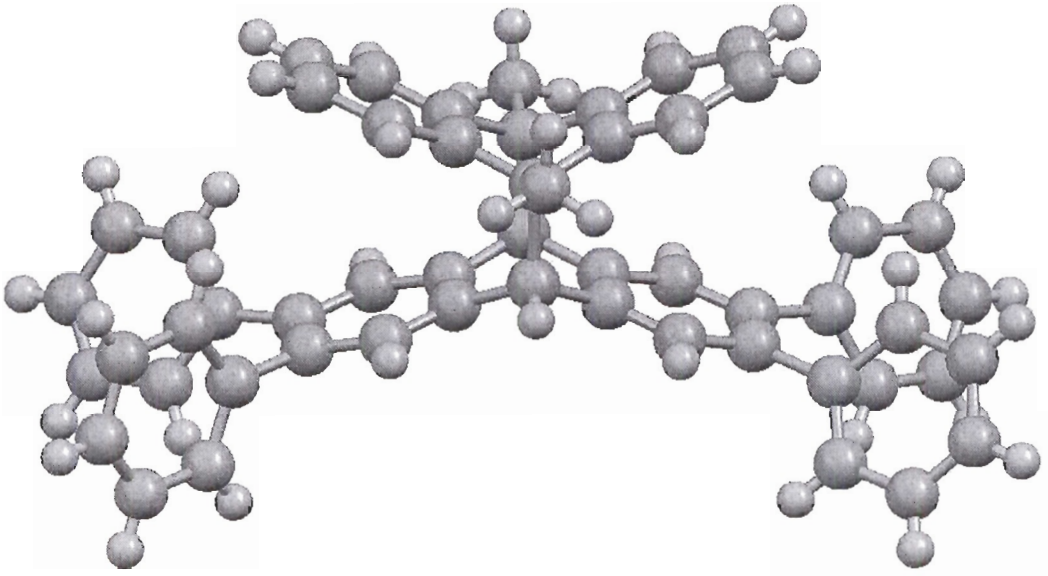
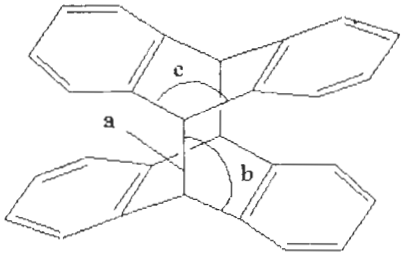


Figure 4.11 Structure of **TPA-DMA** as Determined by X-Ray Diffraction

Final confirmation of the structure of **TPA-DMA** was obtained through single-crystal X-ray crystallography. The X-ray crystal structure of **DMA-A** (dimethylanthracene-anthracene cyclomer) was also obtained. Of note are the negligible differences between the geometries of the **DMA-A** and **TPA-DMA** structures (Table 4.2). The bridgehead 9-9′ and 10-10′ bond lengths of the structures are virtually identical, as are the bond angles formed at these bridgeheads positions. The differences in the deviation from planarity by the anthracene molecules ('anthracene bend' in Table 4.2) are also negligible. The similarity between the central regions of these molecules demonstrates the very

limited effect the pendant phenyl rings of **TPA** have on the structure of the cyclomer. This establishes that these phenyl groups have no significant steric interactions with the anthracene rings of the **DMA** portion of the cyclomer. It also suggests that there are no appreciable electronic effects by the phenyl groups that alter the structure of the cyclomer.



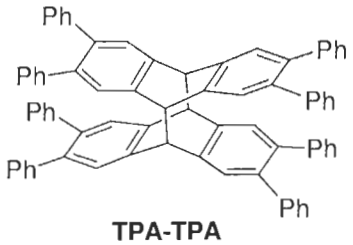
	TPA-DMA	DMA-A
bridgehead bond length (a)	1.63 (+/- 0.022) Å	1.63 (+/- 0.0)Å
bridgehead bond angle (b)	111 (+/- 0.82)°	111 (+/- 0.23)°
anthracene 'bend' (c)	**TPA** 109 (+/- 0.82)° **DMA** 108 (+/- 0.45)°	108 (+/- 0.85)°

Table 4.2 Selected comparisons of the X-ray structures of TPA-DMA and DMA-A

4.3.2.1.1 Dimerisation of 2,3,6,7-Tetraphenylanthracene

Subsequent studies utilising lamps centred at 350 nm revealed that **TPA**, like **DMA**, does form its homodimer when irradiated alone under the appropriate conditions. However, the formation of this dimer is quite slow;

irradiation of a benzene solution of **TPA** at 350 nm for 2 hours led to only 12% of the starting material being converted into this product. As a comparison, the same concentration of anthracene forms dianthracene quantitatively in under 2 hours when irradiated with the lamps centred at 350 nm.



TPA-TPA

Figure 4.12 2,3,6,7-Tetraphenylanthracene dimer 2,2′,3,3′,6,6′,7,7′-Octaphenyldianthracene

It should be stressed that the formation of the homodimers of either **DMA** or **TPA** appears to be highly disfavoured and were rarely observed. When in the presence of other reactive anthracene species, these products were almost never observed, suggesting that these dimers only form when no other reactive species are present.

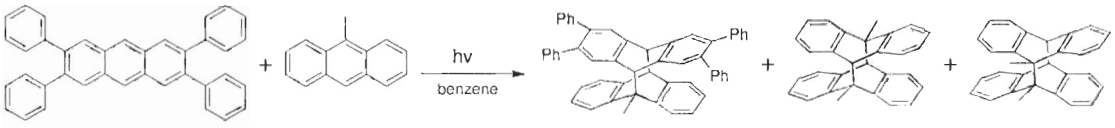
4.3.2.2 Studies into the Formation of Additional Cyclomers

The previous Section (4.3.2.1) demonstrated how the orthogonal bulk of **DMA** and **TPA** could be used to impose a strict regime of reactivity upon these compounds. However, before this or a related system could be used in the

design of functional materials, a more thorough study of substituted anthracenes needed to be undertaken. Most importantly, studies to further elucidate the steric requirements needed to ensure selectivity were carried out, as were experiments to examine the compatibility of groups other than methyl substituents at the 9- and 10-positions. Also of interest was the effect peripherally (2-,3-substituted) aryl groups would have on the reactivity. These studies are summarised in Table 4.3.

	Anthracene **A**	2,3,6,7-Tetraphenylanthracene **TPA**	2,3-Diphenylanthracene **DPA**	2-Phenylanthracene **MPA**	2,3-Diphenyl-9,10-Dimethylanthracene **DMDPA**	2,9,10-Trimethylanthracene **TMA**	2-Anisole-3,6,7-Triphenylanthracene **TPAA**	9,10-Dimethylanthracene **DMA**	9-Methylanthracene **9MeA**	9,10-Dibutylanthracene **DBA**	9,10-Dimethoxyanthracene **DMeOA**	9,10-Dicyanoanthracene **DCNA**	9-Cyanoanthracene **9CNA**
Anthracene **A**	X												
2,3,6,7-Tetraphenylanthracene **TPA**	X	X											
2,3-Diphenylanthracene **DPA**	X		X										
2-Phenylanthracene **MPA**		X		X									
2,3-Diphenyl-9,10-Dimethylanthracene **DMDPA**	X	X			NR								
2,9,10-Trimethylanthracene **TMA**		X				NR							
2-Anisole-3,6,7-Triphenylanthracene **TPAA**							NR						
9,10-Dimethylanthracene **DMA**	X	X			NR		X	X					
9-Methylanthracene **9MeA**	X	X							X				
9,10-Dibutylanthracene **DBA**		X								NR			
9,10-Dimethoxyanthracene **DMeOA**		X						X			NR		
9,10-Dicyanoanthracene **DCNA**		NR										NR	
9-Cyanoanthracene **9CNA**	X	X						X			X		X

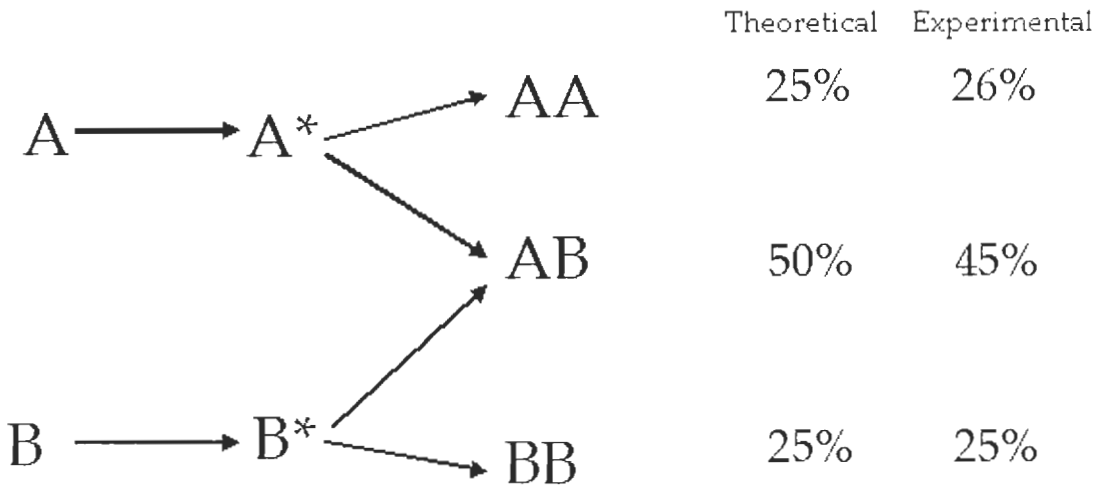
Table 4.3 Summary of attempted anthracene photodimerisations *via* irradiation in a Rayonet Photochemical Reactor© (X = photocycloaddition, NR = no reaction, Blank = not studied)



TPA **9MeA** **TPA-9MeA** ***ht* 9MeA-9MeA** ***hh* 9MeA-9MeA**

Scheme 4.13 Photocycloaddition products of **TPA** and **9MeA**

Studies began by examining the behaviour of 9-methylanthracene (**9MeA**). While 9,10-dimethylanthracene does not form its homodimer except under forcing conditions, the same does not hold true for **9MeA,** which quite readily undergoes photodimerisation.[3] Interestingly, when **9MeA** was irradiated with either unsusbstituted anthracene or **TPA,** the cross cyclomer was preferentially formed. When an equimolar (4+4 mM in benzene) solution of **9MeA** was reacted with anthracene for 140 min under lamps centred at 300 nm 45% of the resulting product mixture was the cross cyclomer, with the two homodimers of the **9MeA** head-to-head (hh) and head-to-tail (ht) and dianthracene formed in 7%, 19% and 25%, respectively. A similar phenomenon was observed in the related reaction of **9MeA** with **TPA**, under the same conditions (140 min, 4+4 mM, 300 nm, benzene) yielding 51% cross-cyclomer and only 10% (2% *hh*, 8% *ht*) of **9MeA** homodimers (Scheme 4.13).



Scheme 4.14 Comparison of theoretical and experimental photodimer product mixtures found during the irradiation of **9MeA** and anthracene

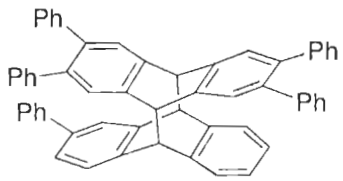
Scheme 4.14 compares the theoretical and experimental mixture of photocyclomer products for the reaction of anthracene with **9MeA**. Two assumptions were made to obtain these theoretical values: i) the excited states two chromophores must have an equal likelihood of population under these conditions, and ii) the barriers to the reaction must be very similar. Judging by the experimental results, this seems to be the case in this example. In the reaction of **TPA** with **9MeA** the situation is slightly different, as **TPA** will not form a homodimer when irradiated at 300 nm, so the ratio of cross-cyclomer to homodimer should be roughly 3:1. However, the ratio in this case was found to be 5:1 cross-cyclomer to homodimer, suggesting a preferential reaction between the **TPA** and **9MeA**. This was most likely due to a greater absorption at 300 nm

by **TPA** resulting in the **TPA** being preferentially excited, and as **TPA** will not form a homodimer under these conditions, it results in the crossdimer being preferentially formed over the homodimer of **9MeA**.

While methyl groups at the 9- and 10-positions and phenyl groups at the 2-, 3-, 6- and 7-positions can be used to prevent dimerisation, it was not known to what extent a methyl group at the peripheral 2-position would interact with peripheral phenyl groups found on **TPA**. Would a methyl group be large enough to prevent reaction with **TPA**? To answer this question, 2,9,10-trimethylanthracene (**TMA**) was prepared from 2-methylanthraquinone and its photochemistry investigated. The reactivity of **TMA** alone was first studied. Upon irradiation in the Rayonet at 300 nm, no signs of dimerisation were observed, as was expected owing to its similarity to **DMA**. However, when irradiated in the presence of **TPA** (4+4 mM, 2 h, 300 nm) a cross-cyclomer formed in 68% yield, demonstrating that any interactions between the 2-methyl group of **TMA** and the phenyl groups of **TPA** were not sufficient to prevent reaction.

A similar result was obtained when 2-phenylanthracene (**MPA**) was irradiated in the presence of **TPA**. The cross-cyclomer formed **TPA-MPA** in 55% yield while the homodimer **MPA-MPA** formed in 25% (4+4 mM, 1.5 h, 350 nm). Under these same conditions (8 mM, 1.5 h, 350 nm), **MPA** alone formed its

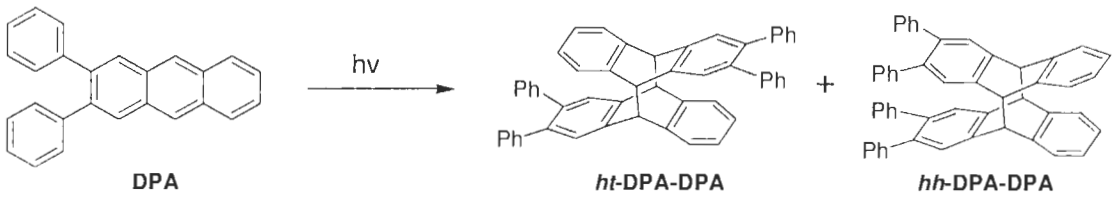
homodimers in 90% yield. The high yield of the cross cyclomer product formation was unexpected, since it was assumed that phenyl groups were of sufficiently bulky to severely hamper dimerisation, as demonstrated by the very sluggish reactivity of **TPA** when irradiated alone.



TPA-MPA

As has been shown through examination of the X-ray structures in this thesis, as well as by previous researchers, dianthracene (and related molecules) bridgehead C-C bond distances do not vary considerably (1.60 – 1.67Å).[127] The effect of the substituents on this bond length tends to be much greater when these groups are placed at the central 9- and 10- positions.[130] This suggests the geometry of the structures of **TPA-TPA** and **TPA-MPA** should be similar, yet **TPA-MPA** forms easily but **TPA-TPA** only forms in limited amounts after extended irradiation. Thus, the reactivity of **MPA** with **TPA** suggests that it is not the structure of the final compound that determines the reactivity, but rather, the ability of the reactive centres to approach one another. It appears to be a kinetic rather than a thermodynamic impediment that is responsible for the reactivity of these compounds. Before dimerisation, the anthracene core is

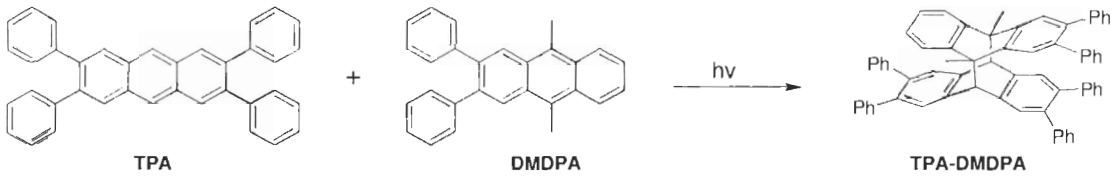
essentially planar; presumably, the [4+4] cycloaddition requires the central regions of the two chromophores to come in close proximity to one another. Therefore, the additional phenyl rings of the tetraphenyl **TPA** would hinder this approach much more so than in the case of **MPA**.



DPA *ht*-**DPA-DPA** *hh*-**DPA-DPA**

Scheme 4.15 Possible dimerisation modes of 2,3-Diphenylanthracene

As four peripheral phenyl substituents (**TPA**) greatly inhibit homodimer formation, and one (**MPA**) does not, the effect of two phenyl groups was investigated next. 2,3-Diphenylanthracene **DPA** was found to undergo facile homodimer formation; after 130 minutes of irradiation at 300 nm, a 2 mM solution of this compound was converted to a single photoproduct in 50% yield (Scheme 4.15). This product was identified as one of the two possible photodimers, the "head-to-tail" or the "head-to-head" product, based on its ^{1}H-NMR spectrum. Although the available information does not allow for the definitive identification as to which of these two photoproducts were formed, steric considerations suggest that the head-to-tail product is likely to be favoured.



TPA + DMDPA → TPA-DMDPA

Scheme 4.16 Photoreaction of **TPA** and **DMDPA**

9,10-Dimethyl-2,3-diphenylanthracene **DMDPA**, like 9,10-dimethylanthracene, but unlike 2,3-diphenylanthracene, failed to undergo any observable photodimer formation, presumably due to the presence of the methyl groups at the 9- and 10-positions. The two phenyl groups of **DMDPA** do not prevent it from forming a cycloadduct with **TPA** in 64% yield (4 + 4 mM, 100 min, 350 nm). The ability of **DMDPA** to react with **TPA** further corroborates the hypothesis that steric crowding of the resulting photodimer by peripheral bulky groups is not sufficient to hinder the formation of these structures.

There are three generalisations to be made of the previous experiments; i) 9,10-dimethyl groups prevent homodimerisation, ii) species with up to two peripheral phenyl groups *will* homodimerise, iii) that two peripheral phenyl groups are not sufficient to prevent reaction with derivatives having four peripheral phenyl groups. This confirms that central substituents have a much greater effect on these photo-cycloadditions, which is not surprising as the 9- and 10-positions are the reactive bond-forming centres.

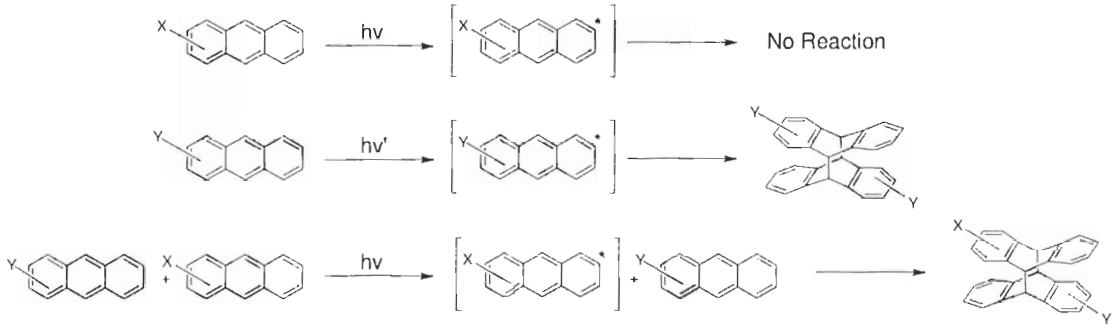
While it has been shown by Bouas-Laurent and coworkers that other symmetrical 9,10-disubstituted anthracenes generally do not homodimerise, what was unknown was whether such anthracenes would react with **TPA**.[3] The photochemical reactions of several other anthracene derivatives of this type were therefore investigated. Earlier reports by Bouas-Laurent demonstrated the preference of 9-cyanoanthracene (**9CNA**) to react with anthracenes containing electron-donating methyl groups.[37] As all of the anthracene derivatives created during the course of this thesis included electron-donating substituents, it seemed apt to perform some preliminary studies using cyano-substituted anthracenes to investigate whether any behaviour similar to that described by Bouas-Laurent would be observed. The mono-substituted **9CNA** did prove reactive with **TPA**, yielding the cross-cyclomer in 42%, while only producing 8% of the 9-cyanoanthracene homodimer (4+4 mM, 140 min, 300 nm). Although its mono-substituted relative, 9,10-dicyanoanthracene (**DCNA**) did not prove reactive at all, forming neither its homodimer nor a cross-cyclomer with **TPA**. It was thought that **DCNA** may quench the excited states of other anthracene molecules present through non-productive routes. However, fluorescence measurements of a series of solutions of **TPA** with varying amounts of **DCNA** did not show any decrease in fluorescence of **TPA** besides the expected effect of dilution.

The reactivities of two other species were also investigated: 9,10-dibutylanthracene (**DBA**) and 9,10-dimethoxyanthracene (**DMeOA**). While both of these species failed to homodimerise when irradiated alone, they both did react with **TPA** when irradiated in a binary mixture, yielding **TPADBA** in 45% (4+4 mM, 100 min, 350 nm) and **TPADMeOA** in 82% (4+4 mM, 100 min, 350 nm).

Also of interest was whether attachment of functional groups on peripheral benzene rings would have an effect on the photochemistry. Accordingly, the monoanisole-triphenyl anthracene **TPAA** was prepared. While in-depth studies of this molecule have not yet been undertaken, preliminary studies suggest that this molecule behaves in a similar manner to the closely related tetraphenylanthracene. This molecule does not appear to homodimerise, yet does readily form a cycloadduct with dimethylanthracene.

4.4 Using Selective Excitation to Control Anthracene Photochemistry

4.4.1 Introduction



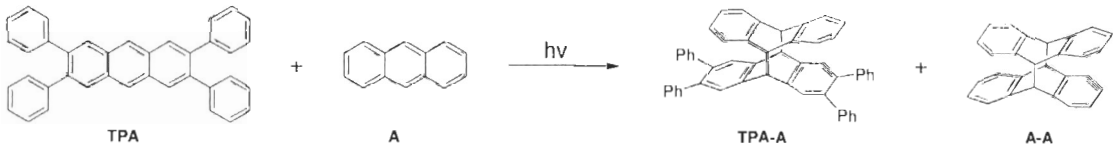
Scheme 4.17 Two anthracene species in which only the one incapable of homodimerisation is excited by irradiation

In the previous Section (4.3) a strategy for restricting [4+4]-photocycloadditions using steric complementarity was described. The same results could, in principle, be obtained using selective excitation. If only one of the two molecules in solution is excited and this excited species is incapable of homodimerisation then the formation of a single photoproduct should result (Scheme 4.17). This strategy is much more flexible than those described previously since it requires only one of the two components to be inert towards homodimer formation. It does, however, require that the two species have distinct absorption spectra to allow one species to be selectively excited in the presence of the other.

4.4.2 Cyclomer Formation

4.4.2.1 Anthracene and 2,3,6,7-Tetraphenylanthracene

The initial photochemical experiments on these compounds were carried out in a Rayonet using lamps centred at either 300 nm or 350 nm. When a 1:1 mixture of 2,3,6,7-tetraphenylanthracene and anthracene were irradiated with light centred at 300 nm, two photoproducts were formed in an approximately 1:9 ratio. These products were identified as dianthracene and the cross-cyclomer **TPA-A**, respectively.



Scheme 4.18 Photodimerisation of anthracene and 2,3,6,7-tetraphenylanthracene

When the mixture of anthracene and **TPA** was irradiated with 350 nm light, both dianthracene and **TPA-A** were again formed, but in a 1:3 ratio rather than the 1:9 ratio observed at 300 nm. As mentioned in the previous Section (4.3) it is possible to form the homodimer of **TPA,** and after extended irradiation periods (>140 min, 350 nm lamps) trace amounts (~3%) of this product were observed. This product (**TPA-TPA**) was never observed when using the lamps centred at 300 nm.

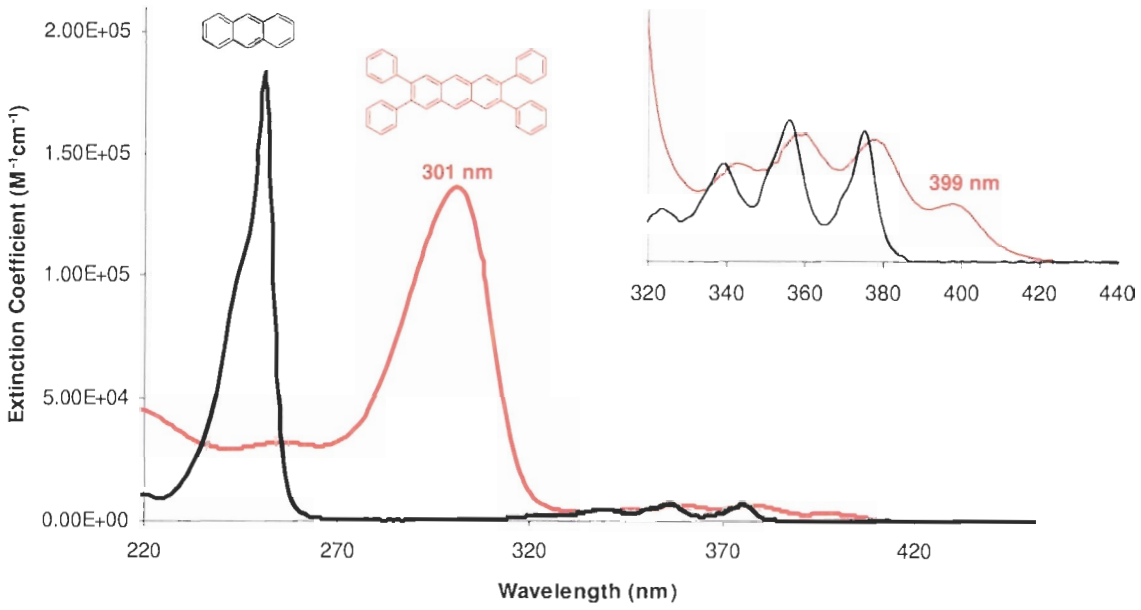


Figure 4.19 UV-visible spectra of **A** and **TPA** recorded in acetonitrile at RT

The greater selectivity for the cyclomer **TPA-A** over dianthracene when light centred at 300 nm was employed most likely resulted from the preferential excitation of **TPA** at these wavelengths (see Figure 4.19). The preference for the cross-cyclomer formation when the 350 nm lamps were used is not as easily explained by selective excitation as both chromophores absorb at this wavelength. Careful examination of the spectral output of the 350 nm lamps (Figure 5.1) in comparison with the absorbance spectra of **TPA** shows that the output of these lamps still overlaps with the large absorbance of **TPA** centred at 300 nm.

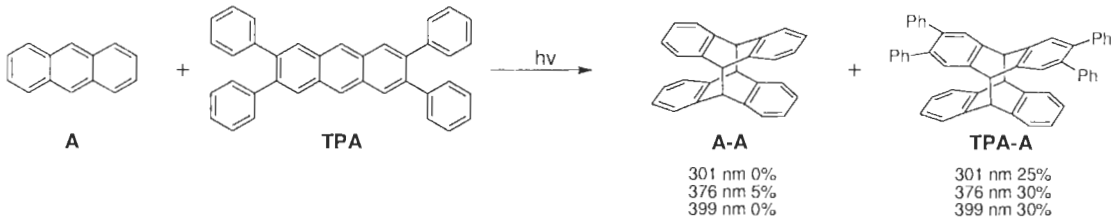
Other factors may also be responsible for the apparent promotion of the **TPA** excited state. For this reason, both the singlet and triplet excited state lifetimes of **TPA** were measured in the laboratory of Cornelia Bohne of the University of Victoria by T. Pace. Measurement of the singlet lifetime of **TPA** showed it to be 7.2 ns in acetonitrile, while the lifetime of anthracene is 5.5 ns (see Section 5.6 for specific experimental details). The longer singlet lifetime of **TPA** may also be partly responsible for the preferential formation of the **TPA-A** cross-cyclomer over dianthracene (especially when irradiated with the 350 nm lamps).

Unfortunately, the lamps employed in these initial experiments deliver light over a relatively broad spectral range (see lamp output spectra in Chapter 5, Figure 5.1), making it difficult to exclusively excite only one chromophore of a binary mixture. In order to explore the effects of selective excitation, it was decided to repeat the experiments described above using a fluorimeter as the light source, enabling irradiation over a much narrower range of wavelengths.

All of the following experiments (those described in Schemes 4.20, 4.22, 4.24, 4.26, and 4.27) were performed in a similar manner. A deuterated chloroform solution of the anthracene derivatives (both at 10 mM) was prepared and transferred into a quartz NMR tube. This solution was then deoxygenated by bubbling N_2 through the solution for ~5 min. Narrow-band irradiation was

obtained by using a fluorimeter as the light source with a 5 nm slit width. Periodic ^{1}H-NMR spectra of the sample mixture were then collected. The sample ratios and yields cited in Schemes 4.20, 4.22, 4.24, 4.26, and 4.27 were measured after 2 hours of irradiation.

Comparison of the absorption spectra of anthracene and **TPA** reveals two distinct regions at which the tetraphenyl **TPA** could be excited without exciting anthracene (Figure 4.19): the region around 300 nm and the bathochromically-shifted S0→S1 anthracene bands around 400 nm.



Scheme 4.20 Selective excitation studies of **TPA** with anthracene

Three solutions of **TPA** and anthracene were prepared; these solutions were irradiated at 301 nm, 376 nm or 399 nm. The sample irradiated at 301 nm exhibited slow formation of a single photoproduct, which was identified as the cross-cyclomer **TPA-A**, while no dianthracene formation was observed. Similar results were found with the sample irradiated at 399 nm; the cross-cyclomer **TPA-A** was formed, with no formation of dianthracene. This is consistent with

expectations, since at these wavelengths only **TPA** should be excited (Figure 4.19). In contrast, irradiation of the third mixture with 376 nm light, a wavelength where both chromophores absorb, causes the formation of both dianthracene (**A-A**) and **TPA-A** in approximately a 1:6 ratio. In addition, trace amounts (< 3%) of **TPA-TPA** were also detected (by ^{1}H-NMR) in the samples excited at 376 and 399 nm, while none of this homodimer was formed when the sample was irradiated at 301 nm.

4.4.2.2 Anthracene and 2,3-Diphenylanthracene Derivatives

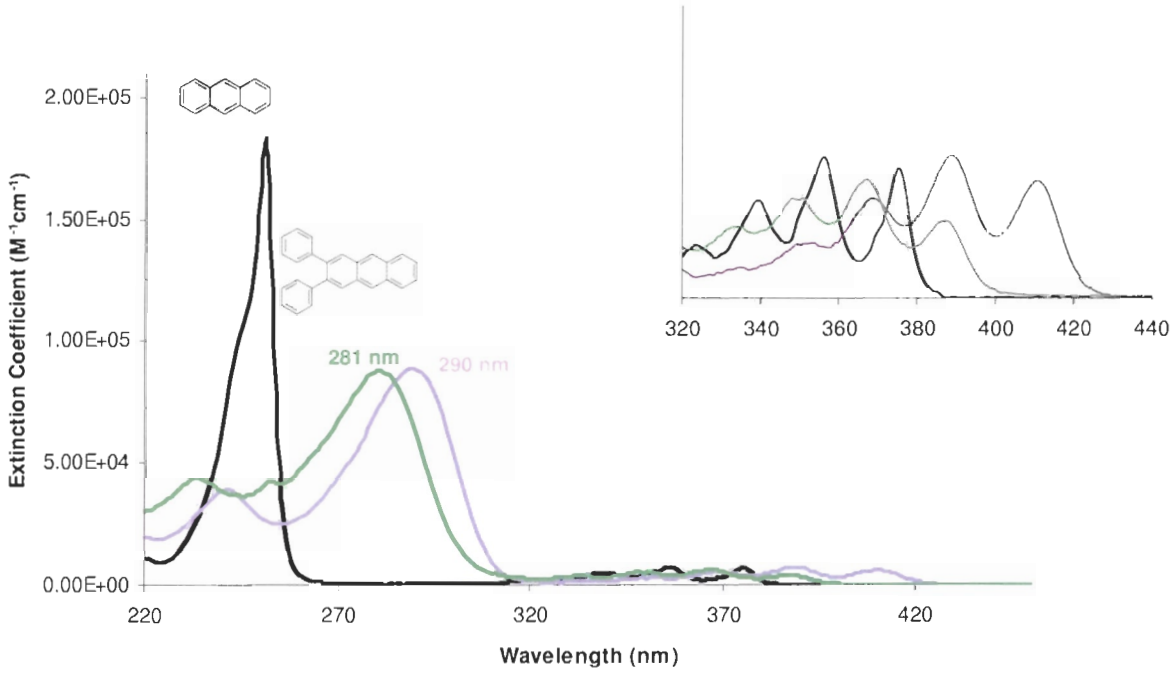
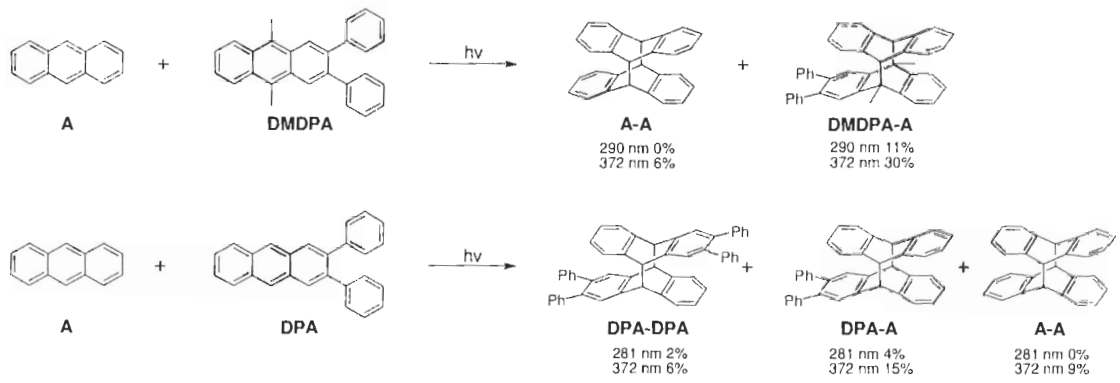


Figure 4.21 Comparison of UV-visible spectra of **DPA**, **DMDPA**, and **A** recorded in acetonitrile at RT

These results demonstrate that the phenyl groups attached to the anthracene core provide enough of a perturbation to the absorption spectrum to allow for selective excitation. Of interest was whether the same strategy could be carried out using analogues that contained fewer pendant phenyl groups. The UV-visible spectra of 2,3-diphenylanthracene **DPA** and 9,10-dimethyl-2,3-diphenylanthracene **DMDPA** are similar to that of **TPA** (Figures 4.19 & 4.21). Both compounds absorb strongly between 270 nm and 300 nm and exhibit a 10-30 nm bathochromic shift in their S0→S1 absorption bands relative to those of anthracene. Accordingly, selective irradiation experiments on mixtures of **DMDPA** and anthracene yield similar results to those carried out with **TPA**. Irradiation at 290 nm, where only **DMDPA** absorbs, led to the exclusive formation of the cross-cyclomer **DMDPA-A**, whereas excitation with 372 nm light yielded **A-A** and the **DMDPA-A** in a 1:5 ratio. The outcome was somewhat more complex when the diphenyl **DPA** and anthracene mixtures were illuminated, since **DPA** is capable of forming its homodimer (Scheme 4.22). Selective excitation of **DPA** with 281 nm light afforded both **DPA-DPA** and **DPA-A** in a 1:2 ratio, while excitation of both chromophores at 372 nm led to the formation of all three possible photoproducts.



Scheme 4.22 Selective excitation studies of **DPA** and **DMDPA** with anthracene

4.4.2.3 Phenyl-Substituted Anthracenes

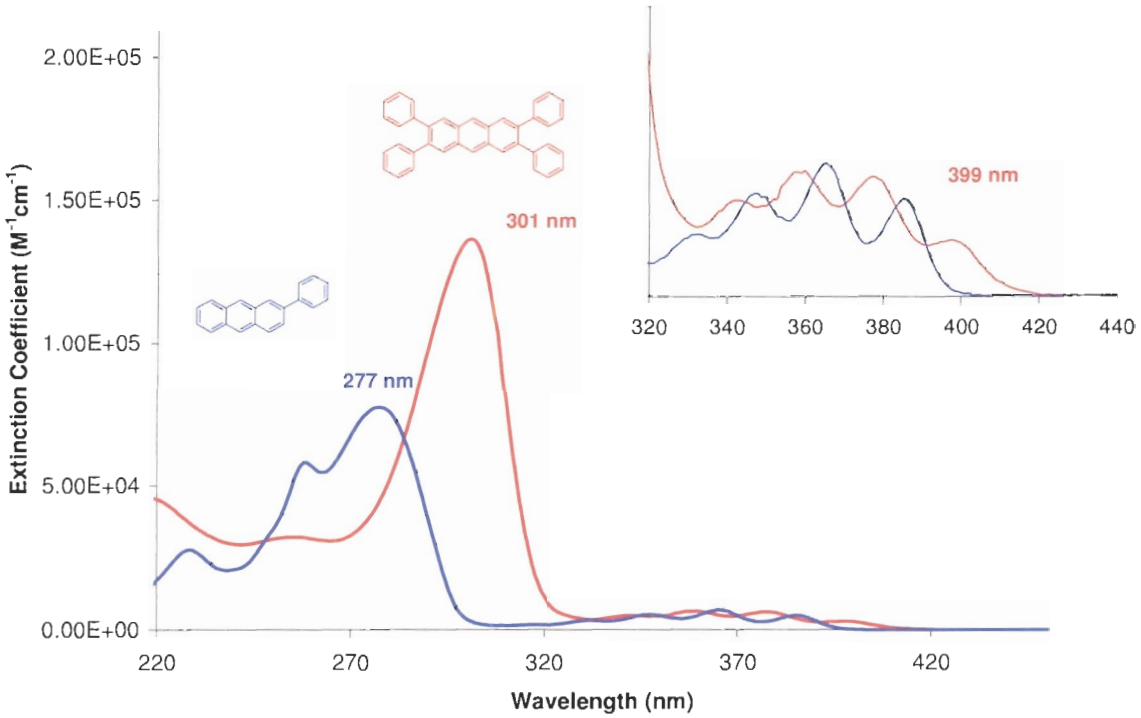
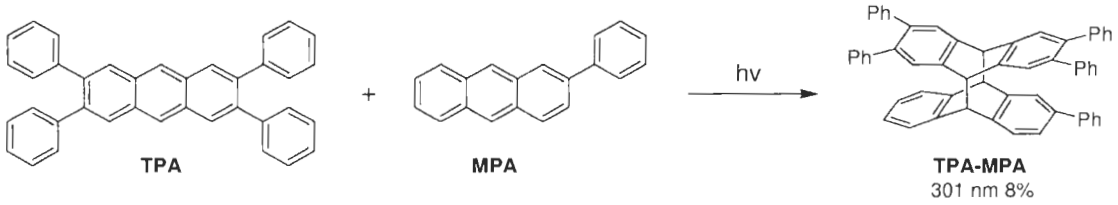


Figure 4.23 Comparison of UV-visible spectra of **TPA** and **MPA** recorded in acetonitrile at RT

All of the previous examples had only one of the two chromophores possessing groups at the periphery. In order to investigate whether it would be possible to achieve the same selectivity using two choromophores both containing pendent phenyl groups, the reaction of **TPA** with 2-phenylanthracene (**MPA**) was examined next. It was found that the absorption band of **TPA** at 301 nm had minimal overlap with the equivalent band of the monophenyl **MPA**,

which was centred at 277 nm (Figure 4.23). Accordingly, irradiation at 301 nm yielded the cross-cyclomer **TPA-MPA** as the only product.



Scheme 4.24 Selective excitation study of **TPA** with a phenyl substituted anthracene **MPA**

4.4.2.4 Anthracene and 9,10-Disubstituted Anthracenes

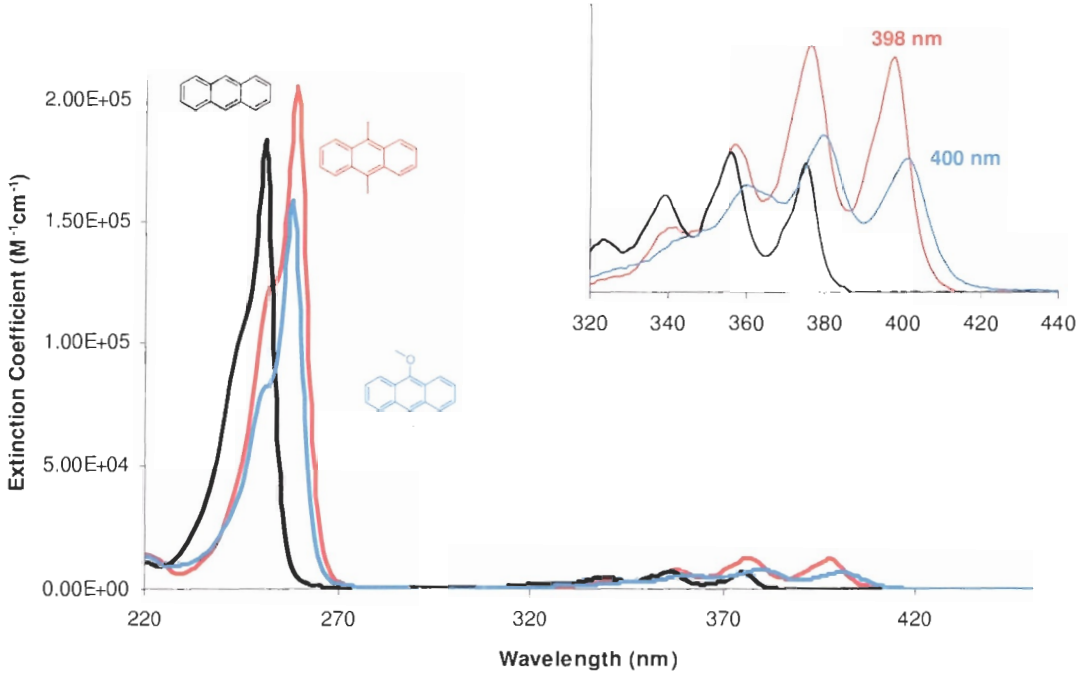
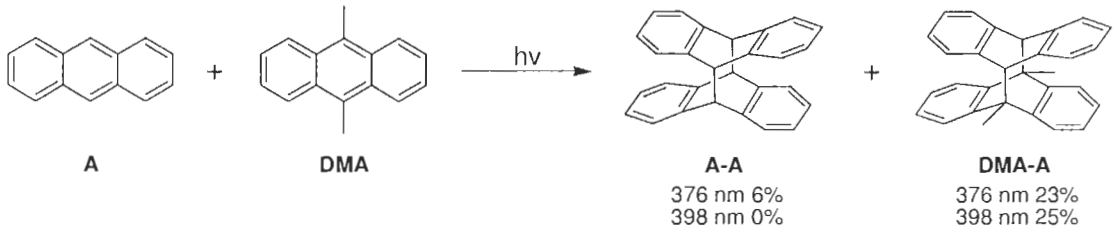


Figure 4.25 Comparison of UV-visible spectra of **DMA** and **DMeOA** with **A** recorded in acetonitrile at RT

Using selective irradiation to restrict the outcome to the creation of cross-cyclomers is not limited to phenyl-substituted anthracenes. The UV-visible absorption spectrum of 9,10-dimethylanthracene is similar to that of anthracene, but with peaks that are red-shifted by approximately 20 nm relative to those of the latter. It should therefore be possible to selectively excite **DMA** in the presence of anthracene. Indeed, irradiation of a mixture of **DMA** and anthracene at 398 nm led to the formation a single observed photoproduct that was identified as **DMA-A**. When this mixture was irradiated at 376 nm, both dianthracene and the mixed cyclomer were formed, as expected.

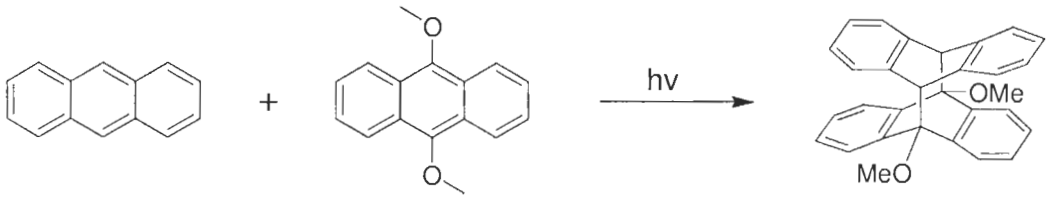


Scheme 4.26 Selective excitation of a centrally substituted anthracene **DMA**

The same outcome is observed over a range of concentrations, although, as expected, the reaction is much slower in dilute solution than in more concentrated samples. For example, when both chromophores were present at initial concentrations of 4 mM, only about 30% of **DMA** was consumed after 2

hours, while approximately 80% of this starting material had reacted after the same period from a solution containing 10 mM of each reagent.

In the examples described above, the initial concentrations of both chromophores were equal. In order to determine whether the same selectivity would be observed if one of the two chromophores was present in large excess, a solution containing 4 mM **DMA** and 11 mM anthracene was irradiated with 398 nm light. During the initial stages of this experiment, the cross-cyclomer was formed as the exclusive product. Despite the low concentration of **DMA**, its conversion to **DMA-A** was complete in less than 2 hours, presumably due to the large excess of anthracene available for reaction. Only after **DMA** had been completely consumed was dianthracene observed to slowly form in trace quantities.



A + **DMeOA** → **DMeOA-A**

400 nm 18%

Scheme 4.27 Selective excitation study of an anthracene with alkoxy substituents

This strategy can also be extended to other substituted derivatives, such as 9,10-dimethoxyanthracene, which does not homodimerise, yet is known to form cross-cyclomers with anthracene.[3] Selective excitation of this chromophore with 400 nm light in the presence of anthracene led to the formation of the cross-cyclomer; again, no dianthracene was observed.

4.5 Thermally Induced Reversibility

While all the dimers presented in the previous Sections (4.3 and 4.4) were relatively stable, allowing them to be purified and handled without any special precautions, it is known that dianthracenes can be reverted to their monomers through heating.[3] Studies of this phenomenon were carried out primarily on the cyclomer **TPA-DMA**. Compound **TPA-DMA** was found to possess considerable stability at low temperatures; indeed, no decomposition was observed at temperatures below 100°C.

The study of the thermal reversion of this compound was performed more thoroughly by ^{1}H-NMR spectroscopy (Figure 4.28). Dissolving this compound in deuterated DMSO made it possible to both record NMR spectra and heat the sample *in situ*.

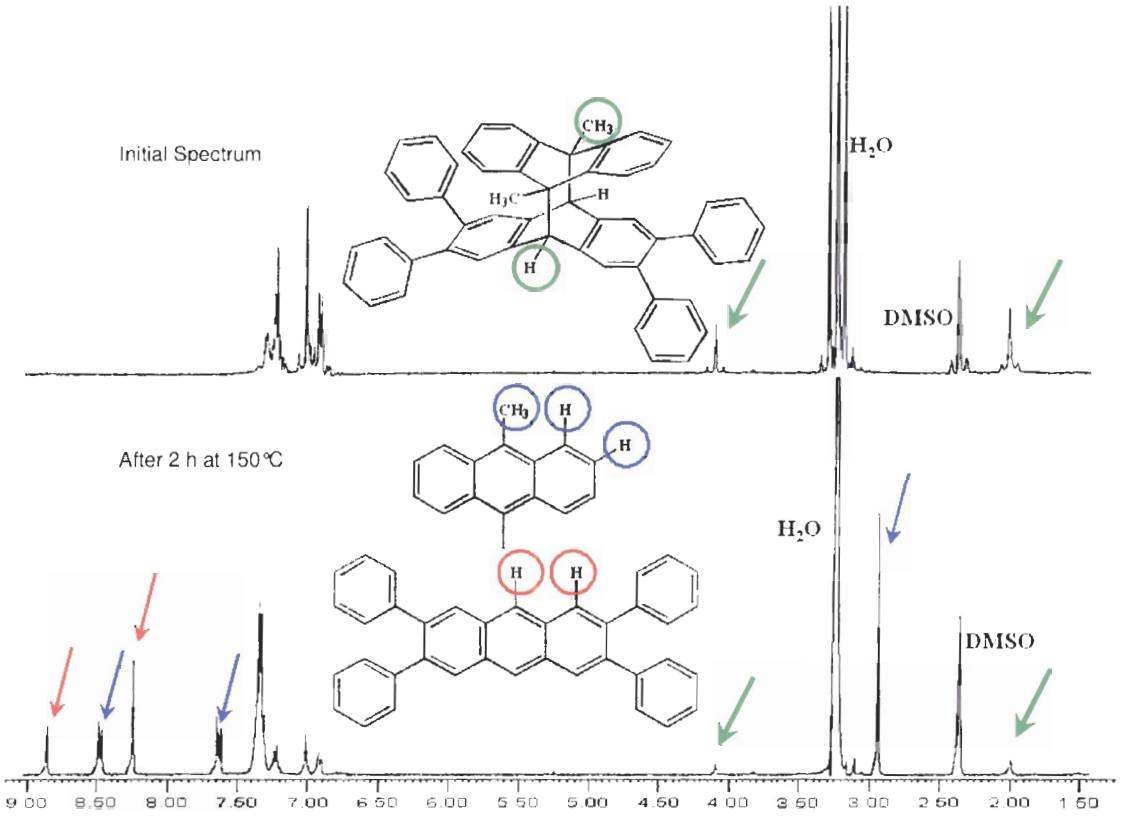


Figure 4.28 ^{1}H-NMR spectra of the thermally-induced reversion of the dimer **TPA-DMA** to its component monomers (spectra recorded in deuterated DMSO at RT)

After heating a sample of **TPA-DMA** at 135°C for 15.5 h, only 15% of the dimer had been converted to the monomers **DMA** and **TPA**. Increasing the temperature to 150°C greatly accelerates the rate of decomposition and approximately 50% of **TPA-DMA** is consumed after 70 min. This reaction was 93% complete after 150 min at this temperature. The reversion proceeds cleanly, with only the two monomers being reformed without any unwanted side products appearing (Figure 4.28). This suggests that the cyclomer formation and

its reversion to monomers could be cycled without losing fidelity. This rate of fragmentation is similar to that of the head-to-tail dimer of 9-methylanthracene, which also has two methyl groups at the bridgehead positions.[128] This suggests the presence of the peripheral phenyl groups does not destabilise the photodimer. The slow decomposition of this compound at low temperatures indicates that dimers of this type could be used to construct relatively robust structures.

4.6 Photochemical Reversibility

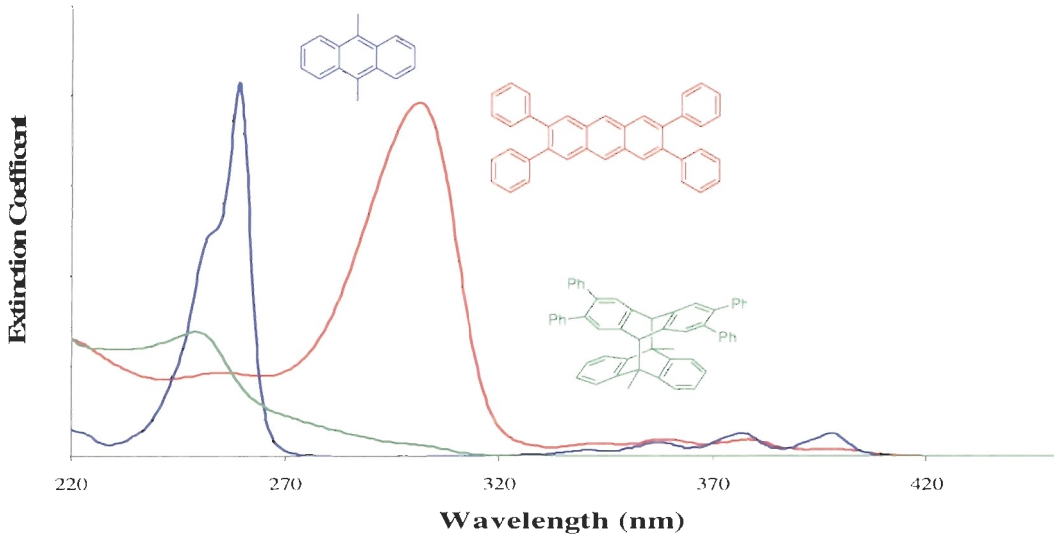


Figure 4.29 UV-visible spectra of **DMA**, **TPA** and their cross-cyclomer (**TPA-DMA**)

As is typical for dianthracenes, the UV–visible absorption spectrum of **TPA-DMA** is blue-shifted relative to both monomers **DMA** and **TPA** with a λ_{max} of 252 nm. This hypsochromic shift is typical anytime conjugation through a π-system is truncated.

In order to study the photoreversion of the **TPA-DMA** dimer, a sample was dissolved in spectral-grade acetonitrile and irradiated with 252 nm light in a fluorimeter. This process was monitored by UV-visible spectroscopy, specifically, through observation of the characteristic S0→S1 anthracene peaks of the two monomers (**TPA** and **DMA**). These absorbances became progressively more intense with longer exposure times (Figure 4.30), and photoreversion was 56% complete after 90 min.

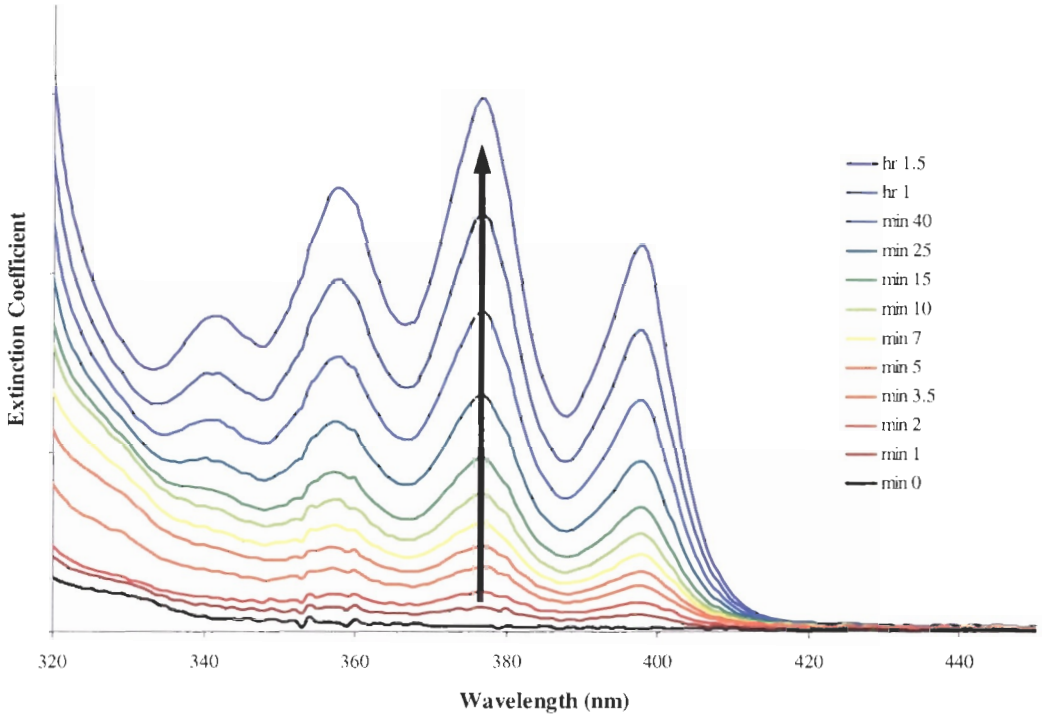


Figure 4.30 Reversion of dimer **TPA-DMA** through short wavelength irradiation recorded in acetonitrile at RT

4.7 Formation of Endoperoxides

Endoperoxide formation did not pose any significant problems in the majority of the studies. However, in some instances it was observed in reactions involving the 9,10-disubstituted **DMA**, **DBA** and **DMeOA** derivatives. Some unidentified degradation products observed during the heating of the **DBA-TPA** cross-cyclomer may also have been due to endoperoxides.

4.8 Conclusions

The highly substituted anthraquinones created in Chapters 2 and 3 were converted to anthracenes following two general strategies: either direct reduction to the anthracene equivalent or through a reductive addition to the anthraquinone to create a centrally-substituted anthracene. Both of these methods gave acceptable yields, providing all of the anthracene structures required.

The photochemistry of these anthracene derivatives were then investigated using both broad-band and selective irradiation. Two methods of enforcing selectivity in these reactions were described. The first method relied on the steric demands of both chromophores in a binary mixture. The second approach required only one of the species to be inactive towards homodimerisation, relying instead on selectively exciting only this one chromophore of the two chromophores in the binary mixture.

Both of these methods demonstrated a selectivity in their reactivity that had not been previously shown. While only one of the cross-cyclomers was shown to be reversible through both thermal and photochemical means, it is reasonable that the reversion of all of the cyclomers to their monomeric components should be possible. Preliminary studies into the stability of these

compounds showed them to be sufficiently stable to be useful in the production of robust functional materials.

The 'steric-controlled' approach relied on the steric bulk of the anthracene pairs being orthogonal to one-another. The steric demands of these anthracenes were designed to prevent any self-association while allowing differing anthracene structures to approach with limited hindrance. By this method, 5 pairs of anthracene derivatives (**TPA** paired with **DMA, DMDPA**, **TMA**, **DBA**, and **DMeOA**) were found to form cross-cyclomers without any homodimerisation.

The 'selective-excitation' strategy relied on two key features of the molecule being excited: a) it must absorb in a range where the other chromophore does not, and b) it must be relatively inert towards homodimer formation. Initial studies indicated that this strategy is fairly general, and works either when the excitation wavelength is blue- or red-shifted relative to S0→S1 absorption bands of anthracene. These perturbations in the absorption spectra may be caused by a variety of peripherally or centrally located substituents. The added flexibility provided by this strategy should facilitate the design of modular reversible materials whose structures can be altered using light. Moreover this method enables the preparation of even more thermally robust

cyclomers such as **TPA-A**, which lacks functional groups at the 9,10-positions that are known to destabilise dianthracenes.

4.9 Future Work

It has been demonstrated that substituted anthracenes can be designed to react in a controlled manner during irradiation. These systems were designed for eventual use in the production of functional materials. The next step should be to create functional materials based on these systems. Incorporation into polymer synthesis could allow production of reversible AB diblock co-polymers, for example. Of course, the ability to reversibly bring together two molecules in a controlled selective manner could be applied in any number of ways.

In terms of more immediate studies, further research into both the cyclomer formation and their reversibility should be undertaken, especially in terms of extending the variety of anthracene substitution patterns. Chapters 2 and 3 described the production of many anthraquinones that have not yet been reduced to their equivalent anthracenes, yet could have many interesting features. In particular the mono-anisole **50** and the naphthyl derivative **43** may prove interesting. The mono-anisole **50** was designed to allow for incorporation into polymer networks and functional materials. The naphthyl derivative **43**

might have interesting photochemistry, especially the possibility that the pendant naphthyl groups may undergo alternate photochemical reactions.

Another interesting avenue may be to explore whether the selective excitation of these chromophores can be extended to include using 2-photon absorption as the method of excitation. 2-Photon irradiation may allow additional wavelengths to be used to excite these chromophores. This may prove useful by allowing the anthracene derivative of interest to be excited at wavelengths at which neither anthracene derivatives nor other molecules absorb, resulting in a more efficient and cleaner reaction. It may be possible to find two or more anthracene derivatives that have very similar UV-visible absorbance profiles that do not allow the application of the 'selective excitation' approach yet have different 2-photon absorbance cross-sections. A system such as this would still allow 'selective excitation' of chromophores even though they possess identical UV-visible spectra.

CHAPTER 5: EXPERIMENTAL

This chapter describes the methods used in the synthesis, purification and characterisation of the compounds discussed in this thesis.

5.1 Materials and Methods

NMR characterisation of products were confirmed using either a Bruker AMX-400 400 MHz spectrometer (400 MHz ^{1}H and 100 MHz ^{13}C) or a Varian Unity Inova 500 MHz spectrometer equipped with a 5 mm inverse detection probe (500 MHz ^{1}H and 125 ^{13}C MHz). Infrared spectra were recorded with a Thermo Nicolet Nexus 670 FT-IR E.S.P. spectrometer; samples were prepared as compressed KBr pellets. Microanalyses (C, H, N) were performed at Simon Fraser University by Mr. Miki Yang. Low Resolution Mass Spectrometry was performed on a Hewlett Packard 5985 mass spectrometer (EI 70 eV). Secondary Ion Mass Spectrometry (HRMS(LSIMS)) and FAB(LSIMS) were performed on a Kratos Concept H double focussing mass spectrometer using *m*-nitryl benzyl alcohol as a matrix and polyethylene glycol as a calibrant. MALDI-TOF mass spectra were carried out using a Perspective Voyager-DE STR from PE Applied Biosystems with a nitrogen laser (337 nm) and using 2,5-dihydroxybenzoic acid

as the matrix. Melting Points were determined either on a Fisher Johns Melting Point Apparatus or utilising an Olympus BX50 polarising microscope with a Linkam 94 heating stage and are uncorrected. Fluorimetry was performed on a PTI C60 Photon Counting Spectrofluorimeter. UV-visible spectrometry was performed on a Cary 100 UV-Vis Spectrophotometer.

All chemicals except those noted below were used as provided from the supplier. The *p*-benzoquinone and 1,4-napthoquinone were sublimed prior to use. Tetrahydrofuran and diethyl ether were dried over sodium using benzophenone as an indicator, under an inert atmosphere of nitrogen gas. Diisopropylamine was dried over magnesium sulphate, and distilled at a reduced pressure. Benzaldehyde was distilled at a reduced pressure. When used in Suzuki reactions, H_2O and DME were deoxygenated before use through a minimum of 3 freeze-pump-thaw cycles.

5.2 Syntheses Reported in Chapter 2

5.2.1 Sulfone Construction

2,3,4,5-tetrabromothiophene (16)

30 mL (378 mmol) of thiophene was diluted in 75 mL of acetic acid and 75 mL (1.5 mol) of Br_2 was then added. This solution was then heated at reflux for 16 h at which time another portion of 25 mL (500 mmol) of Br_2 was added and the solution was again heated at reflux for another 20 h. After this combined period of 36 h the solution was allowed to cool to room temperature. Upon cooling, the solid 2,3,4,5-tetrabromothiophene crystalised out of solution. The product was collected by filtration and washed with copious amounts of water to yield 134 g (351 mmol, 93%) of slightly rust coloured crystalline flakes.

MS: (EI) M^+ 400 (100%), 402 (63%), 398 (63%), 404 (18%), 396 (17%), $(M\text{-}Br)^+$ 321 (39%), 319 (37%), 323 (14%), $(M\text{-}2Br)^+$ 240 (34%), 242 (18%), 238 (18%), $(M\text{-}3Br)^+$ 161 (32%), 160 (6%), 162 (4%), $(M\text{-}4Br)^+$ 80 (61%), Br^+ 81 (40%), 79 (35%)

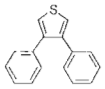
3,4-dibromothiophene (17)

92 g of zinc was added to a rapidly stirred mixture of 200 mL H_2O and 125 mL acetic acid, this suspension was then brought to reflux; 115 g (298

mmol) of 2,3,4,5-tetrabromothiophene was then carefully added. After heating for 30 minutes, the suspension was cooled and the organic (thiophenes) and aqueous (water and acetic acid) layers were separated. The organic solution contained a mixture of the desired 3,4-dibromothiophene and 3-bromothiophene, which were separated by vacuum distillation using a vacuum pump, dry acetone cooled collecting bath and low heat (~35°C) to yield 28.2 g of pure 3,4-dibromothiophene (117 mmol, 39%) as a clear odorous liquid.

^{1}H-NMR: (ppm) (D_6-acetone) 7.74 s [129]; MS: (EI) M^+ 242 (100%), 244 (51%), 240 (56%)

3,4-diphenylthiophene (18)



In a Schlenk flask 6 g (2.7 mL, 24.8 mmol) of 3,4-dibromothiophene, 7.6 g (62 mmol) of phenylboronic acid, and 25 g (202 mmol) of Na_2CO_3 were mixed and placed under nitrogen. To this mixture 20 mL of 1,2-dimethoxyethane and 60 mL of H_2O (both degassed through a minimum of three freeze-pump-thaw cycles) were added *via* a syringe, 140 mg (0.12 mmol) of $Pd(P(Ph)_3)_4$ was also added, this final mixture was then sealed and heated at 75°C under an N_2 atmosphere for 160 h. Upon completion of heating, the solution was cooled and the organic and aqueous layers were separated. The

aqueous layer was then extracted with diethyl ether (3 X 75 mL). These organic layers were then combined, dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude solid was then recrystallised from ethanol yielding the desired product as off-white flakes in 85% (5.0 g) yield.

^{1}H-NMR: (ppm) ($CDCl_3$) 7.32 s (2H), 7.24-7.26 m (s6H), 7.18-7.21 m (4H); MS: (EI) M^+ 236 (100%), 235 (70%), 234 (29%), 237 (19%); mp: 114-115°C, lit. 113.5 –114°C[130]

3,4-diphenylthiophene-1,1-dioxide (14) and 3,4-dibromothiophene-1,1-dioxide (15)

Hydrogen Peroxide and Trifluoroacetic Anhydride Method

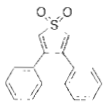
The preparation of both disubstituted thiophene dioxides **14** and **15** was carried out as follows. To dry Schlenck glassware, 10 mL of 30% hydrogen peroxide was added. The solution was cooled to -10°C; to this 25 mL of trifluoroacetic anhydride was slowly added. The 3,4-disubstitutedthiophene was then added (2.5 g, 10 mmol) this solution was allowed to warm to room temperature and stirred for 3.5 h. The acidic mixture was carefully neutralised to pH ~6 with judicious addition of a saturated $NaHCO_3$ solution (usually about

120 mL). The organic and aqueous layers were separated, the aqueous layer was then extracted with CH_2Cl_2 (3 X 50 mL). The combined organic layers were then dried over $MgSO_4$ and the solvent removed *in vacuo*. The resulting flaky solid was recovered in yields ranging from 32 – 70% in the case of the dibromo variant and 50 – 91% in the case of the diphenyl.

Dimethyldioxirane Method

Either 3,4-disubstituted thiophene (250 mg, 1 mmol) was dissolved in a minimum of CH_2Cl_2 (approximately 2 mL), this solution was then added to a freshly distilled dimethyldioxirane solution and allowed to react for 30 min. After this period the solvent was removed *in vacuo* yielding 71% of either 3,4-disubstitutedthiophene-1,1-dioxide of sufficient purity to be used in further reactions.

3,4-diphenylthiophene-1,1-dioxide (14)



Pale orange crystalline solid.

^{1}H-NMR: (ppm) ($CDCl_3$): 6.63 s (2H), 7.27–7.30 m (3H), 7.36–7.40 m (3H), 7.04 –7.06 m (4H); MS: (EI) M^+ 268 (100%), 269 (20%); mp: 162 - 164°C, lit. 171.5 – 172.5°C[131]

3,4-dibromothiophene-1,1-dioxide (15)

 Orange crystalline solid

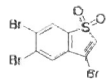
^{1}H-NMR: (ppm) ($CDCl_3$) 6.96 s; MS: (CI) 277.2 (52%), 275.3 (100%), 273.1 (50%); mp: 102-104°C, lit. 104-106°C [87]

dimethyldioxirane

 Dimethyldioxirane was produced following a modified version of the procedure of Murray[132]. In a 2-neck 2 litre round bottom flask fitted with a condenser, down tube, and collecting funnel, 52 mL of acetone, 80 mL of H_2O and 48 g of $NaHCO_3$ were added. Over a 10 min period 100 g of Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was carefully added, after this addition the system was evacuated (water aspirator). The distillate was collected in a flask maintained at -78°C by a dry-ice/acetone bath. The distillate contained ~50-65 mL of a ~0.06-0.1 M dimethyldioxirane solution.

Slightly yellow solution with a distinctive bitter smell. ^{1}H-NMR: (ppm) (D_6-acetone) 1.65 s (consistent with Murray[132])

3,5,6-tribromobenzo[*b*]thiophene-1,1-dioxide (22)



To 20 mL of acetic acid 107 mg (0.39 mmoL) of **15** was added. This solution was heated at reflux for 48 h. The solution was then cooled and poured into H_2O (100 mL) and extracted with CH_2Cl_2 (75 mL), the organic portion was then further washed with H_2O (3 X 75 mL). The product was then purified *via* silica gel chromatography, eluting with 80% CH_2Cl_2 and 20% hexanes, yielding 33 mg (0.16 mmoL, 84%) of the desired product

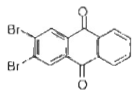
Orange crystalline solid. ^{1}H-NMR: (ppm) ($CDCl_3$) 7.99 s (1H), 7.80 s (1H), 7.00 s (1H); MS: (CI) $(M+H)^+$ 405 (100%), 403 (97%), 407 (35%)

5.2.2 Preparation of Naphtho- and Anthraquinones

In a typical procedure the sulfone (100 mg, 0.37 mmol) and benzoquinone (80 mg, 0.74 mmol) or naphthoquinone (115 mg, 0.74 mmol) were dissolved in 20 mL acetic acid and the solution was heated at reflux for 48 h. The solution was then cooled and poured into H_2O (100 mL) and extracted with CH_2Cl_2 (75 mL), the organic portion was then further washed with H_2O (3 X 75 mL). The products were then separated *via* silica gel chromatography, analytical samples were further recrystallised from an appropriate solvent.

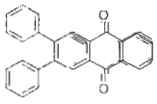
Some of the studies discussed in Chapter 2 examined the effects of varying the ratios of reactants and changes in solvent, specifically from acetic acid to toluene. However, in preparing compounds for analyisis, the synthesis, work-up, and purification followed procedures that were not significantly altered from that described above.

2,3-dibromoanthraquinone (20)



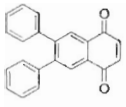
Pale Grey Solid; ^{1}H-NMR: (ppm) ($CDCl_3$) 8.51 s (2H), 8.31-8.41 dd (3.36 Hz, 5.80 Hz) (4H), 7.81-7.88 dd (3.36 Hz, 5.80 Hz) (4H); ^{13}C-NMR: solubility of compound too low to obtain; FT-IR: (cm^{-1}) 1678 C=O stretch; MS: (CI) $(M+H)^+$ 367 (100%), 365 (57%), 369 (53%); mp: 279-280°C, Lit. 279-281°C[133]; chromatography eluent 1:1 hexanes:CH_2Cl_2, recrystallised from EtOH

2,3-diphenylanthraquinone (21)



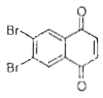
Yellow Solid; ^{1}H-NMR: (ppm) ($CDCl_3$) 8.36 s (2H), 8.34 dd (3.36 Hz, 5.80 Hz) (2H), 7.80-7.84 dd (3.36 Hz, 5.80 Hz) (2H), 7.20-7.30 m (10H); ^{13}C-NMR: (ppm) ($CDCl_3$) 183.0, 146.4, 139.6, 134.1, 132.2, 129.7, 128.3, 127.7, 127.3; FT-IR: (cm^{-1}) 1676 C=O stretch; MS: (EI) M^+ 360; mp: 203-206°C, Lit. 211-212°C[134]; chromatography eluent toluene, recrystallised from EtOH

6,7-diphenylnaphthoquinone (23)



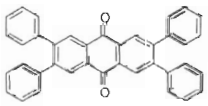
Yellow Solid; ^{1}H-NMR: (ppm) (CD_2Cl_2) 8.11 s (2H), 7.17-7.29 m (10H), 7.00 s (2H); ^{13}C-NMR: (ppm) ($CDCl_3$) 184.9, 146.2, 139.5, 138.8, 130.6, 129.6 128.8, 128.2, 127.7; FT-IR: (cm^{-1}) 1668 C=O stretch; MS: (EI) M^+ 310; HRMS: Calcd. 310.0994, found: 310.0996; mp: 123-125°C; chromatography eluent toluene, recrystallised from EtOH

6,7-dibromonaphthoquinone (24)



Pale Grey Solid; ^{1}H-NMR: (ppm) ($CDCl_3$) 8.29 s (2H), 6.99 s (2H); ^{13}C-NMR: (ppm) ($CDCl_3$) 183.2, 138.6, 132.0, 131.7, 131.0; FT-IR: (cm^{-1}) 1655 C=O stretch; MS: (CI) $(M+H)^+$ 317 (100%), 315 (51%), 319 (47%) mp: 171-173°C, Lit. 171-172°C[135]; chromatography eluent 1:1 hexanes:CH_2Cl_2, recrystallised from EtOH

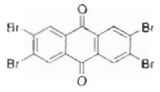
2,3,6,7-tetraphenylanthraquinone (25)



Yellow Solid; ^{1}H-NMR: (ppm) (D_6-acetone) 8.39 s (4H), 7.22-7.29 m (20H); ^{13}C-NMR: (ppm) ($CDCl_3$) 182.8, 146.4, 139.6, 132.4, 129.7, 128.2, 127.7; FT-IR: (cm^{-1}) 1672 C=O stretch; MS: (EI) M^+ 512; HRMS: calcd.

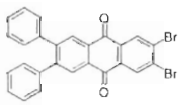
512.1776, found: 512.1774; mp: 323-324°C; chromatography eluent toluene, recrystallised from EtOH

2,3,6,7-tetrabromoanthraquinone (26)



Pale Grey Solid; ^{1}H-NMR: (ppm)($CDCl_3$) 8.50 s (4H); ^{13}C-NMR: solubility of compound too low to obtain; FT-IR: 1670 C=O stretch; MS: (CI) $(M+H)^+$ 525 (100%), 523 (77%), 527 (70%), 526 (18%), 529 (17%); EA: Calcd. for $C_{14}H_4Br_4O_2$ C 32.10% H 0.77% Found C 32.04% H 0.81%; mp: >350°C, Lit. 387-390°C [136]; recrystallised from acetone then toluene; no chromatography was performed on this compound due to its extremely poor solubility.

2,3-dibromo-6,7-diphenylanthraquinone (27)

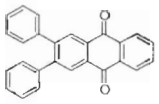


Yellow Solid; ^{1}H-NMR: (ppm) (CD_2Cl_2) 8.55 s (2H), 8.33 s (2H), 7.21-7.30 m (10H); ^{13}C-NMR: due to low solubility could not be obtained; FT-IR: (cm^{-1}) 1676, C=O stretch; MS: (EI) M^+ 518 (100%), 517 (51%), 519 (49%); HRMS: calcd. 515.9361, found 515.9364; EA: Calcd. for $C_{26}H_{42}Br_2O_2$ C 60.26% H 2.72% Found C 59.90% H 2.79%; mp: 280°C decomp.; chromatography eluent 1:1 hexanes:toluene, recrystallised from EtOH

5.3 Syntheses found in Chapter 3

5.3.1 Preparation of Naphtho- and Anthraquinones

2,3-diphenylanthraquinone (21)



To a solution of naphthoquinone (814 mg, 5.2 mmol) in 130 mL acetic acid was added 644 mg (2.6 mmol) 4-hydroxy-3,4-diphenylcyclopent-2-enone and 90 mg (0.52 mmol) *p*-toluenesulfonic acid. This mixture was then heated at reflux for 39 h. The resultant solution was cooled to room temperature, poured into water (150 mL) and then extracted with CH_2Cl_2 (3 x 100 mL). The organic portion was dried over $MgSO_4$ and the solvent then removed *in vacuo*. This mixture of products was then purified through silica gel chromatography eluting with toluene to yield 390 mg (1.1 mmol, 42%) of the desired product 2,3-diphenylanthraquinone. Further recrystallisation from ethanol provided for an analytically pure sample.

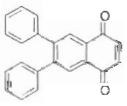
Yellow Solid; ^{1}H-NMR: (ppm) ($CDCl_3$) 8.36 s (2H), 8.35 dd (3.36 Hz, 5.80 Hz) (2H), 7.82 dd (3.36 Hz, 5.80 Hz) (2H), 7.20-7.30 m (10H); ^{13}C-NMR: (ppm) ($CDCl_3$) 183.0, 146.4, 139.6, 134.1, 132.2, 129.7, 128.3, 127.7, 127.3; FT-IR: (cm^{-1}) 1676 C=O stretch; MS: (EI) M^+ 360; mp: 203-206°C, Lit. 211-212°C [65]

6,7-diphenylnaphthoquinone (23) and

2,3,6,7-tetraphenylanthraquinone (25)

To a solution of 1,4-benzoquinone (713 mg, 6.6 mmol) in 180 mL acetic acid was added 836 mg (3.3 mmol) 4-hydroxy-3,4-diphenylcyclopent-2-enone and 65 mg (0.38 mmol) *p*-toluenesulfonic acid. This mixture was then heated at reflux for 49 h. The resultant solution was cooled to room temperature, poured into water (150 mL) and then extracted with CH_2Cl_2 (3 x 100 mL). The organic portion was dried over $MgSO_4$ and the solvent then removed *in vacuo*. This mixture of products was then purified through silica gel chromatography eluting with toluene. The early fractions contained 2,3,6,7-tetraphenylanthraquinone and the later 6,7-diphenylnaphthoquinone **23**. This yielded 220 mg (0.46 mmol, 28%) of 2,3,6,7-tetraphenylanthraquinone **25**, and 150 mg (0.48 mmol, 15%) of 6,7-diphenylnaphthoquinone. Further recrystallisation from ethanol provided analytically pure samples.

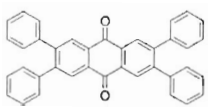
6,7-diphenylnaphthoquinone (23)



Yellow Solid; ^{1}H-NMR: (ppm) (CD_2Cl_2) 8.11 s (2H), 7.17-7.29 m (10H), 7.00 s (2H); ^{13}C-NMR: (ppm) ($CDCl_3$) 184.9, 146.2, 139.5, 138.8,

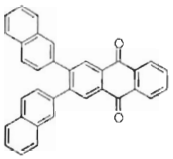
130.6, 129.6 128.8, 128.2, 127.7; FT-IR: (cm^{-1}) 1668 C=O stretch; MS: (EI) M+ 310; HRMS: Calcd. for $C_{22}H_{14}O_2$ 310.0994, found: 310.0996; mp: 123-125°C.

2,3,6,7-tetraphenylanthraquinone (25)



Yellow Solid; ^{1}H-NMR: (ppm) (D_6-acetone) 8.39 s (4H), 7.22-7.29 m (20H); ^{13}C-NMR: (ppm) ($CDCl_3$) 182.8, 146.4, 139.6, 132.4, 129.7, 128.2, 127.7; FT-IR: (cm^{-1}) 1672 C=O stretch; MS: (EI) M^+ 512; HRMS: calcd. for $C_{38}H_{24}O_2$ 512.1776, found: 512.1774; mp: 323-324°C.

2,3-di(naphthalen-2-yl)anthraquinone (43)

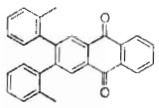


To a solution of naphthoquinone (200 mg, 1.3 mmol) in 20 mL acetic acid was added 220 mg (0.65 mmol) 1,2-di(naphthalen-2-yl)ethane-1,2-dione and 25 mg (0.14 mmol) *p*-toluenesulfonic acid, was then reacted according to the method described above. The resulting mixture of products was then purified through silica gel chromatography eluting with hexanes:toluene (1:1). This yielded 55 mg (0.12 mmol, 18%) of the desired

product 2,3-di(naphthalen-2-yl)anthracene-9,10-dione, further recrystallisation from ethanol afforded an analytically pure sample.

^{1}H-NMR: (ppm) ($CDCl_3$) 8.53 s (2H), 8.38 dd (2H, J=3.3 Hz, J=5.8 Hz), 7.96 s (2H), 7.85 dd (2H, J=3.3 Hz, J=5.8 Hz), 7.81 dd (2H, J=3.4 Hz, J=6.0 Hz), 7.76 dd (2H, J=3.4 Hz, J=6.0 Hz), 7.59 d(2H, J=8.6 Hz), 7.48 dd (4H, J=3.2 Hz, J=6.2 Hz), 7.17 dd (4H, J=1.7 Hz, J=8.5 Hz) ^{13}C-NMR: (ppm) ($CDCl_3$) 183.0, 146.4, 137.3, 134.2, 133.8, 133.3, 132.6, 132.4, 130.1, 128.9, 128.3, 127.7, 127.4, 127.3, 126.5, 126.3; MS (MALDI-TOF) $(M+2H)^+$ 462 (100%); EA calcd. for: $C_{34}H_{20}O_2$ C 88.67 H 4.38 found: C 88.51 H 4.58; mp: 238°C

2,3-di*o*-tolylanthraquinone (44)

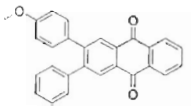


To a solution of naphthoquinone (440 mg, 2.8 mmol) in 30 mL acetic acid was added 400 mg (1.4 mmol) 1,2-dio-tolylethane-1,2-dione and 35 mg (0.20 mmol) *p*-toluenesulfonic acid; this mixture was then reacted according to the method described above. The resulting mixture of products was then purified through silica gel chromatography eluting with toluene. This yielded 90 mg (0.23 mmol, 17%) of the desired product 2,3-di*o*-tolylanthracene-

9,10-dione, further recrystallisation from ethanol afforded an analytically pure sample.

^{1}H-NMR: (ppm) ($CDCl_3$) 8.34 dd (2H, J=3.3 Hz, J=5.7 Hz), 8.28 s (2H), 7.82 dd (2H, J=3.3 Hz, J=5.7 Hz), 7.13 s (4H), 7.03 broad s & 6.91 broad s (combined 4H), 2.11 s (6H); ^{13}C-NMR: (ppm) ($CDCl_3$) 183.1, 147.3(broad), 139.1(broad), 135.3, 134.1, 133.8, 131.9, 130.2, 129.8, 127.8, 127.2, 125.2, 20.2(broad); MS: (EI) M^+ 388 (100%) EA calcd. for: $C_{28}H_{20}O_2$ C 86.57 H 5.19 found: C86.38 H 5.27; mp: 247°C

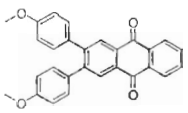
2-(4-methoxyphenyl)-3-phenylanthraquinone (45)



To a solution of naphthoquinone (380 mg, 2.4 mmol) in 20 mL acetic acid was added 336 mg (1.2 mmol) 4-hydroxy-(3 and 4)-(4-methoxyphenyl)-3-phenylcyclopent-2-enone and 50 mg (0.29 mmol) p-toluenesulfonic acid; this mixture was then reacted according to the method described above. The resulting mixture of products was then purified through silica gel chromatography eluting with toluene. This yielded 87 mg (0.22 mmol, 18%) of the desired product 2-(4-methoxyphenyl)-3-phenylanthracene-9,10-dione, further recrystallisation from ethanol provided an analytically pure sample.

Light Yellow Solid; ^{1}H-NMR: (ppm) ($CDCl_3$) 8.36–8.34 m (4H), 7.82 dd (2H, J=3.3 Hz, J=5.8 Hz), 7.30-7.29 m (3H), 7.23 dd (2H, J=3.0 Hz, J=6.7 Hz), 7.14 d (2H, J=8.7 Hz) 6.80 d (2H, J=8.7 Hz) 3.80 s (3H); ^{13}C-NMR: (ppm) ($CDCl_3$) 183.3, 183.2, 159.5, 146.5, 146.3, 140.1, 134.33, 134.30, 134.0, 133.9, 132.5, 132.1, 131.1, 130.0, 129.8, 129.7, 128.5, 127.8, 127.5, 113.9, 55.5; MS: (EI) M^+ 390 (100%); EA calcd. for: $C_{27}H_{18}O_3$ C 83.06 H 4.65 found: C 82.80 H 4.89; mp: 89-91°C

2,3-bis(4-methoxyphenyl)anthraquinone (46)

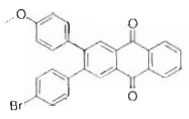


To a solution of naphthoquinone (380 mg, 2.4 mmol) in 20 mL acetic acid was added 372 mg (1.2 mmol) 4-hydroxy-3,4-bis(4-methoxyphenyl)cyclopent-2-enone and 50 mg (0.29 mmol) p-toluenesulfonic acid; this mixture was then reacted according to the method described above. The resulting mixture of products was then purified through silica gel chromatography eluting with a 4:1 mixture of hexanes:ethyl acetate. This yielded 41 mg (0.1 mmol, 8%) of the desired product 2,3-bis(4-methoxyphenyl)anthracene-9,10-dione. Further recrystallisation from ethanol provided an analytically pure sample.

Yellow Solid; ^{1}H-NMR: (ppm) ($CDCl_3$) 8.34 dd (2H, J=3.3 Hz, J=5.8 Hz), 8.31 s (2H), 7.81 dd (2H, J=3.3 Hz, J=5.8 Hz), 7.16 d (4H, J=8.7 Hz), 6.82 d (4H,

J=8.7 Hz), 3.82 s (6H) ; ^{13}C-NMR: (ppm) ($CDCl_3$) 183.0, 159.2, 145.9, 134.0, 133.8, 132.1, 131.9, 130.9, 129.5, 127.2, 113.8, 55.2 ; MS: (CI) $(M+H)^+$ 421 (100%), 422 (29%) EA calcd. for: $C_{28}H_{20}O_4$ C 79.98 H 4.79 found: C 80.13 H 4.90; mp: 168°C.

2-(4-bromophenyl)-3-(4-methoxyphenyl)anthraquinone (47)



To a solution of naphthoquinone (380 mg, 2.4 mmol) in 20 mL acetic acid was added 432 mg (1.2 mmol) 3-(4-bromophenyl)-4-hydroxy-4-(4-methoxyphenyl)cyclopent-2-enone and 50 mg (0.29 mmol) p-toluenesulfonic acid; this mixture was then reacted according to the method described above. The resulting mixture of products was then purified through silica gel chromatography eluting with toluene. This yielded 120 mg (0.26 mmol, 21%) of the desired product 2-(4-bromophenyl)-3-(4-methoxyphenyl)anthracene-9,10-dione, further recrystallisation from ethanol afforded an analytically pure sample.

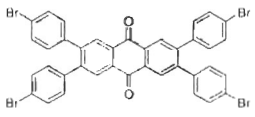
^{1}H-NMR: (ppm) ($CDCl_3$) 8.34 dd (2H, J=3.1 Hz, J=5.4 Hz), 8.33 s (1H), 8.30 s (1H), 7.83 dd (2H, J=3.3 Hz, J=5.8 Hz), 7.43 d (2H, J=8.4 Hz), 7.14-7.09 m (4H), 6.83 d (2H, J=8.7 Hz), 3.82 s (3H); ^{13}C-NMR: (ppm) ($CDCl_3$) 183.2, 183.1, 159.6, 146.3, 145.1, 139.0, 134.41, 134.39, 133.9, 132.7, 132.2, 131.75, 131.70, 131.4, 131.1, 129.8, 129.7, 127.5, 122.3, 114.1, 55.5; CI: $(M+H)^+$ 470 (100%), 468 (80%), 469 (60%), 471

(58%), 472 (13%) EA calcd. for: $C_{27}H_{17}BrO_3$ C 69.10 H 3.65 found: C 69.27 H 3.72; mp: 215-216°C

2,3,6,7-tetrakis(4-bromophenyl)anthraquinone (48) and 6,7-bis(4-bromophenyl)naphthoquinone (49)

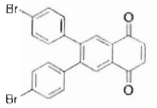
To a solution of benzoquinone (158 mg, 1.46 mmol) in 20 mL acetic acid was added 300 mg (0.74 mmol) 3,4-bis(4-bromophenyl)-4-hydroxycyclopent-2-enone and 20 mg (0.11 mmol) *p*-toluenesulfonic acid, the mixture was then reacted according to the method described above. The resulting mixture of products was then purified through silica gel chromatography eluting with toluene. This yielded 40 mg (0.05 mmol, 9%) of 2,3,6,7-tetrakis(4-bromophenyl)anthraquinone (**48**) as a yellow solid and (0.03 mmol, 3%) of 6,7-bis(4-bromophenyl)naphthoquinone (**49**) as a light yellow solid.

2,3,6,7-tetrakis(4-bromophenyl)anthraquinone (48)



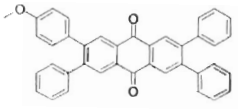
^{1}H-NMR: (ppm) ($CDCl_3$) 8.35 s (4H), 7.46 d (8H, J=8.4 Hz) 7.10 d (8H, J=8.4 Hz)

6,7-bis(4-bromophenyl)naphthoquinone (49)



^{1}H-NMR: (ppm) ($CDCl_3$) 8.10 s (2H), 7.44 d (4H, J=8.4 Hz) 7.09 d (4H, J=8.4 Hz), 6.94 s (2H)

2-(4-methoxyphenyl)-3,6,7-triphenylanthraquinone (50)

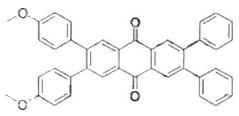


To a solution of 6,7-diphenylnaphthoquinone (469 mg, 1.6 mmol) in 20 mL acetic acid was added 281 mg (1.0 mmol) 4-hydroxy-(3 and 4)-(4-methoxyphenyl)-3-phenylcyclopent-2-enone and 65 mg (0.38 mmol) *p*-toluenesulfonic acid, this mixture was then reacted according to the method described above. The resulting mixture of products was then purified through silica gel chromatography eluting with toluene. This yielded 140 mg (0.26 mmol, 26%) of the desired product 2-(4-methoxyphenyl)-3,6,7-triphenylanthracene-9,10-dione, further recrystallisation from ethanol allowed an analytically pure sample.

Yellow Solid; ^{1}H-NMR: (ppm) ($CDCl_3$) 8.40 s (2H), 8.38 d (2H, J=2.9 Hz), 7.31-7.23 m (15H), 7.17 d (2H, J=8.8 Hz) 6.82 d (2H, J=8.8 Hz) 3.81 s (3H); ^{13}C-NMR: (ppm) ($CDCl_3$) 183.1, 183.0, 159.5, 146.61, 146.58, 146.4, 146.3, 140.1, 139.9, 132.7, 136.67, 132.3, 132.1, 131.2, 130.0, 129.9, 129.8, 129.7, 128.5, 128.4, 127.9, 127.8,

113.9, 55.5; MS: (MALDI-TOF) M^+ 543 (100%); EA calcd. for: $C_{39}H_{26}O_3$ C 86.32 H 4.83 found: C 85.97 H 5.03; mp: 230°C

2,3-bis(4-methoxyphenyl)-6,7-diphenylanthraquinone (51)



To a solution of 6,7-diphenylnaphthoquinone (200 mg, 0.65 mmol) in 25 mL acetic acid was added 240 mg (0.77 mmol) 4-hydroxy-3,4-bis(4-methoxyphenyl)cyclopent-2-enone and 17 mg (0.1 mmol) p-toluenesulfonic acid, this mixture was then heated at reflux under for 48 h. The resultant solution was cooled to room temperature, poured into water (75 mL) and then extracted with CH_2Cl_2 (3 x 75 mL). The organic portion was dried over $MgSO_4$ and the solvent then removed *in vacuo*. This product was passed through a short plug of silica gel eluting with toluene yielding a mixture primarily of unreacted 6,7-diphenylnaphthoquinone and the desired product (145 mg). This mixture of products was then purified through silica gel chromatography eluting with a 4:1 mixture of hexanes : ethyl-acetate. This yielded 50 mg (0.09 mmol, 13%) of the desired product 2,3-bis(4-methoxyphenyl)-6,7-diphenylanthracene-9,10-dione; further recrystallisation from ethanol allowed an analytically pure sample.

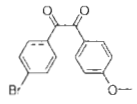
Yellow Solid; ^{1}H-NMR: (ppm) ($CDCl_3$) 8.39 s (2H), 8.35 s (2H), 7.30-7.22 m (10H), 7.18 d (4H, J=8.8 Hz) 6.83 d (4H, J=8.7 Hz), 3.82 s (6H); ^{13}C-NMR: (ppm) ($CDCl_3$) 183.1, 159.4, 146.6, 146.1, 139.9, 132.7, 132.4, 132.3, 131.1, 129.90, 129.86, 129.80, 128.4, 127.9, 114.0, 55.5; MS: (MALDI-TOF) $(M+2H)^+$ 574 (100%); EA calcd. for $C_{40}H_{28}O_4$ C 83.90 H 4.93 found: C 84.20 H 5.16; mp: 235°C

5.3.2 Preparation of Ethane Diones *via* a Benzoin Condensation

2-Naphthaldehyde (5 g, 32 mmol) and sodium cyanide (1 g, 20 mmol) were dissolved in 20 mL ethanol and 10 mL water. After refluxing for 1.5 h the solution was poured into water and extracted with dichloromethane, yielding the coupled benzil product in (4.4 g, 14 mmol) 87% crude yield. This product was then dissolved in 25 mL pyridine and 15 mL water in the presence of $CuSO_4$ (1 g); after refluxing this solution overnight the desired ethane dione was recovered through extraction with dichloromethane and washing with water in 73% yield (3.2 g, 10 mmol).

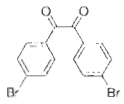
A slight modification was required for the preparation of the remaining ethane diones this involved using potassium cyanide instead of sodium cyanide and refluxing for 24 h instead of 1.5 h to affect the coupling.

1-(4-bromophenyl)-2-(4-methoxyphenyl)ethane-1,2-dione



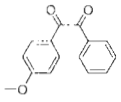
Pale yellow solid; ^{1}H-NMR: (ppm) ($CDCl_3$) 7.93 d (2H, J=8.9 Hz), 7.84 d (2H, J=8.6 Hz), 7.65 d (2H, J=8.6 Hz), 6.98 d (2H, J=8.9 Hz), 3.89 s (3H); mp: 135°C, lit. 136-137°C[137]

1,2-bis(4-methoxyphenyl)ethane-1,2-dione



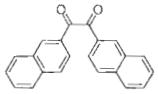
Pale grey solid; ^{1}H-NMR: (ppm) ($CDCl_3$) 7.95 d (4H, 8.8 Hz), 6.97 d (4H, 8.9 Hz), 3.89 s (6H); mp: 131°C, lit 133°C[138]

1-(4-methoxyphenyl)-2-phenylethane-1,2-dione (42)



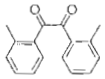
Pale yellow solid; ^{1}H-NMR: (ppm) ($CDCl_3$) 7.96 d (2H, J=8.9Hz), 7.65 d (2H, J=8.6 Hz), 7.51 m (3H), 6.98 d (2H, J=8.9 Hz), 3.89 s (3H); mp: 58.5 – 60°C, lit. 61°C[139]

1,2-di(naphthalen-2-yl)ethane-1,2-dione



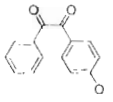
Off-white crystals; ^{1}H-NMR: (ppm) ($CDCl_3$) 8.45 s (2H), 8.15 dd (2H, J=1.6 Hz, J=8.6 Hz) 7.99 d (2H, J=8.7 Hz), 7.90 d (4H, J=8.8 Hz), 7.64 t (2H, J=7.6 Hz), 7.55 t (2H, J=7.6 Hz); ^{13}C-NMR: (ppm) ($CDCl_3$) 194.8, 136.4, 133.6, 132.4, 130.5, 130.0, 129.6, 129.2, 128.0, 127.2, 123.8; EA calcd. for: $C_{22}H_{14}O_2$ C 85.14 H 4.55 found: C 85.41 H 4.65; mp: 155°C, lit. 155-156°C[140]

1,2-dio-tolylethane-1,2-dione



Pale yellow crystals; ^{1}H-NMR: (ppm) ($CDCl_3$) 7.66 d (2H, J=7.8 Hz), 7.49 t (2H, J=7.5 Hz), 7.35 d (2H, J=7.6 Hz), 7.28 m (2H), 2.71 s (6H); mp: 88-89°C, lit. 92°C[141]

5.3.3 Preparation of 1-(4-methoxyphenyl)-2-phenylethane-1,2-dione *via* a Hagihara-Sonogashira Coupling (42)

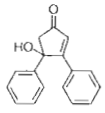


To dried Schlenk glassware was added 4-iodoanisole (3.2 g 13.8 mmol), tetrakis(triphenylphosphine)palladium (59 mg, 0.05 mmol), and copper(I)iodide (815 mg, 4.3 mmol). Phenylacetylene (1.75 mL, 16 mmol), 50 mL dry tetrahydrofuran and 10 mL dry di-isopropylamine were added *via* syringe and the resulting mixture was heated at reflux under N_2 for 45 h. After filtering

through a silica gel plug eluting with dichloromethane the organic extracts were freeze-dried *in vacuo*. This product was then oxidized immediately using iodine in a dimethylsulfoxide solution at reflux for 44 h. After extraction and washing with dichloromethane, water, and brine solutions the organic portion was washed again with saturated potassium iodide then recrystallised from a methanol/water mixture, yielding the desired product in 59% yield (1.7 g, 8.2 mmol).

^{1}H-NMR: (ppm) ($CDCl_3$) 7.96 d (2H, J=8.9Hz), 7.65 d (2H, J=8.6 Hz), 7.51 m (3H), 6.98 d (2H, J=8.9 Hz), 3.89 s (3H); mp: 58.5–60°C, lit. 61°C[142]

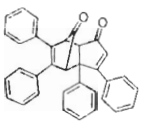
4-hydroxy-3,4-diphenylcyclopent-2-enone (30)



To 200 mL anhydrous ethanol and 16 mL of acetone, 20 g (95 mmoL) of benzil and 1.6 g of KOH were added. This solution was stirred for one week at room temperature. At this point, the solution was poured into water (200 mL), this caused a solid to precipitate from solution. After vacuum filtration and washing with water the desired product was obtained in 95% yield (22.3 g, 89 mmoL).

Pale yellow solid, ^{1}H-NMR: (ppm) ($CDCl_3$) 7.50-7.52 m (2H), 7.44-7.47 m (2H), 7.27-7.37 m (6H), 6.71 s (1H), 3.02 d (1H, J=18.5 Hz), 2.90 d (1H, J=18.5 Hz)[143]

Dimer of 3,4-diphenylcyclopenta-2,4-dienone (32)



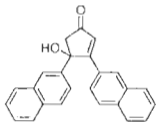
To 10 mL of acetic acid 100 mg (0.4 mmol) of 4-hydroxy-3,4-diphenylcyclopent-2-enone and 7 mg (0.04 mmol) *p*-toluenesulfonic acid was added. This mixture was then heated at reflux for 22 h. The resultant solution was cooled to room temperature, poured into water (50 mL) and then extracted with CH_2Cl_2 (3 x 50 mL). The organic portion was dried over $MgSO_4$ and the solvent then removed *in vacuo*. Recrystallisation from ethanol provided for an analytically pure sample in 73% yield (68 mg).

Yellow solid, ^{1}H-NMR: (ppm) ($CDCl_3$) 6.80-7.43 m (21H), 4.37 s (1H), 3.75 d (1H, J=4.8 Hz), 3.08 d (1H, J=4.8 Hz)[144]

5.3.4 General Preparation of Substituted Hydroxycyclopentenones

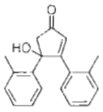
1,2-di(naphthalen-2-yl)ethane-1,2-dione (3.2 g, 10 mmol) was stirred for a week at room temperature in an ethanolic solution of potassium hydroxide (560 mg, 10 mmol) and acetone (12 mL, 160 mmol). This solution was then poured into water (150 mL) and extracted with dichloromethane (3 X 75 mL), yielding the desired 4-hydroxy-4-(naphthalen-2-yl)-3-(naphthalen-2′-yl)cyclopent-2-enone in 69% (2.4 g, 6.9 mmol) yield.

4-hydroxy-4-(naphthalen-2-yl)-3-(naphthalen-2′-yl)cyclopent-2-enone (34)



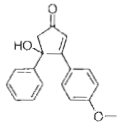
^{1}H-NMR: (ppm) ($CDCl_3$) 8.19 d (2H, J=11.5 Hz), 7.85-7.40 m (12H), 6.90 s (1H), 3.13 d (1H, J=18.6 Hz), 3.02 d (1H, J=18.6 Hz)

4-hydroxy-3,4-dio-tolylcyclopent-2-enone (36)

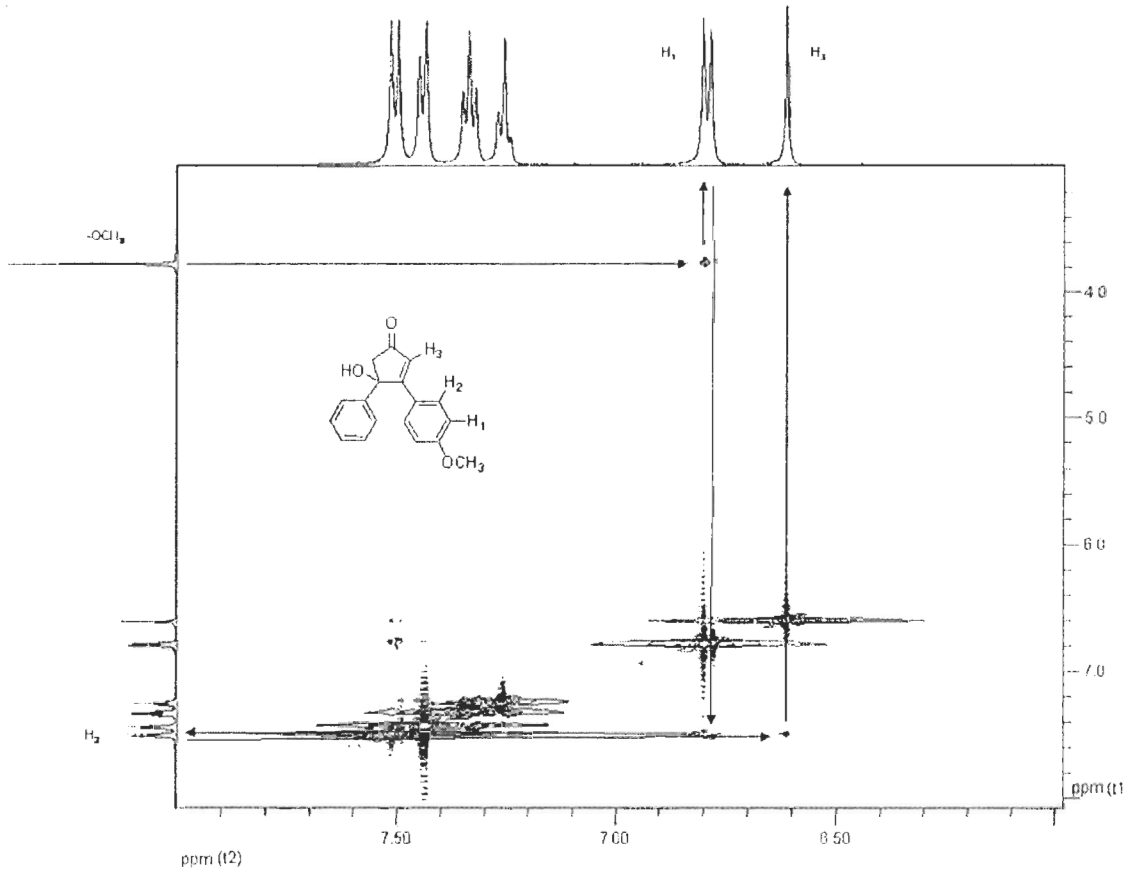


^{1}H-NMR: (ppm) ($CDCl_3$) 7.55-7.53 m (2H), 7.20-7.14 m (4H). 6.99-6.97 m (2H), 6.40 s (1H), 3.07 d (1H, J=18.6 Hz), 2.98 d (1H, J=18.6 Hz), 2.41 s (3H), 2.31 s (3H)

4-hydroxy-3-(4-methoxyphenyl)-4-phenylcyclopent-2-enone (37a)

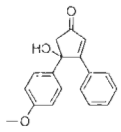


^{1}H-NMR: (ppm) ($CDCl_3$) 7.51 dt (2H, J=9.0 Hz, J=2.1 Hz), 7.45 dt (2H, J=7.3 Hz, J=1.6 Hz), 7.35 td (2H, J=7.6 Hz, J=1.8 Hz), 7.28-7.25 m (3H), 6.66 s (1H), 3.79 s (3H), 2.88 d (1H, J=18.4 Hz), 2.53 br (1H): ^{13}C-NMR: (ppm) ($CDCl_3$) 205.1, 173.8, 161.9, 144.6, 131.5, 129.0, 127.6, 127.1, 124.4, 123.8, 114.1, 81.7, 56.9, 55.6; EA calcd. For $C_{18}H_{16}O_3$: C 77.12 H 5.75 found: C 76.91 H 5.80 mp: 150.5-152.5^{o}C



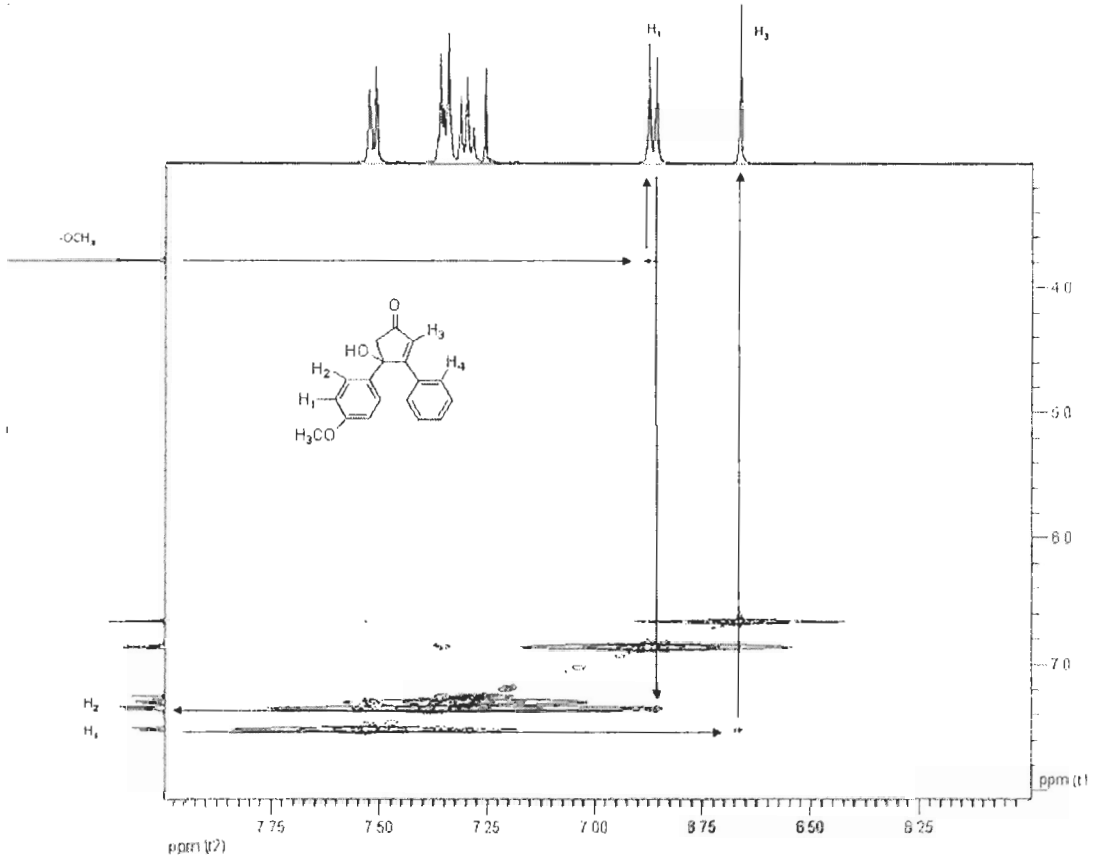
NOESY spectrum of **37a** arrows show correlations from through space couplings. Note that proton **H3** can be correlated back to the methoxy group.

4-hydroxy-4-(4-methoxyphenyl)-3-phenylcyclopent-2-enone (37b)



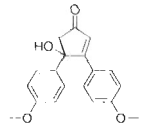
^{1}H-NMR: (ppm) ($CDCl_3$) 7.52 dt (2H, J=7.1 Hz, J=1.3 Hz), 7.37-7.35 m (3H), 7.30 td (2H, J=7.4 Hz, J=1.5 Hz), 6.87 dt (2H J=8.8 Hz, J=2.5 Hz) 6.66 s (1H), 3.79 s (3H), 3.00 d (1H, J=18.5 Hz), 2.88 d (1H, J=18.5 Hz), 2.65 br

(1H): ^{13}C-NMR: (ppm) ($CDCl_3$) 205.3, 174.1, 159.1, 136.3, 131.6, 131.1, 129.4, 129.2, 129.0, 125.7, 114.4, 81.7, 56.9, 55.6; EA calcd. For $C_{18}H_{16}O_3$: C 77.12 H 5.75 found: C 76.99 H 5.82 mp: 194-195°C



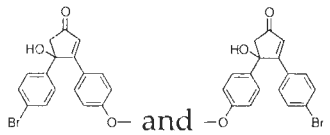
NOESY spectrum of **37b** arrows show correlations from through space couplings. Note that proton $\mathbf{H_3}$ cannot be correlated back to the methoxy group, but is instead correlated to $\mathbf{H_4}$.

4-hydroxy-3,4-bis(4-methoxyphenyl)cyclopent-2-enone (38)



^{1}H-NMR: (ppm) ($CDCl_3$) 7.52 d (2H, J=9.0 Hz), 7.34 d (2H, J=8.8 Hz), 6.83 dd (4H, J=8.9 Hz, J=20.5 Hz), 6.60 s (1H), 3.79 s (3H), 3.78 s (3H), 2.98 d (1H, J=18.5 Hz), 2.85 d (1H, J=18.5 Hz)

3-(4-bromophenyl)-4-hydroxy-4-(4-methoxyphenyl)cyclopent-2-enone and 4-(4-bromophenyl)-4-hydroxy-3-(4-methoxyphenyl)cyclopent-2-enone (39)

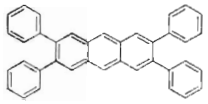


^{1}H-NMR: (ppm) ($CDCl_3$) 7.52-7.43 m (4H), 7.34-7.32 m (2H), 6.86 d (J=9.0 Hz) or 6.82 d (J=8.9 Hz) (2H), 6.66 s or 6.64 s (1H), 3.79 s (3H), 2.97 d (1H, J=18.6 Hz), 2.83 d (1H, J=18.5 Hz)

5.4 Syntheses found in Chapter 4

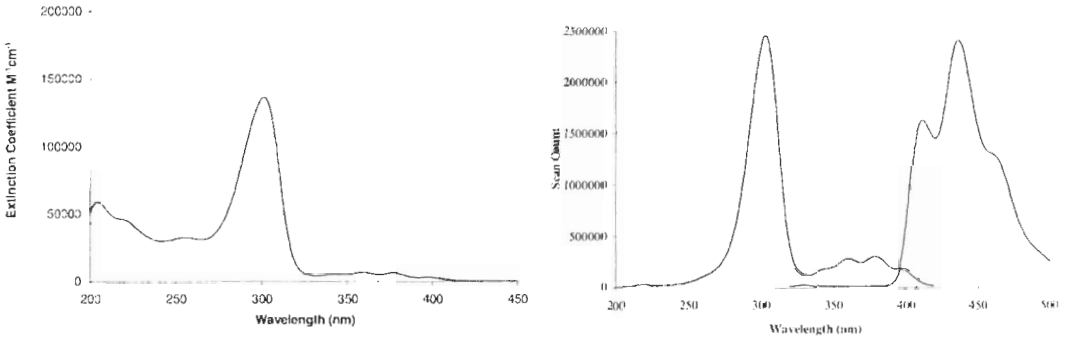
5.4.1 Preparation of Substituted Anthracenes

2,3,6,7-tetraphenylanthracene (TPA)



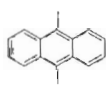
In an oven-dried 100 mL Schlenk tube 2,3,6,7-tetraphenylanthraquinone (420 mg, 0.82 mmol) was dissolved in 20 mL dry tetrahydrafuran cooled to -78°C by a dry ice/acetone bath. To this solution 310 mg (2.3 mmol) of lithium aluminum hydride and 545 mg (14 mmol) of aluminum trichloride were carefully added. This mixture was then allowed to warm to room temperature and then heated under reflux for 22 hours under N_2. The solution was then cooled and poured into diethyl ether (50 mL) and carefully quenched with water (50 mL). After extraction with three further portions of diethyl ether (50 mL each), the ethereal layer was dried with magnesium sulfate, and concentrated *in vacuo*. This crude product was then dissolved in 30 mL xylenes and 400 mg Pd/C was added to the solution, which was then heated at reflux for 6 days. The product was then eluted through a silica gel column with toluene and then recrystallised from acetone yielding 300 mg (0.62 mmol, 76%) of the desired product as a yellow solid.

^{1}H-NMR: (ppm) (D_6-acetone) 8.71 s (2H), 8.15 s (4H), 7.28-7.30 m (20H); ^{13}C-NMR: (ppm) ($CDCl_3$) 141.6, 139.3, 131.7, 130.2, 129.8, 128.1, 126.7, 126.2; FT-IR: 2922 C-H stretch MS: (MALDI-TOF) M^+ 482 (100%), UV-Vis: λ_{max}=301 nm (ε=136,000 $M^{-1}cm^{-1}$); EA calcd.: C 94.57 H 5.43 found: C 94.32 H 5.59 mp: 298-299°C



Both UV-Vis and fluorescence spectra were recorded in spectral-grade acetonitrile at concentrations of 6.4 x 10^{-5} and 1.9 x 10^{-7} M, respectively.

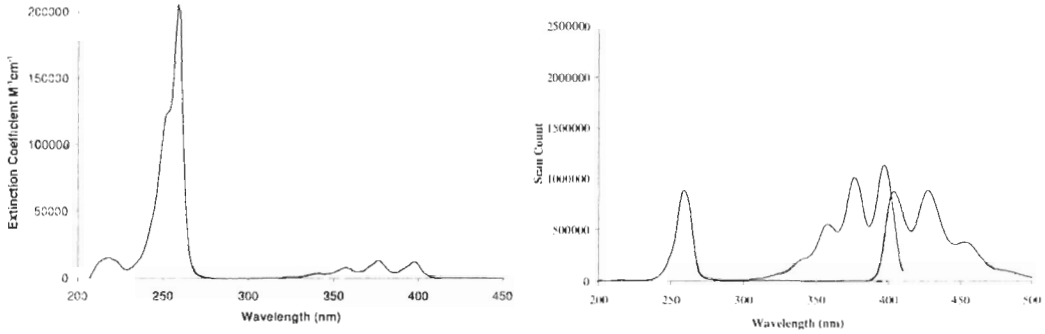
9,10-dimethylanthracene (DMA)



To 80 mL dry Et_2O in oven-dried glassware was added 2 g (80 mmol) of crushed magnesium turnings. The solution was cooled to 0°C in an ice bath and 6 mL (80 mmol) methyl iodide was added dropwise. Once the

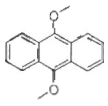
Grignard reagent had visibly formed (assumed from magnesium turning consumption), 2 g (9.6 mmol) of anthraquinone was added while under a stream of nitrogen. This solution was then stirred at room temperature (25°C) for 17 hours. The reaction mixture was then carefully quenched with a saturated aqueous NH_4Cl solution. The ethereal portion was then separated and dried with magnesium sulfate, and the ether was removed *in vacuo*. This yielded the crude of 9,10-dimethyl-9,10-dihydroxy-anthracene, which was used without further purification. This product was then dissolved in 60 mL glacial acetic acid and 20 mL concentrated hydrochloric acid with 20 g $SnCl_2$ was added and the solution was heated at reflux for 3.5 hours. The mixture was then cooled to room temperature and poured into 500 mL H_2O and stirred for a further 2 hours. The solution was then filtered and recrystalized from 95% ethanol; the solid portion contains unreacted impurities. The mother liquor was evaporated and the product passed through a short plug of silica (eluting with toluene) to yield 900 mg (4.4 mmol, 46%) of the pure 9,10-dimethylanthracene.

^{1}H-NMR ($CDCl_3$): (ppm) 8.34 dd (J=3.3 Hz, J=6.9 Hz, 4H), 7.52 dd (J=3.2 Hz, J=6.9 Hz, 4H), 3.11 s (6H); UV-Vis: λ_{max}=259 nm (ε=206,000 $M^{-1}cm^{-1}$); mp: 180-182°C, lit. 180-181°C[145]



Both UV-Vis and fluorescence spectra were recorded in spectral-grade acetonitrile at concentrations of 9.9×10^{-6} and 2.1×10^{-7} M, respectively.

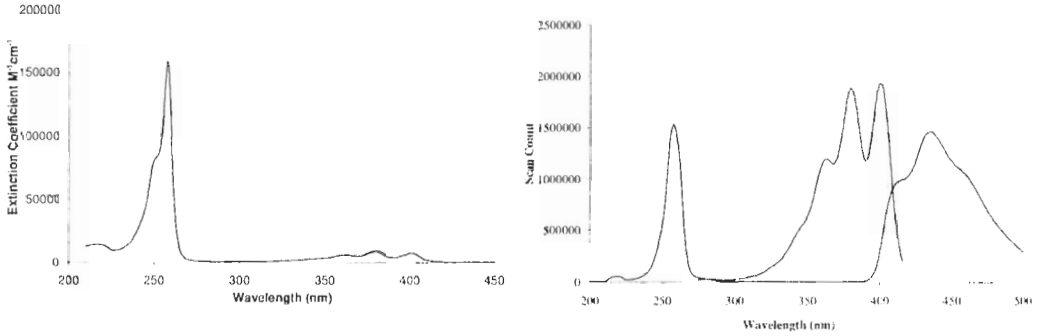
9,10-dimethoxyanthracene (DMeOA)



To a mixture of 20 mL THF and 10 mL H_2O was added 1 g (4.8 mmol) of anthraquinone and 620 mg (1.9 mmol) tetrabutylammonium bromide. To this was added 5 g of $Na_2S_2O_4$ dissolved in 50 mL H_2O; after stirring for 30 min 6.2 g of KOH dissolved in 50 mL of H_2O was then added. After another 15 min of stirring, 10 mL (13.25 g, 105 mmol) of dimethyl sulphate added, and the solution was then allowed to stir at room temperature for a further 17 h. The solution was then poured into a H_2O/CH_2Cl_2 (100 mL of each) solution; the layers were then separated and the aqueous layer extracted with CH_2Cl_2 (3 X 50 mL) the combined organic portions were dried over $MgSO_4$ and the solvent removed *in vacuo*. After first recrystallising from EtOH and then

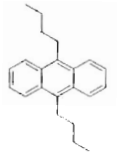
subjecting the resultant solid to silica gel chromatography (toluene as eluent) the desired product was obtained as a light yellow solid in 72% yield (820 mg, 3.4 mmol).

^{1}H-NMR ($CDCl_3$): (ppm) 8.30 dd (J=3.1 Hz, J=6.7 Hz, 4H), 7.50 dd (J=3.1 Hz, J=6.7 Hz, 4H), 4.13 s (6H)[146]; UV-Vis: λ_{max}=258 nm (ε=158,000 $M^{-1}cm^{-1}$); mp: 199-200°C, lit. 198-199°C[147]



Both UV-Vis and fluorescence spectra were recorded in spectral-grade acetonitrile at concentrations of 9.8 x 10^{-6} and 2.3 x 10^{-7} M, respectively.

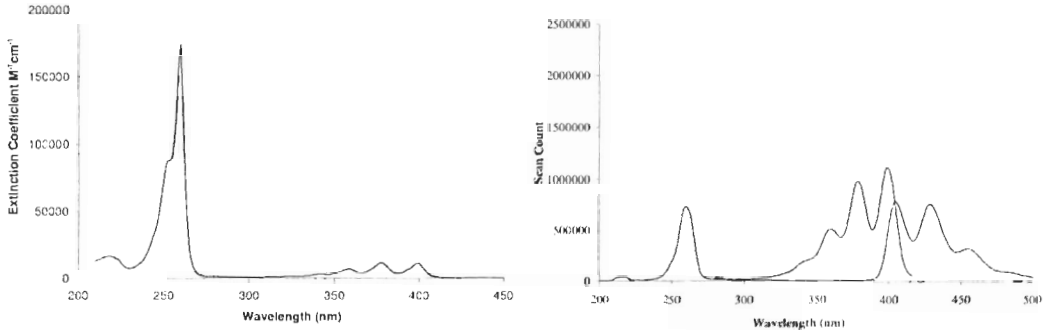
9,10-dibutylanthracene (DBA)



To 40 mL of dry Et_2O 2 g (6 mmol) of 9,10-dibromoanthracene was added. This solution was cooled to -78°C in an acetone-dry ice bath, and *n*-butyllithium (3.2 mL of 2.5 M solution) was slowly added. This solution was then allowed to stir for 30 min at which time 1.35 mL (1.7 g, 12.4 mmol) of 1-bromobutane was added and the solution was allowed to warm to room temperature, and then heated at reflux for 21 h. The solution was then cooled and poured into Et_2O (75 mL) and carefully quenched with H_2O (75 mL). The organic and aqueous layers were then separated, the aqueous layer was then extracted with Et_2O (3 X 50 mL) the combined organic layers were then dried over $MgSO_4$ and the solvent removed *in vacuo* to yield 1.8 g of product. This solid was then purified to separate the desired product from starting material and partially reacted material by silica gel chromatography using a 1:1 mixture of hexanes : toluene. This gave 650 mg (2.2 mmol, 37%) of the desired product as bright yellow-green needles.

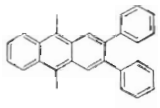
^{1}H-NMR ($CDCl_3$): (ppm) 8.31 dd (J=3.3 Hz, J=6.9 Hz, 4H), 7.49 dd (J=3.1 Hz, J=6.7 Hz, 4H), 3.58-3.61 m (4H), 1.78-1.82 m (4H), 1.58-1.65 m (4H), 1.04 t

(J=7.3 Hz, J=14.7 Hz, 6H); UV-Vis: λ_{max}=260 nm (ε=173,000 $M^{-1}cm^{-1}$); mp: 103-104°C Lit. 104-105°C [148].



Both UV-Vis and fluorescence spectra were recorded in spectral-grade acetonitrile at concentrations of 9.5 x 10^{-6} and 2.3 x 10^{-8} M, respectively.

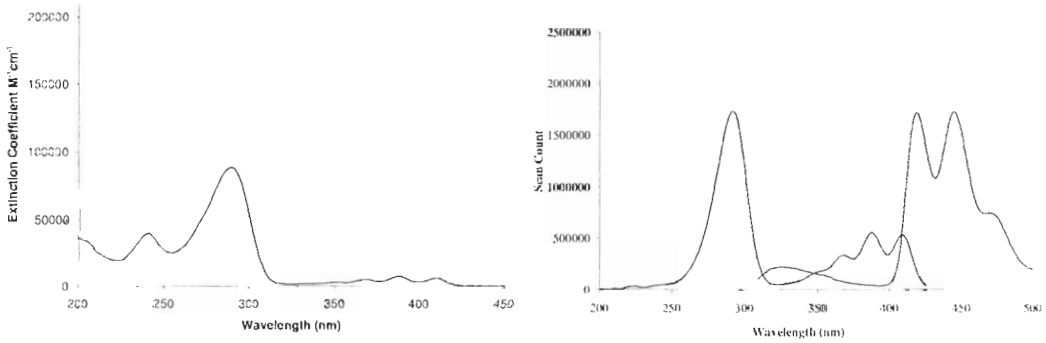
9,10-dimethyl-2,3-diphenylanthracene (DMDPA)



In an oven-dried 100 mL round bottom flask kept under N_2 2,3-diphenylanthraquinone (300 mg, 0.83 mmol) was dissolved in 30 mL dry diethyl ether. This mixture was cooled to 0°C, and 1.4 M MeLi in diethylether (2.65 mL, 3.7 mmol) was slowly added. After addition, the solution was allowed to warm to room temperature while stirring. After 90 minutes, 30 mL of a 10% HCl solution saturated with $SnCl_2$ was added and allowed to stir for a further 60

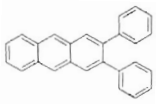
minutes. This solution was then diluted with water (75 mL) and extracted with diethyl ether (3 x 75 mL). After drying the ethereal layer with magnesium sulfate the solution was concentrated *in vacuo*. This crude product was then directly applied to a SiO_2 column and eluted with a mixture of hexanes and toluene (1:1) to afford 70 mg (20 mmol, 23%) of the desired product as a yellow solid.

^{1}H-NMR: (ppm) ($CDCl_3$) 8.36 s (2H), 8.34 dd (2H, J=3.3 Hz, J=6.9 Hz), 7.53 dd (2H, J=3.3 Hz, J=6.9 Hz), 7.33–7.25 m (10H), 3.14 s (6H); ^{13}C-NMR: (ppm) ($CDCl_3$) 142.1, 138.2, 130.5, 130.3, 129.5, 128.7, 128.1, 127.3, 126.8, 125.6, 125.1, 14.4; FT-IR: (cm^{-1}) 3077, 3050, 3017, 2920, 1598, 1490, 1443, 1386, 1021, 876, 766, 742, 699, 638, 595, 544; MS: (EI) M^+ 358 (100%); UV-Vis: λ_{max}=289 nm (ε=88,000 $M^{-1}cm^{-1}$); EA calcd. for: $C_{28}H_{22}$ C 93.81 H 6.19 found: C 93.57 H 6.30; mp: 204–205°C



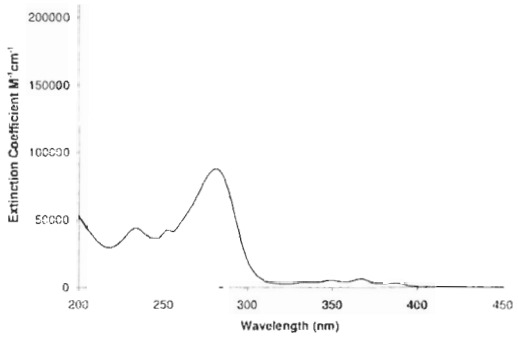
Both UV-Vis and fluorescence spectra were recorded in spectral-grade acetonitrile at concentrations of 1.1 x 10^{-5} and 2.0 x 10^{-7} M, respectively.

2,3-diphenylanthracene (DPA)



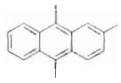
In an oven-dried 100 mL Schlenk tube 2,3-diphenylanthraquinone (200 mg, 0.56 mmol) was dissolved in 30 mL dry tetrahydrafuran, and this mixture was then cooled to -78°C in a dry ice/acetone bath. To this was carefully added 210 mg (1.6 mmol) of lithium aluminum hydride and 373 mg (9.8 mmol) of aluminum trichloride. This mixture was then allowed to warm to room temperature and then heated at reflux for 22 hours under N_2. The solution was then cooled and poured into diethyl ether (50 mL) and carefully quenched with water (50 mL). After extraction with three further portions of diethyl ether (50 mL each) the ethereal layer was dried with magnesium sulfate, and concentrated *in vacuo*. This crude product was then dissolved in 20 mL xylenes, and 200 mg Pd/C was then added to the solution, which was then heated at reflux for 134 hours. The product was then eluted through a SiO_2 column with a solvent gradient beginning with pure hexanes and moving to a 1:1 mixture of hexanes and toluene. This resulted in the 150 mg (82%) of the desired product as a yellow solid.

^{1}H-NMR: (ppm) ($CDCl_3$) 8.47 s (2H), 8.06 s (2H), 8.02 dd (2H, J=3.3 Hz, J=6.4 Hz), 7.48 dd (2H, J=3.2 Hz, J=6.5 Hz), 7.28–7.23 m (10H); ^{13}C-NMR: (ppm) ($CDCl_3$) 141.5, 139.0, 132.1, 130.0, 129.6, 128.3, 127.9, 126.6, 126.2, 125.5; FT-IR; (cm^{-1}) 3054, 3017, 2916, 1598, 1490, 1427, 1068, 1020, 957, 903, 772, 739, 699, 564, 467; MS: (EI) M^+ 330 (100%); UV-Vis: λ_{max}=281 nm (ε=87,000 $M^{-1}cm^{-1}$); EA calcd. for: $C_{26}H_{18}$ C 94.51 H 5.49 found: C 94.17 H 5.65; mp: 98-100°C



The UV-Vis spectrum was recorded in spectral-grade acetonitrile at a concentration of 1.1 x 10^{-5} M.

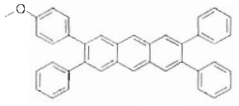
2,9,10-trimethylanthracene (TMA)



In an oven-dried 100 mL round bottom flask kept under N_2, 40 mL of dry diethyl ether was charged with 240 mg (10 mmol) of ground magnesium shavings. To this was added 0.6 mL (10 mmol) of methyl iodide. Once the Grignard reagent had formed (assumed by consumption of visible magnesium shavings) 300 mg (1.35 mmol) of 2-methylanthraquinone was added. After the solution had been heated at reflux for 42 h it was cooled and 55 mL of a 10% HCl solution saturated with $SnCl_2$ was added and allowed to stir for a further 20 h at room temperature. This solution was then diluted with water (75 mL) and extracted with diethyl ether (3 x 75 mL). After drying the ethereal layer with magnesium sulphate, the solution was concentrated *in vacuo*. This crude product was then directly applied to a silica gel column and eluted with a mixture of hexanes and toluene (9:1) 90 mg (41 mmol, 30%) of the desired product was recovered as a yellow solid.

^{1}H-NMR: (ppm) ($CDCl_3$) 8.32-8.30 m (2H), 8.24 d (2H, J=9.0 Hz), 8.07 s (1H), 7.47 – 7.50 m (2H), 3.08 s (3H), 3.07 s (3H), 2.59 s (3H); mp: 97°C, lit. 96°C[149]

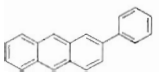
2-(4-methoxyphenyl)-3,6,7-triphenylanthracene (TPAA)



In an oven-dried 100 mL Schlenk tube, 2-(4-methoxyphenyl)-3,6,7-triphenylanthraquinone (200 mg, 0.37 mmol) was dissolved in 20 mL dry tetrahydrafuran then cooled to -78°C in a dry ice/acetone bath. To this solution 135 mg (1.0 mmol) of lithium aluminum hydride and 440 mg (11 mmol) of aluminum trichloride were carefully added. This mixture was then allowed to warm to room temperature and heated at reflux for 26 hours under N_2. The solution was then allowed to cool, poured into diethyl ether (50 mL), and carefully quenched with water (50 mL). After extraction with three further portions of diethyl ether (50 mL each) the ethereal layer was dried with magnesium sulfate, and finally concentrated *in vacuo*. This crude product was then dissolved in 30 mL xylenes and 200 mg Pd/C was added to the solution, which was then heated at reflux for 113 hours. The product was then cooled to room temperature and eluted through a plug of SiO_2 with toluene. This resulted in the 160 mg of the desired product, which was then recrystallised from acetone yielding 135 mg (0.26 mmol, 70%) of the desired product as a yellow solid.

^{1}H-NMR: (ppm) ($CDCl_3$) 8.37-8.40 m (3H), 7.31-7.16 m (20H), 6.83-6.81 m (2H), 3.81 s (3H)

2-phenylanthracene (MPA)



2-Phenylanthracene was prepared by first converting 2-aminoanthraquinone to 2-iodoanthraquinone and then carrying out a Suzuki coupling with phenylboronic acid to produce 2-phenylanthraquinone, which was then reduced to the anthracene.

2-iodoanthraquinone

2-Aminoanthraquinone (5 g, 22.3 mmol) was suspended in a mixture of 15 mL HCl and 15 mL ice. In a separate container 2.7 g (40 mmol) of $NaNO_2$ was dissolved in 15 mL of H_2O. While maintaining the 2-aminoanthraquinone solution in an ice bath the $NaNO_2$ solution was added slowly over a 20-minute period. This solution was then allowed to stir for another 1 hour at 5°C and then carefully poured into a solution of KI (6.6 g, 40 mmol) in 50 mL of H_2O and allowed to stir for a further 30 minutes. The crude product was then sublimed under vacuum to yield 1.3 g (3.9 mmol, 17%) of the pure 2-iodoanthraquinone.

^{1}H-NMR: (ppm) ($CDCl_3$) 8.64 d (1H, J=1.8 Hz), 8.30 m (2H), 8.15 dd (1H, J=1.8 Hz, J=8.2 Hz), 7.99 d (1H, J=8.2 Hz), 7.82 dd (2H, J=3.3 Hz, J=5.8 Hz); mp: 173 - 175°C, lit. 175 –176°C[150]

2-phenylanthraquinone

To a Schlenk flask, 500 mg (1.5 mmol) of 2-iodoanthraquinone, 270 mg (2.25 mmol) of phenylboronic acid, 1.85 g (15 mmol) of $Na_2CO_3 \cdot H_2O$, 20 mg (0.03 mmol) of $PdCl_2(PPh_3)_2$ were added to 10 mL of H_2O and 4 mL of 1,2-dimethoxyethane. This solution was sealed and heated to 80°C for 48 h. The solution was then cooled to RT, and poured into Et_2O and H_2O (30 mL each). The ethereal layer was separated and the aqueous layer was extracted with Et_2O (3 X 30 mL). The combined ethereal extracts were dried over $MgsO_4$ and concentrated *in vacuo* resulting in the desired product in 74% yield (470 mg, 1.65 mmol). This product was used without further purification.

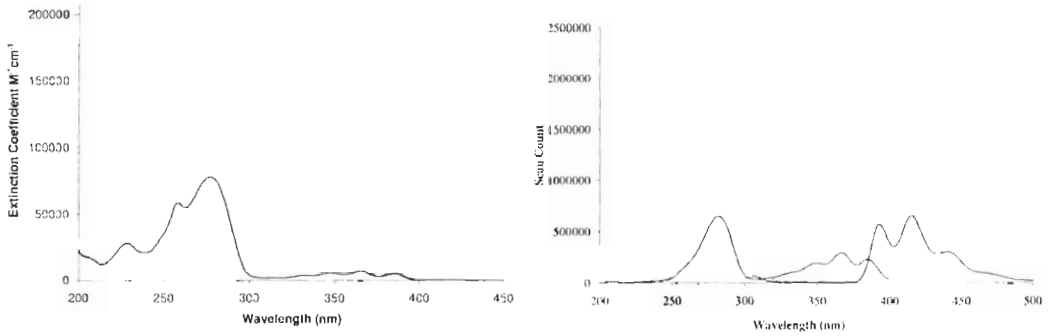
^{1}H-NMR: (ppm) ($CDCl_3$) 8.55 d (1H, J=1.9 Hz), 8.39 d (1H, J=8.1 Hz), 8.35 m (2H), 8.03 dd (1H, J=1.9 Hz, J=8.1 Hz), 7.82 dd (1H, J=1.2 Hz, J=2.5 Hz), 7.82 d (1H, J=9.1 Hz), 7.74 d (2H, J=7.1 Hz), 7.53 t (2H, J=7.3 Hz), 7.47 dt (1H, J=4.7 Hz, J=1.9 Hz); mp: 162 - 164°C, lit. 163-164°C[151]

2-phenylanthracene

In an oven-dried 100 mL Schlenk tube, 2-phenylanthraquinone (300 mg, 1.06 mmol) was dissolved in 20 mL dry tetrahydrafuran cooled to -78°C by a dry ice/acetone bath. To this solution 500 mg (3.8 mmol) of lithium aluminum hydride and 875 mg (18.8 mmol) of aluminum trichloride were carefully added,

this mixture was then allowed to warm to room temperature and heated at reflux for 24 hours under N_2. The solution was then cooled and poured into diethyl ether (50 mL) and carefully quenched with water (50 mL). After extraction with three further portions of diethyl ether (50 mL each) the ethereal extracts were dried with magnesium sulfate, and finally concentrated *in vacuo*. This crude product was then dissolved in 50 mL xylenes and 420 mg Pd/C was added to the solution, which was then heated at reflux for 9 days. The product was then cooled to room temperature and eluted through a plug of SiO_2 with toluene. This resulted in the 170 mg of the desired product, which was recrystallised from acetone yielding 100 mg (0.39 mmol, 37%) of the desired product as a yellow solid.

^{1}H-NMR: (ppm) ($CDCl_3$) 8.48 s (1H), 8.45 s (1H), 8.21 s (1H), 8.09 d (1H, J=8.9 Hz), 8.02 dd (1H, J=1.2 Hz, J=4.3 Hz), 8.02 d (1H, J=9.7 Hz), 7.75-7.80 m (3H), 7.51 t (2H, J=7.6 Hz), 7.47 dd (1H, J=1.1 Hz, J=3.4 Hz), 7.47 d (1H, J=9.7 Hz), 7.40 tt (1H, J=7.4 Hz, J=1.2 Hz); UV-Vis: λ_{max}=277 nm (ε=77,000 $M^{-1}cm^{-1}$); mp: 206-207°C, lit. 207-208°C[152]



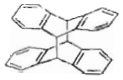
Both UV-Vis and fluorescence spectra were recorded in spectral-grade acetonitrile at concentrations of 1.4×10^{-5} and 2.2×10^{-8} M, respectively.

5.4.2 Dianthracene Cyclomers

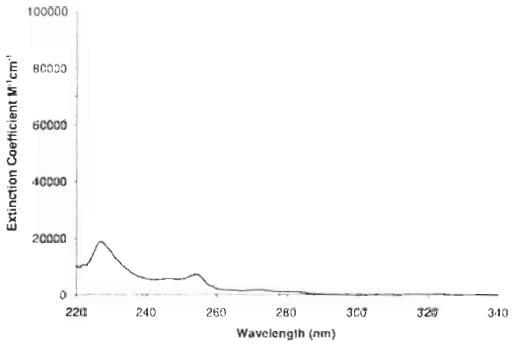
5.4.2.1 Note on ^{1}H-NMR Characterisation of Anthracene Photoproducts

All photoproducts share two distinctive and characteristic features in their ^{1}H-NMR spectra. All exhibit a broad envelope of resonances roughly between 7.20 and 6.80 ppm, unfortunately these are not useful in determining the identity of the photoproduct as there is significant overlap of the signals. The second and more diagnostic resonances are due to the bridgehead protons; these signals appear between 3.9-5 ppm and are always sharp and do not overlap between species.

dianthracene (A-A)



^{1}H-NMR: (ppm) ($CDCl_3$) 6.92 dd (8H, J=3.3 Hz, J=5.3 Hz), 6.81 dd (8H, J=3.2 Hz, J=5.4 Hz), 4.55 s (4H) [153]; UV-Vis: λ_{max}=227 nm (ε=19,000 $M^{-1}cm^{-1}$).



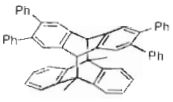
The UV-Vis spectrum was recorded in spectral-grade dichloromethane at a concentration of 7.1 x 10^{-5} M.

5.4.2.2 Dianthracene Cyclomer Syntheses

The following syntheses are not representative of the conditions used in the studies of reactivity of these anthracenes. They have been optimised for production of the desired dianthracene cyclomers. A description of the

techniques used in the qualitative studies discussed in Chapter 4 can be found following this section.

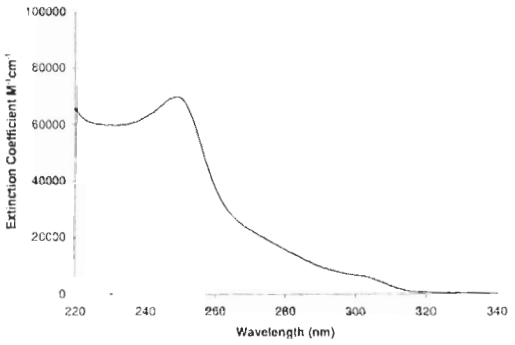
9,10-dimethyl-2′,3′,6′,7′-tetraphenyldianthracene (TPA-DMA)



A solution of 2,3,6,7-tetraphenylanthracene (20 mg, 0.04 mmol) and 9,10-dimethylanthracene (8.5 mg, 0.04 mmol) in 5 mL benzene placed in a Schlenk flask was deoxygenated by carrying out three freeze-pump-thaw cycles. The flask was then sealed under an N_2 atmosphere and the solution irradiated in a Rayonet Photochemical Reactor© fitted with ten RPR-3000 lamps for 150 minutes to yield **TPA-DMA** in 83% yield (based on ^{1}H-NMR). Recrystallisation from acetone yielded 13 mg of the purified product as a white crystalline solid (47% yield).

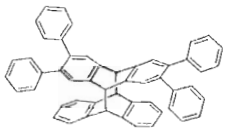
^{1}H-NMR: (ppm) (CD_2Cl_2) 7.26 (dd, J=3.3, 5.7 Hz, 4H), 7.17-7.15 (m, 12H), 6.98 (dd, J=3.3, 5.7 Hz, 4H), 6.95 (s, 4H), 6.94 (dd, J=2.8, 6.4 Hz, 8H), 4.08 (s, 2H), 2.19 (s, 6H); ^{13}C-NMR: (ppm) (CD_2Cl_2) 148.2, 143.8, 143.7, 139.7, 131.7, 130.9, 129.5, 128.0, 127.3, 125.9, 64.3, 53.4, 28.2; MS: (FAB) (**TPA**)$^+$ 482.1 (50%), (**TPA-DMA**)$^+$ 688.2 (1%); (MALDI-TOF) (**TPA**)$^+$ 482 (40%), (DMA)$^+$ 206 (100%); (CI) (**DMA**+H)$^+$ 207 (100%); UV-Vis: λ_{max}=249 nm (ε=69,000 $M^{-1}cm^{-1}$); FT-IR (cm^{-1}): 2916, 2843,

1675, 1584, 1474, 1447, 1333, 1239, 1074 1021, 766, 702; EA: calcd. for $C_{54}H_{40}$ C 94.15 H 5.85 found: C 94.04 H 6.20; mp: 107°C (decomp.)



The UV-Vis spectrum was recorded in spectral-grade acetonitrile at a concentration of 3.5 x 10^{-5} M.

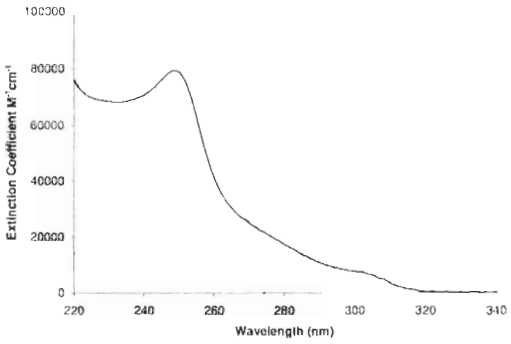
2,3,6,7-tetraphenyldianthracene (TPA-A)



In an oven-dried 100 mL Schlenk flask 55 mg (0.11 mmol) of 2,3,6,7-tetraphenylanthracene (**TPA**) and 20 mg (0.11 mmol) of anthracene were dissolved in 10 mL of spectral-grade benzene. Oxygen was removed from the sample through a minimum of three freeze-pump-thaw cycles. The sample was then irradiated for 2.5 h with 350 nm lamps in a Rayonet Photochemical Reactor©. After irradiation the solvent was removed at room

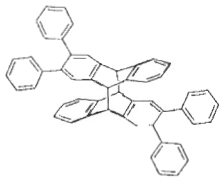
temperature *in vacuo*. The solid was then purified through silica gel chromatography eluting with a 3:1 mixture of hexanes and toluene followed by recrystallisation from ethanol, yielding 12 mg (0.02 mmol) 33%.

^{1}H-NMR: (ppm) ($CDCl_3$) 7.16-7.13m (12H), 7.00 dd (4H, J=3.3 Hz, J=5.4), 6.98 s(4H), 6.92 dd (8H, J=3.3 Hz, J=7.5 Hz), 6.88 dd (4H, J=3.2 Hz, J=5.4 Hz), 4.68 d (2H, J=10.9 Hz), 4.61 d (2H, J=10.9 Hz); ^{13}C-NMR: (ppm) ($CDCl_3$) 143.3, 142.4, 141.7, 137.8, 129.8, 129.3, 127.6, 127.3, 126.1, 125.6, 53.7, 53.1; MS: (FAB) **TPA**$^{+}$ 482; UV-Vis: λ_{max}=248 nm (ε=79,000 $M^{-1}cm^{-1}$); EA: calcd. for $C_{52}H_{36}$ C 94.51 H 5.49 found: C 94.36 H 5.51



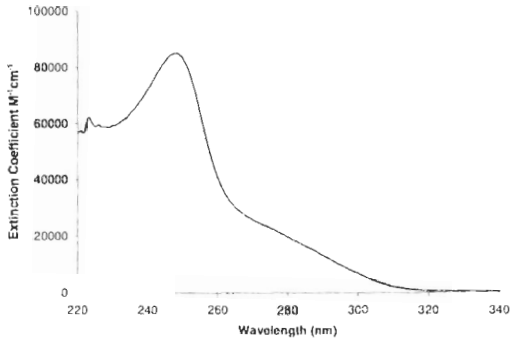
The UV-Vis spectrum was recorded in spectral-grade acetonitrile at a concentration of 3.5 x 10^{-6} M.

2,2′,3,3′-tetraphenyldianthracene (DPA-DPA)



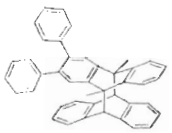
In an oven-dried 100 mL Schlenk flask 73 mg (0.22 mmol) of 2,3-diphenylanthracene (**DPA**) was dissolved in 42.5 mL of HPLC-grade acetonitrile. Oxygen was removed from the sample through a minimum of three freeze-pump-thaw cycles. The sample was then irradiated for 3 h with 350 nm lamps in a Rayonet Photochemical Reactor©. During irradiation, clear flaky crystals of pure **di-DPA** formed. The solvent was then removed through gravity filtration yielding 42 mg (0.06 mmol) 58% after rinsing with ethanol.

^{1}H-NMR ($CDCl_3$) 7.13-7.10 m (8H), 7.01 s (4H), 7.00 dd (4H, J=3.3 Hz, J=5.4 Hz), 6.92 dd (8H, J=1.8 Hz, J=7.5 Hz), 6.88 dd (4H, J=3.2 Hz, J=5.4 Hz), 4.65 s (4H); ^{13}C-NMR ($CDCl_3$) 129.8, 129.3, 127.6, 127.4, 126.1,125.7, 53.4 (Note: due to the limited solubility of this compound, we were unable to observe the signals for quaternary carbons); MS: (MALDI-TOF) **DPA** $(M+H)^+$ 331; UV-Vis: λ_{max}=248 nm (ε=84,700 $M^{-1}cm^{-1}$); EA: calcd. for $C_{52}H_{36}$ C 94.51 H 5.49 found: C 94.17 H 5.70



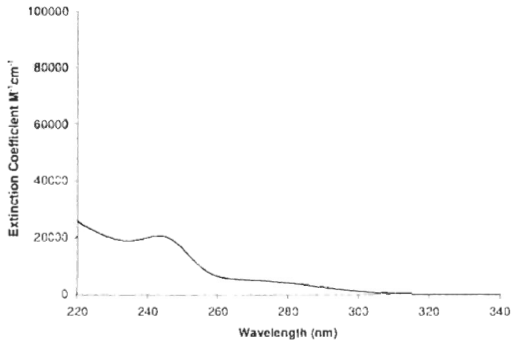
The UV-Vis spectrum was recorded in spectral-grade dichloromethane at a concentration of 1.1×10^{-4} M.

9,10-dimethyl-2,3-diphenyldianthracene (DMDPA-A)



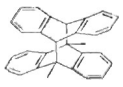
In an oven-dried 100 mL Schlenk flask 340 mg (0.95 mmol) of 9,10-dimethyl-2,3-diphenylanthracene (**DMDPA**) and 85 mg (0.48 mmol) of anthracene were dissolved in 20 mL of spectral-grade benzene. Oxygen was removed from the sample through a minimum of three freeze-pump-thaw cycles. The sample was then irradiated for 285 min with 350 nm lamps in a Rayonet Photochemical Reactor©. After irradiation the solvent was removed at room temperature *in vacuo*. The solid was then purified through silica gel chromatography eluting with a 3:1 mixture of hexanes:toluene yielding 60 mg (0.11 mmol) 46% of a white solid.

^{1}H-NMR ($CDCl_3$) 7.21-7.16 m (8H), 7.14 s (2H), 6.96-6.90 m (10H), 6.86 dd (2H, J=3.2 Hz, J=5.4 Hz), 6.83 dd (2H, J=3.2 Hz), 3.98 s (2H), 2.19 s (6H); ^{13}C-NMR ($CDCl_3$) 146.3, 145.8, 143.1, 142.9, 142.2, 137.5, 130.1, 127.9, 127.2, 127.1, 126.5, 126.4, 125.9, 125.84, 125.78, 124.1, 63.5, 51.4, 26.9; MS: (FAB) **DMDPA** (M^+) 358; UV-Vis: λ_{max}=244 nm (ε=20,300 $M^{-1}cm^{-1}$); EA: calcd. for $C_{42}H_{32}$ C 93.99 H 6.01 found: C 93.84 H 6.22



The UV-Vis spectrum was recorded in spectral-grade acetonitrile at a concentration of 9.3 x 10^{-5} M.

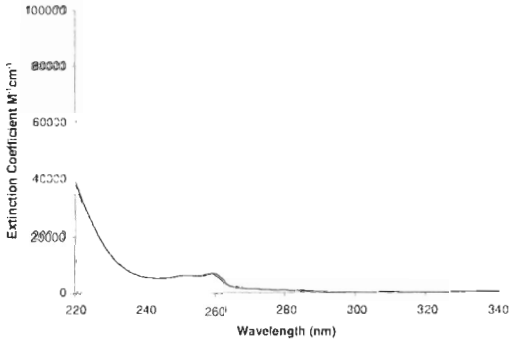
9,10-dimethyldianthracene (DMA-A)



In an oven-dried 100 mL Schlenk flask 190 mg (0.92 mmol) of 9,10-dimethylanthracene (**DMA**) and 80 mg (0.45 mmol) of anthracene were

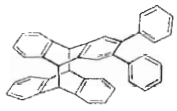
dissolved in 10 mL of spectral-grade benzene. Oxygen was removed from the sample through a minimum of three freeze-pump-thaw cycles. The sample was then irradiated for 4.5 h with 350 nm lamps in a Rayonet Photochemical Reactor©. During irradiation large slightly yellow rhombic crystals of pure **DMA-A** formed yielding 110 mg (0.29 mmol) 63% after removing the solvent through gravity filtration and rinsing with acetone.

^{1}H-NMR ($CDCl_3$) 7.15 dd (4H, J=3.4 Hz, J=5.7 Hz), 6.89 m (8H), 6.80 dd (4H, J=3.3 Hz, J=5.4 Hz), 3.94 s (2H), 2.15 s (6H); ^{13}C-NMR ($CDCl_3$) 146.4, 142.9, 1 126.8, 125.6, 125.3, 123.7, 63.2, 51.2, 26.8; MS: (MALDI-TOF) **DMA** $(M+H)^+$ 207, anthracene (M^+) 178; (FAB) **DMA** (M^+) 206; UV-Vis: λ_{max}=259 nm (ε=6,500 $M^{-1}cm^{-1}$); EA: calcd. for $C_{30}H_{24}$ C 93.71 H 6.29 found: C 93.81 H 6.23



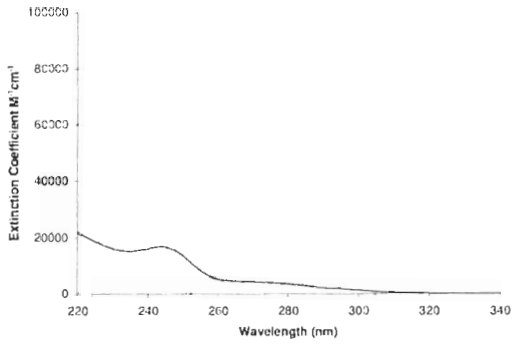
The UV-Vis spectrum was recorded in spectral-grade acetonitrile at a concentration of 6.9×10^{-5} M.

2,3-diphenyldianthracene (DPA-A)



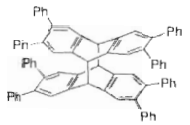
In an oven-dried 100 mL Schlenk flask 95 mg (0.29 mmol) of 2,3-diphenylanthracene (**DPA**) and 160 mg (0.90 mmol) of anthracene were dissolved in 30 mL of spectral-grade benzene. Oxygen was removed from the sample through a minimum of three freeze-pump-thaw cycles. The sample was then irradiated for 5 h with 350 nm lamps in a Rayonet Photochemical Reactor©. After irradiation the solvent was removed at room temperature *in vacuo*. The solid was then purified by recrystallising twice from acetone yielding 17 mg (0.03 mmol, 21%) of a white solid.

^{1}H-NMR ($CDCl_3$) 7.08-7.06 m (6H), 6.90-6.87 m (8H), 6.85-6.83 m (4H), 6.80-6.76 m (6H), 4.59 d (4H, J=3.7 Hz); ^{13}C-NMR ($CDCl_3$) 143.7, 143.6, 143.5, 142.9, 141.9, 137.8, 130.0, 129.5, 127.8, 127.5, 127.34, 127.31, 126.3, 125.9, 125.8, 125.7, 53.9, 53.6; MS: (MALDI-TOF) **DPA** (M^+) 331, anthracene (M^+) 178; UV-Vis: λ_{max}=244 nm (ε=16,500 $M^{-1}cm^{-1}$); EA: calcd. for $C_{40}H_{28}$ C 94.45 H 5.55 found: C 94.14 H 5.80



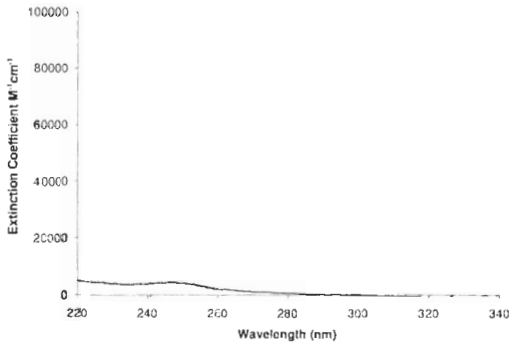
The UV-Vis spectrum was recorded in spectral-grade acetonitrile at a concentration of 1.3×10^{-4} M.

2,2′,3,3′,6,6′,7,7′-octaphenyldianthracene (TPA-TPA)



In an oven-dried 100 mL Schlenk flask 175 mg (0.36 mmol) of 2,3,6,7-tetraphenylanthracene (**TPA**) was dissolved in 30 mL of spectral-grade benzene. Oxygen was removed from the sample through a minimum of three freeze-pump-thaw cycles. The sample was then irradiated for 13 h with 350 nm lamps in a Rayonet Photochemical Reactor©. After irradiation, the solvent was removed at room temperature *in vacuo*. The solid was then purified through silica gel chromatography eluting with a 3:1 mixture of hexanes and toluene yielding 95 mg (0.10 mmoL) 55% of a white solid.

^{1}H-NMR (ppm) ($CDCl_3$) 7.15- 7.11 m (24H), 7.10 s (8H), 6.95 dd (16H, J=3.3 Hz, J=4.8 Hz), 4.75 s (4H); ^{13}C-NMR ($CDCl_3$) 142.5, 141.7, 138.5, 130.1, 129.8, 127.9, 126.4, 53.4; MALDI-TOF: **TPA** (M^+) 482; UV-Vis: λ_{max}=249 nm (ε=4,200 $M^{-1}cm^{-1}$); Anal. Calcd. for $C_{52}H_{36}$: C 94.51 H 5.49 found: C 94.28 H 5.56



The UV-Vis spectrum was recorded in spectral-grade acetonitrile at a concentration of 1.1 x 10^{-5} M.

5.4.2.3 Rayonet Irradiation

Under most circumstances the two anthracene species were dissolved in spectral-grade benzene both at a 4 mM concentration. In most cases the volume of solvent was 1.25 – 5 mL. The sample was then degassed through a minimum of 3 freeze-pump-thaw cycles. A Rayonet Photochemical Reactor© with ten bulbs either RPR3000A (300 nm) or RPR35000A (350 nm) was used as the

irradiation chamber. Upon completion of irradiation (usually 2 h) the solvent was removed *in vacuo* at room temperature. Analysis of the resulting product mixture was accomplished through ^{1}H-NMR.

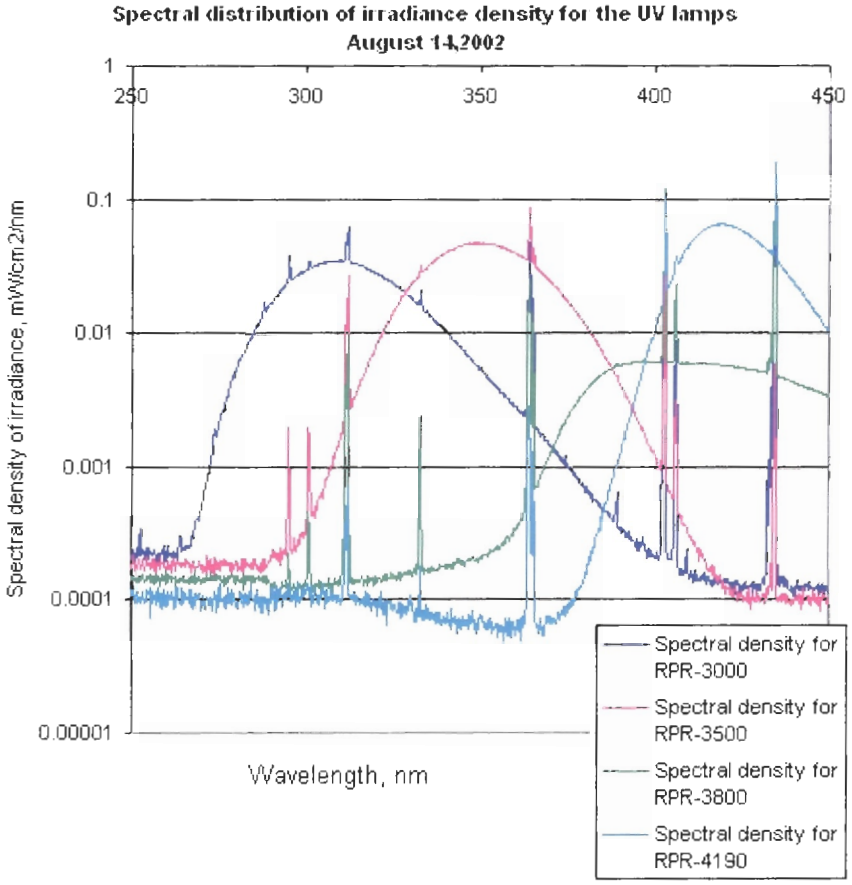


Figure 5.1 Lamp output of Rayonet Photochemical Reactor© (only RPR-3000 or RPR-3500 bulbs were used in the studies described in this thesis, image supplied by and reproduced with permission from the Southern New England Ultra Violet Company, www.rayonet.org)

5.4.2.4 Selective Irradiation

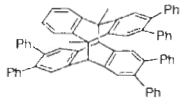
The two anthracene species were dissolved in deuterated chloroform, usually each at 10 mM concentration; 1 mL of this solution was transferred into a quartz NMR tube. After bubbling N_2 through the solution for ~2 min the tube was capped and sealed with parafilm. A fluorimeter with the slit width set to 5 nm was used as the light source. Periodically during the irradiation, ^{1}H-NMR spectra were collected to monitor the progress of the reaction.

5.4.2.5 Dianthracene Cyclomers Produced During the Qualitative Studies in Chapter 4

The following dianthracene compounds were formed during the qualitative photochemical studies described in Chapter 4 and as such the quantities produced were not sufficient to purify and characterise to the same extent as those in Section 5.4.2.2.

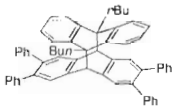
All of the following ^{1}H-NMR spectra were obtained by first removing the solvent used during the photochemical studies by first freezing the solvent using liquid nitrogen and then placing the frozen solution under vacuum (vacuum pump). When all of the solvent was removed the solid was then redissolved in deuterated chloroform.

2,2′,3,3′,6,7-hexaphenyl-9,10-dimethylanthracene (DMDPA-TPA)



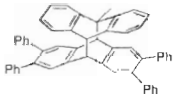
^{1}H-NMR (ppm) ($CDCl_3$) 7.17-6.93 m (40H), 4.12 s (2H), 2.23 s (6H)

9,10-dibutyl-2′,3′,6′,7′-tetraphenyldianthracene (DBA-TPA)



^{1}H-NMR (ppm) ($CDCl_3$) 7.22-7.06 m (32H), 2.67 m (4H), 1.73 m (4H), 1.47 m (4H), 0.89 t (6H, J=7.3 Hz)

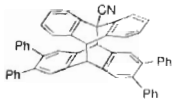
9-methyl-2′,3′,6′,7′-tetraphenyldianthracene (TPA-9MA)



^{1}H-NMR (ppm) ($CDCl_3$) 4.66 s (2H), 4.09 s (1H), 2.177 s (3H)

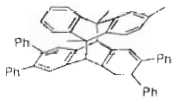
The aromatic resonances could not be determined due to overlap with the resonances of the **9MA** homodimer.

9-cyano-2′,3′,6′,7′-tetraphenyldianthracene (TPA-9CNA)



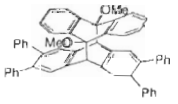
^{1}H-NMR (ppm) ($CDCl_3$) 5.01 s (1H), 4.67, 4.18 poorly resolved singlets (2H) The aromatic resonances could not be determined due to overlap with the resonances of the **9CNA** homodimer.

2,9,10-trimethyl-2′,3′,6′,7′-tetraphenyldianthracene (TPA-TMA)



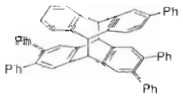
^{1}H-NMR (ppm) ($CDCl_3$) 7.20-6.85 m (45H), 3.97 s (2H), 2.13 s (3H), 2.10 s (3H), 2.09 s (3H)

9,10-dimethoxy-2′,3′,6′,7′-tetraphenyldianthracene (TPA-DMeOA)



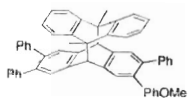
^{1}H-NMR (ppm) ($CDCl_3$) 7.15-6.91 m (32H), 4.36 s (2H), 3.54 s (6H)

2,2′,3,6,7-pentaphenyldianthracene (TPA-MPA)



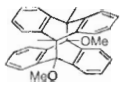
^{1}H-NMR (ppm) ($CDCl_3$) 7.18-6.81 m (54H), 4.682, 4.677, 4.671 poorly resolved singlets (4H)

2-(4-methoxyphenyl)-9′,10′-dimethyl-3,6,7-triphenyldianthracene (TPAA-DMA)



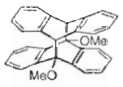
^{1}H-NMR (ppm) ($CDCl_3$) 7.23-6.69 m (37H), 4.06 s (2H), 3.76 s (3H), 2.19 s (6H)

9,10-dimethyl-9′,10′-dimethoxydianthracene (DMA-DMeOA)



^{1}H-NMR (ppm) ($CDCl_3$) 7.13 dd (4H, J=3.3 Hz, J=5.7 Hz), 7.04 dd (4H, J=3.4 Hz, J=5.8 Hz), 6.94 dd (4H, J=3.3Hz, J=5.7Hz), 6.77 dd (4H, J=3.3Hz, J=5.8Hz), 3.11 s (6H), 2.10 s (6H)

9,10-dimethoxydianthracene (DMeOA-A)

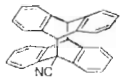


^{1}H-NMR (ppm) ($CDCl_3$) 7.23 dd (4H, J=3.3Hz, J=5.7Hz), 7.00 dd (4H, J=3.2Hz, J=5.8Hz), 6.85 dd (4H, J=3.3Hz, J=5.4Hz), 6.73 dd (4H, J=3.2Hz, J=5.4Hz), 4.23 s, (2H), 3.49 s (6H)

2,7′-diphenyldianthracene (MPA-MPA) plus assumed isomers

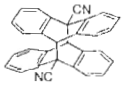
^{1}H-NMR (ppm) ($CDCl_3$) 7.43-6.77 m (24H), 4.64, 4.624, 4.621 poorly resolved singlets (4H)

9-cyanodianthracene (9CNA-A)



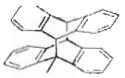
^{1}H-NMR (ppm) ($CDCl_3$) 4.87 s (1H), 4.61 d (1H, J=11.1 Hz), 4.53 (1H, J=11.1 Hz) The aromatic resonances could not be determined due to overlap with the resonances of the homodimers.

9,9′-dicyanodianthracene (9CNA-9CNA)



^{1}H-NMR (ppm) ($CDCl_3$) 7.36-7.34 m (4H), 6.97-6.87 m (12H), 4.82 s (2H)

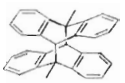
9-methyldianthracene (9MeA-A)



^{1}H-NMR (ppm) ($CDCl_3$) 4.56 s (2H), 3.96 s (1H) The aromatic resonances could not be determined due to overlap with the resonances of the homodimers. The methyl resonances of the crossdimer **9MeA-A** and the homodimers could not be conclusively determined.

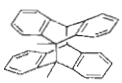
9,9′-dimethyldianthracene (*hh*- and *ht*-9MeA-9MeA)

ht-9MeA-9MeA



4.56 s

hh-9MeA-9MeA



4.00 s

These species were reported by Wu and as such were not reproduced in the laboratory.[126]

5.5 X-Ray Crystallographic Analysis of TPA-DMA and DMA-A

All X-ray crystallography preparation, acquisition, and structure determination was graciously performed by Michael J. Katz. Crystallographic data for **DMA-A** and **TPA-DMA** are tabulated in Table 5.1. The crystals were mounted on glass fibers using epoxy adhesive. Crystal descriptions for each compound are as follows: **DMA-A** was a pale yellow crystal having dimensions 0.60 x 0.60 x 0.06 mm^3, and **TPA-DMA** was a pale yellow crystal having dimensions 0.69 x 0.19 x 0.15 mm^3. The data for **DMA-A** and **TPA-DMA** were collected at room temperature using the diffractometer control program DIFRAC and an Enraf Nonius CAD4F diffractometer employing graphite monochromated Mo Kα radiation.[154] The following data ranges were recorded: 1 = $4° \leq 2\theta \leq 54°$; 2 = $4° \leq 2\theta \leq 45°$. The data was corrected by integration for the effects of absorption using a semi-empirical psi-scan method with the following transmission ranges: 1 = 0.782478 – 0.976048; 2 = 0.911445 – 0.974815. Data reduction included corrections for Lorentz and polarization effects.[155] Final unit-cell dimensions were determined based on the following well-centered reflections: 1 = 22 reflections with range $35° \leq 2\theta \leq 40°$; 2 = 22 reflections with range $23° \leq 2\theta \leq 33°$.

The programs used for the absorption correction, and data reduction were from the NRCVAX Crystal Structure System.[156] The structure was solved and refined using CRYSTALS.[156] Diagrams were made using ORTEP and rendered in POV-Ray.[157,158] Complex scattering factors for neutral atoms were used in the calculation of structure factors.[159]

All non-hydrogen atoms for **DMA-A** were refined anisotropically. The structure was solved and refined in P 21/a with 50% occupancy for the necessarily disordered methyl groups C(15) and C(16). While we report this model, for simplicity's sake, we must also comment that two 0,k,0 reflections (0,3,0 and 0,5,0) were measured as weakly observed (whereas there were no significant reflections violating the a-glide condition). A heavily restrained and constrained model in the spacegroup P a, resulting in a 33/67(2) refined partial occupancy ratio of the methyl positions (corresponding to different relative orientations of adjacent molecules of the single diastereomer), produces slightly better aggreement than the P 21/a model, and does fit the observed intensity of the 0,k,0 reflections.

Due to the limited number of reflections and the non-centrosymmetric space groups of **TPA-DMA**, all atoms were refined isotropically with the exception of the chlorine atom from the dichloromethane solvent molecule in

TPA-DMA which was also found to have a partial occupancy of 55.65%. The absolute configuration (*i.e.* the Flack parameter[160]) of **TPA-DMA** could not be unambiguously determined due to the absence of significant anomalous scattering. Hydrogen atoms were placed in geometrically calculated positions, and refined using a riding model, and a constrained isotropic thermal parameter. The final refinement using observed data are as follows: ($I_o \geq 2.50\sigma(I_o)$) and statistical weights included 147 parameters for 1226 unique reflections for 1, and 232 parameters for 1788 unique reflections for **TPA-DMA**. Selected bond lengths and angles are given in Table 5.1.

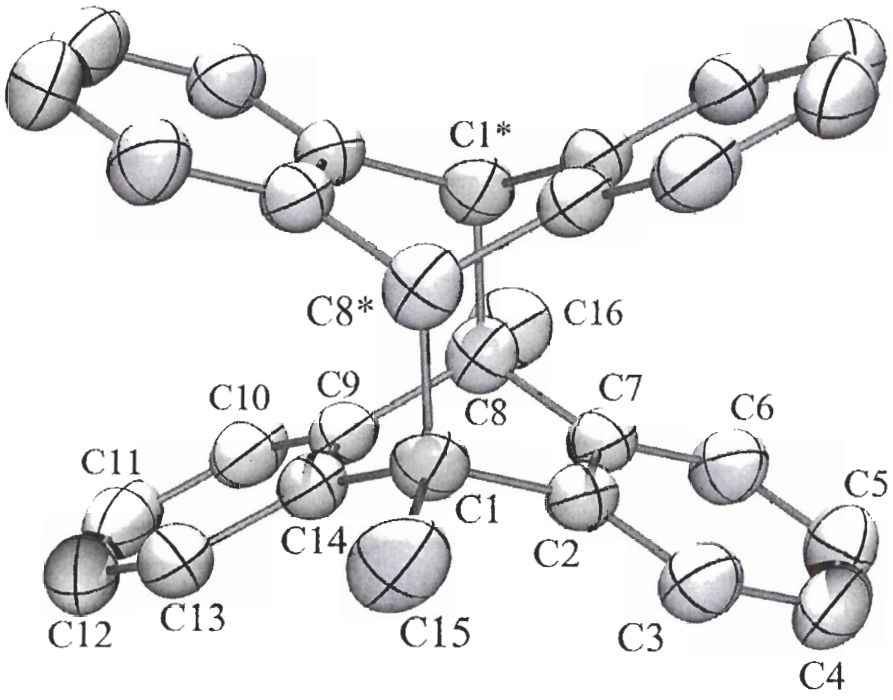


Figure 5.2 Thermal ellipsoid plot of **DMA-A** showing the methyl groups in one of two possible orientations. Thermal ellipsoids at 50%. * = - x + 2, - y, - z + 2

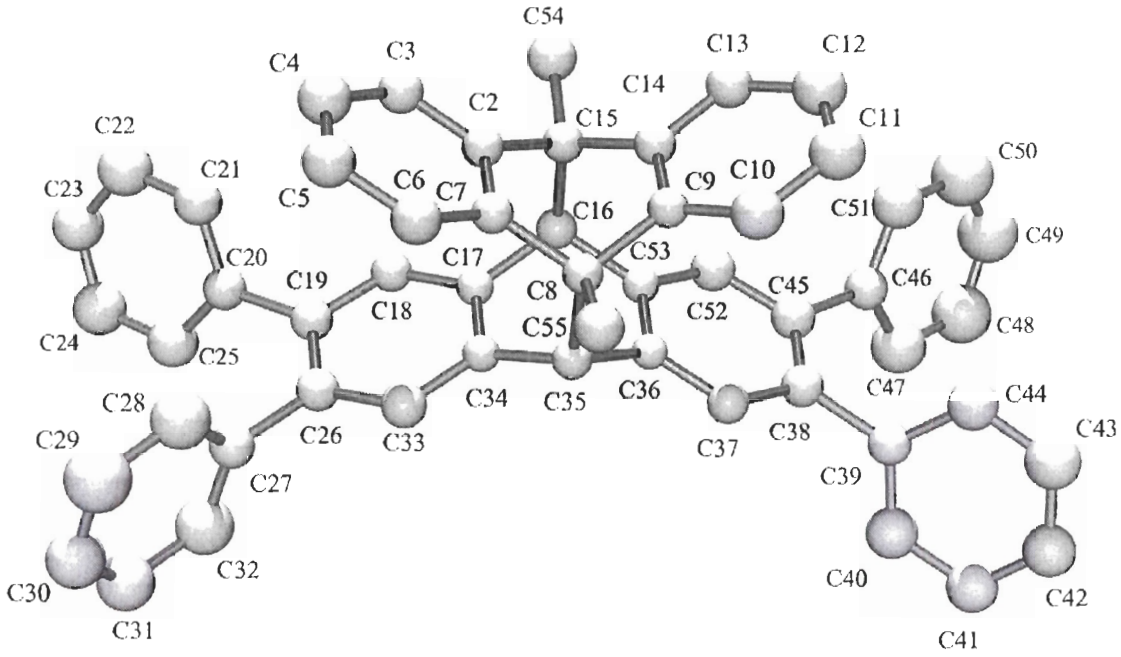


Figure 5.3 Thermal ellipsoid plot of TPA-DMA. Thermal ellipsoids at 50%.

Table 5.1 Crystallographic data for DMA-A and TPA-DMA

	DMA-A	**TPA-DMA**
Empirical formula	$C_{30}H_{24}$	$C_{54}H_{40}\cdot (CH_2Cl_2)_{0.278}$
Formula weight	384.54	712.51
Crystal system	Monoclinic	Monoclinic
Space group	P 2_1/a	I 2
a, Å	8.469(2)	17.899(4)
b, Å	12.824(4)	8.041(3)
c, Å	9.976(2)	27.929(6)

α, °	90	90
β, °	110.729(19)	98.341(16)
γ, °	90	90
V, Å^3	1013.3(5)	3977.2(19)
Z	2	4
T, K	293	293
λ, Å	0.70930	0.70930
$\rho_{calcd.}$, g•cm^{-3}	1.26	1.19
μ, mm^{-1}	0.071	0.103
R[a] ($I > 2.5\sigma(I)$)	0.047	0.089
R_w[a] ($I > 2.5\sigma(I)$)	0.047	0.116
Goodness of fit	2.231	2.771

[a]Function minimized $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = [\sigma^2(F_o) + (m*F_o)^2]$, $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$. m = 0.010 for **DMA-A**, 0.025 for **TPA-DMA**

Table 5.2 Atomic coordinates and temperature factors for DMA-A

Atom	**x/a**	**y/b**	**z/c**	**U(iso)**
C(1)	0.9470(3)	0.12089(17)	0.9687(2)	0.0482
C(2)	1.0249(3)	0.09698(18)	0.8565(2)	0.0448
C(3)	0.9774(3)	0.14752(19)	0.7252(2)	0.0553
C(4)	1.0532(3)	0.1229(2)	0.6275(2)	0.0651
C(5)	1.1743(3)	0.0468(2)	0.6589(3)	0.0662
C(6)	1.2222(3)	-0.0046(2)	0.7886(2)	0.0577
C(7)	1.1472(3)	0.01971(17)	0.8879(2)	0.0459

C(8)	1.1938(3)	-0.03442(18)	1.0318(2)	0.0481
C(9)	1.2129(3)	0.04877(19)	1.1443(2)	0.0489
C(10)	1.3435(3)	0.0509(2)	1.2745(2)	0.0611
C(11)	1.3529(4)	0.1279(3)	1.3742(3)	0.0748
C(12)	1.2290(4)	0.2029(2)	1.3437(3)	0.0749
C(13)	1.0981(4)	0.2022(2)	1.2140(3)	0.0624
C(14)	1.0876(3)	0.12520(18)	1.1124(2)	0.0477
C(15)*	0.8389(7)	0.2200(4)	0.9350(5)	0.0734
C(16)*	1.3505(6)	-0.1048(4)	1.0641(5)	0.0659
H(11)*	0.8923(3)	0.19107(17)	0.9476(2)	0.045(3)
H(31)	0.8909(3)	0.19893(19)	0.7032(2)	0.059(3)
H(41)	1.0213(3)	0.1583(2)	0.5380(2)	0.070(3)
H(51)	1.2264(3)	0.0287(2)	0.5910(3)	0.066(3)
H(61)	1.3072(3)	-0.0584(2)	0.8097(2)	0.063(3)
H(81)*	1.3048(3)	-0.07029(18)	1.0530(2)	0.049(3)
H(101)	1.4308(3)	-0.0010(2)	1.2979(2)	0.065(3)
H(111)	1.4443(4)	0.1297(3)	1.4650(3)	0.079(3)
H(121)	1.2345(4)	0.2552(2)	1.4137(3)	0.078(3)
H(131)	1.0123(4)	0.2547(2)	1.1919(3)	0.072(3)
H(151)*	0.7885(7)	0.2316(4)	1.0062(5)	0.095(3)
H(152)*	0.9092(7)	0.2784(4)	0.9330(5)	0.095(3)
H(153)*	0.7515(7)	0.2132(4)	0.8427(5)	0.095(3)

H(161)*	1.4466(6)	-0.0629(4)	1.0714(5)	0.080(3)
H(162)*	1.3719(6)	-0.1411(4)	1.1528(5)	0.080(3)
H(163)*	1.3302(6)	-0.1548(4)	0.9884(5)	0.080(3)

- Occupancy = 0.5

Table 5.3 Atomic coordinates and temperature factors for TPA-DMA

Atom	**x/a**	**y/b**	**z/c**	**U(iso)**
Cl(1)*	-0.9658(5)	-0.3369(12)	-0.0418(2)	0.0957
C(1)*	-1.000000(10)	-0.211(6)	0.000000(10)	0.084(13)
C(2)	-0.7101(6)	-0.4535(17)	-0.3220(4)	0.037(3)
C(3)	-0.7857(7)	-0.4428(18)	-0.3435(4)	0.044(4)
C(4)	-0.8127(8)	-0.545(2)	-0.3812(5)	0.058(4)
C(5)	-0.7670(8)	-0.661(2)	-0.3978(5)	0.055(4)
C(6)	-0.6908(7)	-0.6752(19)	-0.3759(5)	0.051(4)
C(7)	-0.6612(6)	-0.5712(18)	-0.3388(4)	0.036(3)
C(8)	-0.5806(6)	-0.5743(18)	-0.3151(4)	0.034(3)
C(9)	-0.5798(6)	-0.5592(17)	-0.2609(4)	0.034(3)
C(10)	-0.5335(8)	-0.651(2)	-0.2285(5)	0.056(4)
C(11)	-0.5328(8)	-0.633(2)	-0.1776(5)	0.064(4)
C(12)	-0.5808(8)	-0.518(2)	-0.1613(5)	0.061(4)
C(13)	-0.6280(7)	-0.4250(19)	-0.1946(4)	0.047(4)
C(14)	-0.6272(6)	-0.4410(18)	-0.2443(4)	0.038(3)

C(15)	-0.6760(6)	-0.3366(18)	-0.2805(4)	0.037(3)
C(16)	-0.6256(6)	-0.1946(18)	-0.3010(4)	0.039(3)
C(17)	-0.6297(6)	-0.2056(16)	-0.3546(4)	0.032(3)
C(18)	-0.6841(7)	-0.1218(17)	-0.3870(4)	0.039(3)
C(19)	-0.6931(7)	-0.1489(17)	-0.4368(4)	0.041(3)
C(20)	-0.7599(7)	-0.0730(18)	-0.4674(4)	0.043(3)
C(21)	-0.8297(7)	-0.1024(19)	-0.4566(5)	0.053(4)
C(22)	-0.8932(9)	-0.026(2)	-0.4806(5)	0.072(5)
C(23)	-0.8854(8)	0.085(2)	-0.5179(5)	0.065(4)
C(24)	-0.8187(8)	0.111(2)	-0.5305(5)	0.070(5)
C(25)	-0.7544(8)	0.036(2)	-0.5053(5)	0.062(4)
C(26)	-0.6421(7)	-0.2617(17)	-0.4541(4)	0.041(3)
C(27)	-0.6477(7)	-0.3153(18)	-0.5065(4)	0.044(3)
C(28)	-0.6860(8)	-0.460(2)	-0.5220(5)	0.074(5)
C(29)	-0.6875(9)	-0.518(3)	-0.5712(6)	0.092(6)
C(30)	-0.6510(8)	-0.435(2)	-0.6014(6)	0.073(5)
C(31)	-0.6142(8)	-0.290(2)	-0.5877(6)	0.072(5)
C(32)	-0.6119(8)	-0.228(2)	-0.5393(5)	0.075(5)
C(33)	-0.5886(7)	-0.3436(18)	-0.4209(4)	0.045(4)
C(34)	-0.5826(6)	-0.3189(16)	-0.3725(4)	0.031(3)
C(35)	-0.5332(6)	-0.4211(17)	-0.3364(4)	0.035(3)
C(36)	-0.4986(6)	-0.3091(15)	-0.2957(4)	0.029(3)

C(37)	-0.4266(6)	-0.3239(18)	-0.2745(4)	0.038(3)
C(38)	-0.3975(6)	-0.2376(18)	-0.2324(4)	0.041(3)
C(39)	-0.3166(7)	-0.2738(17)	-0.2098(4)	0.043(4)
C(40)	-0.2564(8)	-0.230(2)	-0.2309(5)	0.062(4)
C(41)	-0.1827(8)	-0.273(2)	-0.2110(5)	0.061(4)
C(42)	-0.1716(8)	-0.363(2)	-0.1710(5)	0.064(4)
C(43)	-0.2283(8)	-0.409(2)	-0.1482(5)	0.071(5)
C(44)	-0.3023(8)	-0.3643(19)	-0.1667(5)	0.057(4)
C(45)	-0.4446(7)	-0.1318(18)	-0.2124(4)	0.046(4)
C(46)	-0.4233(7)	-0.0423(19)	-0.1647(4)	0.046(4)
C(47)	-0.3635(9)	0.075(2)	-0.1588(6)	0.077(5)
C(48	-0.3482(10)	0.157(3)	-0.1131(6)	0.092(6)
C(49)	-0.3901(10)	0.131(3)	-0.0779(6)	0.095(6)
C(50)	-0.4461(10)	0.022(3)	-0.0816(6)	0.098(6)
C(51)	-0.4635(8)	-0.068(2)	-0.1272(5)	0.065(4)
C(52)	-0.5179(7)	-0.1121(19)	-0.2357(5)	0.047(4)
C(53)	-0.5458(6)	-0.2013(16)	-0.2775(4)	0.031(3)
C(54)	-0.7391(8)	-0.246(2)	-0.2585(5)	0.055(4)
C(55)	-0.5404(7)	-0.7328(18)	-0.3274(4)	0.049(4)
H(11)*	-0.960764(10)	-0.143(6)	0.015990(10)	0.104(8)
H(31)	-0.8178(7)	-0.3658(18)	-0.3327(4)	0.060(8)
H(41)	-0.8631(8)	-0.538(2)	-0.3950(5)	0.082(8)

H(51)	-0.7852(8)	-0.733(2)	-0.4238(5)	0.083(8)
H(61)	-0.6601(7)	-0.7572(19)	-0.3869(5)	0.072(8)
H(101)	-0.5016(8)	-0.731(2)	-0.2398(5)	0.077(8)
H(111)	-0.4999(8)	-0.698(2)	-0.1557(5)	0.089(8)
H(121)	-0.5818(8)	-0.505(2)	-0.1283(5)	0.085(8)
H(131)	-0.6615(7)	-0.3510(19)	-0.1834(4)	0.067(8)
H(161)	-0.6466(6)	-0.0881(18)	-0.2932(4)	0.054(8)
H(181)	-0.7165(7)	-0.0483(17)	-0.3747(4)	0.059(8)
H(211)	-0.8352(7)	-0.1779(19)	-0.4319(5)	0.079(8)
H(221)	-0.9405(9)	-0.050(2)	-0.4717(5)	0.107(8)
H(231)	-0.9278(8)	0.139(2)	-0.5343(5)	0.097(8)
H(241)	-0.8138(8)	0.179(2)	-0.5566(5)	0.102(8)
H(251)	-0.7069(8)	0.058(2)	-0.5137(5)	0.084(8)
H(281)	-0.7106(8)	-0.523(2)	-0.5007(5)	0.103(8)
H(291)	-0.7129(9)	-0.619(3)	-0.5808(6)	0.133(8)
H(301)	-0.6514(8)	-0.478(2)	-0.6327(6)	0.108(8)
H(311)	-0.5896(8)	-0.233(2)	-0.6098(6)	0.103(8)
H(321)	-0.5879(8)	-0.130(2)	-0.5301(5)	0.098(8)
H(331)	-0.5551(7)	-0.4189(18)	-0.4329(4)	0.065(8)
H(351)	-0.4930(6)	-0.4704(17)	-0.3526(4)	0.050(8)
H(371)	-0.3940(6)	-0.3959(18)	-0.2886(4)	0.058(8)
H(401)	-0.2642(8)	-0.172(2)	-0.2597(5)	0.090(8)

H(411)	-0.1423(8)	-0.244(2)	-0.2263(5)	0.089(8)
H(421)	-0.1225(8)	-0.395(2)	-0.1578(5)	0.094(8)
H(431)	-0.2194(8)	-0.473(2)	-0.1196(5)	0.105(8)
H(441)	-0.3418(8)	-0.3983(19)	-0.1505(5)	0.083(8)
H(471)	-0.3348(9)	0.093(2)	-0.1837(6)	0.106(8)
H(481)	-0.3081(10)	0.230(3)	-0.1084(6)	0.132(8)
H(491)	-0.3792(10)	0.190(3)	-0.0494(6)	0.141(8)
H(501)	-0.4741(10)	0.004(3)	-0.0564(6)	0.138(8)
H(511)	-0.5025(8)	-0.147(2)	-0.1310(5)	0.097(8)
H(521)	-0.5498(7)	-0.0380(19)	-0.2230(5)	0.063(8)
H(541)	-0.7167(8)	-0.177(2)	-0.2320(5)	0.093(8)
H(542)	-0.7690(8)	-0.182(2)	-0.2828(5)	0.092(8)
H(543)	-0.7709(8)	-0.330(2)	-0.2467(5)	0.093(8)
H(551)	-0.4875(7)	-0.7322(18)	-0.3135(4)	0.090(8)
H(552)	-0.5436(7)	-0.7488(18)	-0.3618(4)	0.090(8)
H(553)	-0.5636(7)	-0.8294(18)	-0.3145(4)	0.091(8)

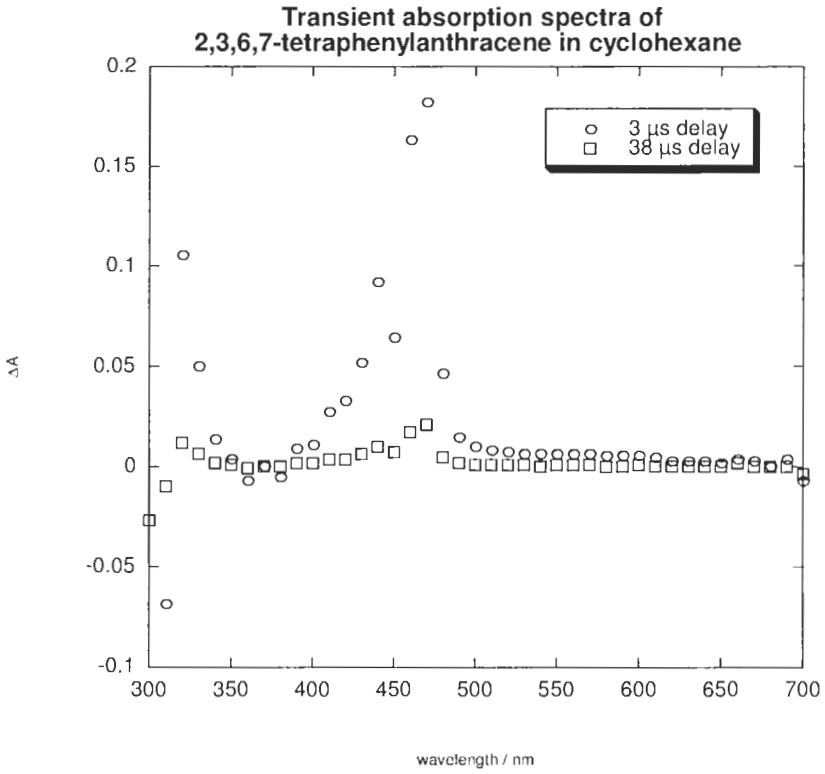
* Occupancy = 0.5565

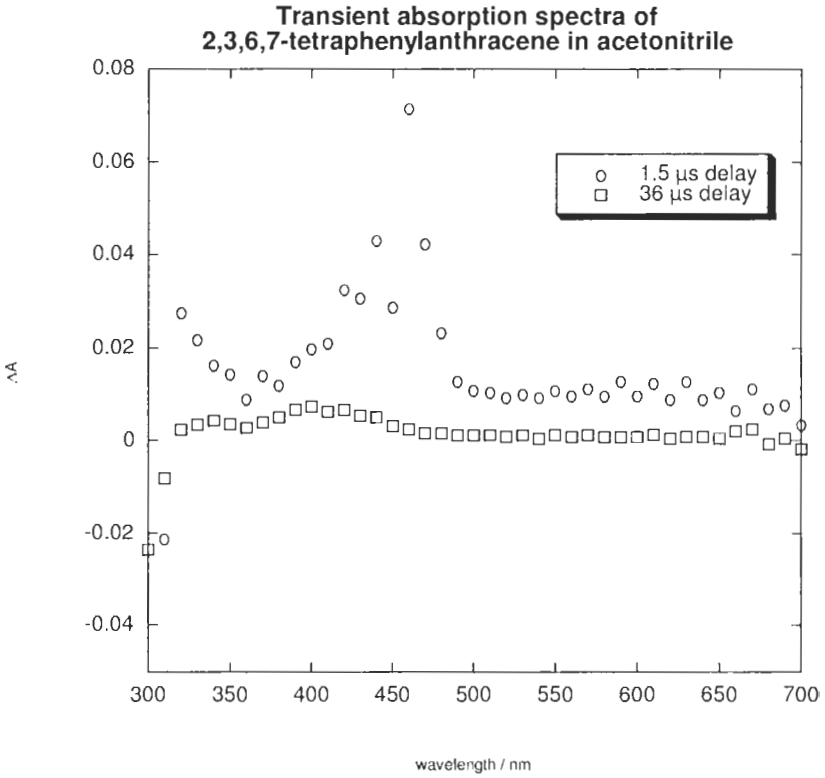
5.6 Singlet and Triplet Lifetime Measurements of TPA

These studies were graciously performed by T. Pace working at the University of Victoria under Cornelia Bohne.

The singlet lifetime of 2,3,6,7-tetraphenylanthracene in the absence of oxygen was obtained in cyclohexane and acetonitrile. The lifetime is 7.17 ± 0.01 ns in cyclohexane and 7.98 ± 0.01 ns in acetonitrile. These lifetimes are longer than that for unsubstituted anthracene (5.5 ns in cyclohexane).[161] The lifetimes were also obtained in air and after bubbling with O_2 in cyclohexane. A linear (3 point) relationship was observed and the estimated rate constant for quenching of the singlet by oxygen in cyclohexane was determined to be diffusion controlled ($k_q = 1 \times 10^{10}\ M^{-1}\ s^{-1}$).

The transient spectra and decay kinetics were measured for 2,3,6,7-tetraphenylanthracene in acetonitrile and cyclohexane. The observed transient spectra were the same at all delays in cyclohexane. Bleaching was observed below 300 nm and sharp absorbance was observed around 470 nm. In acetonitrile bleaching was observed below 300 nm and sharp absorbance was observed around 460 nm, but there also seems to be a broad shoulder centered around 400 nm, visible at longer delays. These maxima are red-shifted in comparison to unsubstituted anthracene, which exhibits sharp absorbance around 420 nm.


Transient absorption spectra of
2,3,6,7-tetraphenylanthracene in cyclohexane
3 µs delay
38 µs delay
ΔA
wavelength / nm


Transient absorption spectra of
2,3,6,7-tetraphenylanthracene in acetonitrile
1.5 µs delay
36 µs delay
ΔA
wavelength / nm

The lifetimes of the transient, assumed to be the triplet, were measured at the absorption maximum in cyclohexane in air and after bubbling with N_2 and O_2. The lifetime of 2,3,6,7-tetraphenylanthracene in cyclohexane in the absence of oxygen was 97 μs. A linear (3 point) relationship was observed and the estimated rate constant for quenching of the triplet by oxygen in cyclohexane was determined to be diffusion controlled (k_q = 1.6 x 109 M^{-1} s^{-1}). The rate constant for quenching of unsubstituted anthracene by oxygen is also estimated to be diffusion controlled (k_q = 3.1 x 109 M^{-1} s^{-1}).

At low concentrations the decay kinetics follow a mono-exponential decay, but at higher concentrations multi-exponential decays are observed, must likely due to triplet-triplet annihilation. Decays were obtained at a range of concentrations in cyclohexane to determine if self-quenching occurs. No change in lifetime was observed up to a concentration of 0.1 mM, and the upper limit for the self-quenching rate constant is therefore 1 x 10^7 M^{-1} s^{-1}. The absence of observable self-quenching is consistent with what is known for anthracene where the self-quenching rate constant for anthracene in cyclohexane is known to be (1.06 ± 0.01) x 10^6 M^{-1} s^{-1}.[162]

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